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Advanced Light Source

Compendium of User Abstracts and Technical Reports 1998

July 1999

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The Web version provides a full-text search of user abstracts as well as searches by beamline, author name, subject area, year, and other parameters.

The Compendium is intended to complement the
Advanced Light Source Activity Report,
which presents an overview of the scientific program,
ongoing research and development efforts, and operations.

Related publications available from the ALS User Services Office

ALS Activity Report 1996/97, 1997/98

ALS Compendium of User Abstracts and Technical Reports 1993–1996, 1997

Workshop on Scientific Directions at the Advanced Light Source:
Summary and Reports of the Working Groups

Soft X-Ray Spectromicroscopy:
Materials Characterization on a Microscale

World Class Protein Crystallography:
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at the Advanced Light Source

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Welcome to our third annual Compendium of research abstracts from the Advanced Light Source (ALS). These are intended to convey results and work in progress of many of our user programs. We thank our users for taking time out of their busy schedules to prepare these abstracts.

The last year or so has seen a substantial growth in the number of ALS users: 764 in 1998, up from 387 in 1997. Undulator Beamline 7.0.1 continues as one of the most oversubscribed and prolific beamlines, demonstrating an urgent need for an additional similar beamline. We have also seen significant shifts in user demographics. About 25% of our users are now in the life sciences, a fact attributable to the full operation of our Macromolecular Crystallography Facility (Beamline 5.0.2), which is solving protein structures at a rapid pace. About 10% of our users are now in environmental science thanks largely to the popularity of the microfocus capabilities of Beamlines 10.3.2 (x-ray), 7.0.1 and 6.1 (soft x-ray), and 1.4 (infrared). All this is to the good; it shows that we are adapting to the scientific imperatives that will prevail in the 21st century.

You are most likely reading all this on the Web or from a CD. We are minimizing the number of hard copies to save some trees! I am grateful to Lori Tamura and her colleagues in our Technical Information Section for their professionalism and painstaking efforts in preparing this Compendium for your reading pleasure.

Neville Smith
ALS Division Deputy for Science

Advanced Light Source

Compendium of User Abstracts and Technical Reports 1998

The Advanced Light Source (ALS), a national user facility located at Ernest Orlando Lawrence Berkeley National Laboratory of the University of California, is available to researchers from academia, industry, and government laboratories. Operation of the ALS is funded by the Department of Energy's Office of Basic Energy Sciences.

This Compendium contains abstracts written by users summarizing research completed or in progress during 1998, ALS technical reports describing ongoing efforts related to improvement in machine operations and research and development projects, and information on ALS beamlines planned through 2000.

Two tables of contents organize the user abstracts by beamline and by area of research, and an author index makes abstracts accessible by author and by principal investigator. Technical details for each beamline, including whom to contact for additional information, can be found in the beamline information section. The most current information on ALS beamlines can be found on the ALS Web pages (<http://www-als.lbl.gov/>).

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Beamline 1.4 Abstracts

Characterizing the Kinetics and Mechanisms of Ion Sorption to Soil Components Employing Infrared and Optical Spectroscopy

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Project Goal:

The overall objective of this research is to use synchrotron-based FTIR spectro-microscopy to aid in the identification of metal and oxyanion sorption products on soil materials. Specifically, our efforts will be focused towards characterization of inorganic contaminant speciation to organic and mineral components within various soil types. This research will benefit from the higher flux and, consequently, greater spatial resolution available with synchrotron radiation.

Our specific goals within the last proposal periods were: 1) to identify sample cells compatible with the endstation spectrometer(s) at Beamline 1.4.3 that were suitable for the analysis of soil materials, and 2) to help establish a wet chemical laboratory adjacent to the beamline. In addition, we evaluated potential experimental and instrumental limitations which could interfere with the proper identification of analyte speciation.

Project Accomplishments:

We have performed preliminary analyses using the NicPlan Microscope available on the spectro-microscopy endstation of Beamline 1.4. Our results suggest that this technique will be successful for the characterization of analyte-soil associations provided that certain experimental and instrumental requirements are satisfied. With respect to instrumentation, reliable control of the atmosphere surrounding the sample is essential due to potential interference from common absorbing species in air, e.g. H₂O and CO₂. In addition, important requirements must be met with respect to sample characteristics. Foremost, for optimal results the particle size distribution of the soil material cannot be significantly smaller than the spatial resolution of the spectrometer. This may limit examination of the clay size fraction (<2 μm), which is generally considered to be the most reactive fraction within a soil. Research should focus on identifying analyte speciation and distribution in heterogeneous materials. Finally, characterization of soil materials reacted with metals or oxyanions suggest that studies examining the latter compounds will prove more fruitful. Our initial hope that the improved spatial resolution available with the synchrotron source would facilitate identification of metal hydroxide precipitation products was unfulfilled. These studies will likely only prove successful when the spectral signature of the reaction product and soil material are significantly different. In most cases, characterization of sorption products for oxyanions such as arsenate, borate and phosphate will not suffer from this limitation.

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Dependence of the fundamental band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on alloy composition and pressure

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III-nitrides have been extensively studied in recently years because of their scientific and technological importance. In particular, the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy system covers a wide ultraviolet (UV) spectral range between the direct band gaps of ~ 3.4 eV for GaN and ~ 6.2 eV for AlN at room temperature, and is very attractive for short-wavelength optical applications such as UV light emitters and UV detectors. In addition, AlGaIn alloys with small mole fractions are used to form strained heterostructures with GaN and InGaIn in light emitting diodes and laser diodes and in GaN/AlGaIn field-effect transistors (FETs). Therefore, it is important to know the fundamental band gap of an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial layer with a given mole fraction and its pressure dependence in order to calculate the band alignment for designing and engineering a device.

In this paper, we report an optical absorption study on $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial films with emphasis on the variation of the band-gap energy with alloy composition and the pressure dependence of the direct band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples with different x . The bowing parameter which characterizes the nonlinear dependence of the fundamental band gap on the alloy composition was derived for the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy system. The pressure coefficients of the direct Γ band gap were determined from the energy shift of the optical absorption edge with pressure for each individual sample.

The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy samples were nominally undoped single-crystal epitaxial films grown by MOCVD on (0001) sapphire substrates. Thin AlN buffers were deposited on the substrates before the growth of the alloy films. The thickness of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers varies from several thousand angstroms to over one micron. The AlN mole fractions of the samples were determined by Rutherford backscattering spectrometry. The experimental uncertainty for the determination of the x value is ± 0.01 . The light source for the optical absorption measurements was the bright continuous UV radiation from a bending magnet in the synchrotron at the Advanced Light Source of Lawrence Berkeley National Laboratory. A detection system consisting of a 0.5-m single-grating monochromator and a UV enhanced CCD detector was used for transmission measurements and for calibration of the light source. Pressure-dependent measurements were carried out using gasketed diamond anvil cells (DAC). All the absorption measurements were carried out at room temperature (295 K).

Figure 1 shows optical transmission spectra taken from several $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples at atmospheric pressure. The band-gap energy is determined as the intersection of linear fits to the steeply declining transmission profile and the baseline above the transmission threshold. The inset of the figure plots the measured transition energies for the samples used in this work as a function of AlN mole fraction. The solid line is a least-square fit to our experimental data using

$$E(x) = E(0) + ax + bx^2, \quad (1)$$

where $E(0) = 3.43$ eV is the band-gap energy of GaN determined by the absorption measurements at room temperature, x is the AlN alloy fraction, and energy is given in eV. With the band-gap energy of AlN fixed at 6.2 eV,⁴ the best fit using least-square fitting yields $a = 1.44$ and $b = 1.33$ eV. The obtained bowing parameter is larger than the value theoretically predicted by first-principle calculations (0.53 eV),⁵ but is in good agreement with experimental values reported by Malikova *et al.* (0.98 eV)⁶ and Agerer *et al.* (1.3 eV).⁷

Under applied pressure, the optical absorption edges shift towards higher energy as the direct band gaps of the alloy samples increase. The pressure-induced energy shifts for the optical transition related to the direct band gap are plotted in Fig. 2 for the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples with $x=0.12, 0.2, 0.4$, and 0.6 . No pressure-dependent results obtained for the $x=0.86$ sample because its band-gap energy is larger than the transmission threshold of the diamond anvils (5.5 eV). The solid lines in Fig. 2 are least-square fits to the experimental data using a linear pressure-dependent fit function:

$$E(P)=E(0)+\alpha P, \quad (2)$$

where the energy E is in eV and the pressure P is in PGa. The pressure coefficients yielded from the best fit to the experimental data are listed in Table I as “measured” α . These values do not exhibit a significant dependence on alloy composition. They are comparable to the pressure coefficients of excitonic transitions associated with the fundamental band gap of GaN^{8-10} and are consistent with our previous photoluminescence results in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys.¹¹

Table I. Pressure coefficients for the fundamental band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayer samples

	$E(0)$ (eV)	$\alpha=dE/dP$ (meV/PGa) (Measured)	$\alpha=dE/dP$ (meV/PGa) (Corrected)
GaN	3.43	39.0 ^a ;38.9 ^{a,b}	41.4 ^{a,b}
$\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$	3.64	37.3	40.4
$\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$	3.88	37.2	40.5
$\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$	4.22	37.6	41.2
$\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$	4.72	37.2	41.5

^aResults were obtained by photoluminescence measurements.

^bRef. 20.

It is known that nitride epitaxial films grown on sapphire substrates are always subjected to slight compression primarily caused by the difference between the thermal-expansion coefficients of the epilayers and the substrates. Application of hydrostatic pressure to such a strained system consisting of materials with different bulk moduli will lead to uniaxial strains that make the epilayer and the substrate experience different effective hydrostatic and axial pressure components.^{12,13} Since the bulk modulus of sapphire (~240 GPa)¹⁴ is larger than that of GaN (~210-237 GPa)^{15,17} and AlN (218 GPa),¹⁸ the deformation of nitride epilayers deposited on sapphire is affected by the compression of the stiffer substrates under hydrostatic pressure. Under hydrostatic pressure conditions, a tensile strain will be induced in the compressively strained $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers to compensate the applied hydrostatic pressure because $\text{Al}_x\text{Ga}_{1-x}\text{N}$ has a larger compressibility. As a result, the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers effectively experience a smaller hydrostatic pressure and an additional (0001) uniaxial stress.

In order to derive the actual pressure coefficients for the AlGaN samples from the measured values, one has to estimate the effective pressure experienced by AlGaN epilayers. The sample volume change with applied pressure can be described using the Murnaghan equation of state:¹⁹

$$V(P)=V(0)[1+(B'/B)P]^{1/B'}, \quad (3)$$

where B is the bulk modulus and B' is its pressure derivative ($=dB/dP$). For a crystal with wurtzite structure, the relative volume change can be related to the variation of lattice parameters a and c as $\Delta V/V=2\Delta a/a+\Delta c/c$. The relative changes of the lattice parameters are related through the elastic stiffness coefficients as $\Delta c/c=-2(C_{13}/C_{33})\Delta a/a$. Using a first-order (linear) approximation, Eq.(3) can be further reduced to

$$a(P)/a(0) = P/[2B (1- C_{13}/C_{33})] \quad (4)$$

Figure 3 plots out the calculated $a(P)/a(0)$ for GaN and AlN as a function of applied hydrostatic pressure using Eq.(4) under two extreme conditions: (1) unstrained (free-standing) $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with their deformation under pressure independent of the volume change of

sapphire, and (2) “pseudomorphically” strained epilayers with their in-plane compressibility completely determined by the compression of sapphire at high pressures. An averaged value of $B=223.5$ GPa from Refs.15-17 was used for GaN in the calculation. The overall effect of mechanical strain is to make a strained layer on a stiffer substrate be compressed less than a free-standing layer at a given externally applied hydrostatic pressure. The effective hydrostatic pressure experienced by the assumed “pseudomorphically” strained $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers is smaller than applied pressure. The stress reduction ranges from ~8-12% depending on the alloy composition. The pressure coefficients for the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples derived from the mechanical correction to the experimental measured values are listed in Table I as “corrected” values.

It has to be pointed out that the “pseudomorphically” strained condition should be relaxed in reality. Perlin *et al.* recently found a 6% reduction of the experimentally measured pressure coefficient for GaN on sapphire (strained) as compared to that for free-standing GaN (unstrained),²⁰ which is smaller than an 8% predicted in Fig. 3 for GaN. One of the possible reasons leading to a smaller effect of stress reduction is that the highly defective AlN buffers are most likely to be, at least partially, plastically deformed under applied pressure. Therefore, we regard the corrected values for the pressure coefficients listed in Table I as the upper limit for the pressure dependence of the fundamental band gaps of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy samples.

In conclusion, optical absorption measurements were performed to study the fundamental band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ as a function of alloy composition and applied pressure. The $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples were found to exhibit a large nonlinear variation of the fundamental band gap with a bowing parameter of 1.33 eV. The fundamental band gaps of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples were found to linearly increase under applied pressure. We derived the pressure coefficients for the direct band gap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ to be around 40-41 meV/PGa from the experimentally measured values by taking into account the difference of compressibility between the epitaxial films and sapphire substrate.

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Figure 1. Transmission spectra taken from several $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial layers at atmospheric pressure. The inset plots the measured band-gap energies as a function of AlN mole fraction. The solid line is the best fit to the experimental data.

Figure 2. The energy positions of the optical transitions associated with the direct band gaps of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples as a function of applied pressure.

Figure 3. Calculated change of in-plane lattice constant a of GaN and AlN with pressure under free-standing and “pseudomorphically” strained conditions using linear elastic approximation. The pressure-induced volume change for free-standing $\text{Al}_x\text{Ga}_{1-x}\text{N}$ lies in between the lines of GaN and AlN.

FT-IR Microscopy of Liquid Microjets

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Motivation

It is well known that the thermodynamic properties of liquid water show anomalous behavior in the deeply supercooled region of the phase diagram. Specifically, the density, heat capacity and isothermal compressibility all show rapid divergence at a singular temperature, $T_s = -45^\circ\text{C}$. In addition, the transport and relaxation properties show similar behavior as T_s is approached. Currently, two thermodynamic scenarios have been postulated to account for the divergent response functions observed in deeply supercooled water.

The Stability Limit Conjecture, proposed by Speedy and coworkers¹, attributes the low temperature behavior of supercooled water to the reentry of the liquid-gas (L-G) spinodal through the negative pressure region of the phase diagram. As a consequence, T_s is the point at which the free energy surface of the liquid terminates at a first order phase transition to crystalline ice. Adequate determination of the proposed L-G spinodal, at negative pressures, is severely complicated by the experimental difficulties in working with superstretched liquids.

Poole et al.² have suggested an alternative explanation—the Critical Point Hypothesis. At T_s , there exists another critical point in the water phase diagram. At $T < T_s$, there is a line of first order phase transitions between two structurally distinct liquid phases. Mishima et al.³ have offered indirect evidence for a liquid-liquid phase transition in the decompression induced melting of Ice IV.

Currently it is not been possible to distinguish between the two scenarios either by Molecular Dynamics simulations or direct experimental investigation. MD simulations are hampered by the slow relaxation processes inherent in supercooled liquids, while experiments have failed to penetrate the homogenous nucleation limit (-40°C , 1 atm).

Preliminary Experimental Results

Liquid jets, technology pioneered by Faubel and coworkers⁴, may provide a novel way to circumvent the many difficulties encountered in studying metastable liquids. Micron-sized liquid jets have been shown to produce deeply supercooled water (-63°C) by large rates of evaporative cooling (10^5 K/sec).⁴ We have endeavored to characterize these jets by Raman Spectroscopy, FT-IR microscopy, and X-Ray absorption in an effort to corroborate the low reported surface temperatures and to hopefully investigate the structure of deeply supercooled water. FT-IR microscopy was used to probe the temperature profile as well as the character of hydrogen bonding in these liquid microjets.

Preliminary experiments conducted on ALS beamline 1.4.3 (spring 1998), with Drs. Wayne McKinney and Michael Martin, have supported the low temperatures previously reported and have provided compelling evidence for a large temperature gradient within the liquid jet. Figure 1 shows the temperature gradient determined by the shift in the OH stretching frequency in a 5% $\text{H}_2\text{O}/\text{D}_2\text{O}$ solution¹. A "sheath" of supercooled water ($\sim -50^\circ\text{C}$), 3 microns from the edge of the jet, appears to surround a warmer core ($\sim 25^\circ\text{C}$). Raman experiments, which give complimentary

information, were conducted at UC Berkeley. However, these experiments lacked the spatial resolution of beamline 1.4.3 and therefore the 3 micron "sheath" of what appears to be supercooled water could not be detected. In this way, the spectromicroscopy facility's spatial as well as spectral resolution has been indispensable in the investigation of liquid microjets.

Fig. 1: Temperature vs. position in a 20 micron jet obtained by infrared absorption of 5% $\text{H}_2\text{O}/\text{D}_2\text{O}$ (v/v).

In addition, we have examined the OH (OD) stretching and bending frequencies in pure H_2O (D_2O). The OH stretch region has been demonstrated to be a highly sensitive probe of hydrogen bonding.² The infrared spectrum taken in the middle of the jet is consistent with room temperature liquid water. In contrast, water within the 3-5 micron "sheath" show significant spectral perturbations that may be due to enhanced hydrogen bonding. Specifically, the OH stretching frequencies, shown in Fig. 2, are dramatically red-shifted from the normal room temperature water that is observed in the middle of the jet. This shift may be consistent with the microscopic picture of cage-like structures theorized to be present in deeply supercooled water. In addition, the sharp peak observed around 3600 cm^{-1} is not observed in the room temperature liquid and may be a surface localized mode or perhaps a unique feature of the deeply supercooled state.

Future Directions

The experiments and data described above are still in the initial stages. Further experiments are needed to map out the temperature profile across as well as down the axis of the microjet. To better understand the cooling mechanism, a variety of jet sizes (5 to 30 microns in diameter) will be used. Furthermore, we would like to extend our studies to the intermolecular vibrational modes ($<1000\text{ cm}^{-1}$) of both H_2O and D_2O , which are extremely sensitive probes of the hydrogen-bonding environment within the liquid.⁶

In general, liquid microjet technology coupled with the high spatial and spectral resolution of beamline 1.4.3 may provide a powerful new tool in the investigation of metastable liquids.

Fig. 2: The infrared OH stretch region of water measured near the edge of a 20 micron liquid microjet

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High-frequency electron beam motion observed and resolved.

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After implementing several changes to the beamline to reduce the coupling to external physical vibrations, a new much higher frequency source of noise was observed on the measured IR spectra at ALS Beamline 1.4.3. Figure 1 shows two examples of this noise where 128 FTIR scans were obtained and then another 128, with the two measurements ratioed to one another. This results in a signal to noise spectra around a 100% line (if there is no noise, the result should be a perfectly straight line). The data show that the noise is not uniform throughout the spectral region, but is instead much more pronounced in the 2 – 8 kHz region. These frequencies are much higher than the physical motion of a mirror could produce, so we had to assume that the extra noise was coming from motion of the electron beam itself.

Figure 1. FTIR Spectra showing extra noise in the 2 – 8 kHz frequency regime.

The frequency dependence of this noise as a function of beam current was measured by placing a spectrum analyzer directly on the IR detector output and stopping the scanning mirror in the interferometer. The frequency spectrum was observed to change as the beam decayed, further indicating that the source is on the electron beam. During 2-bunch mode operations (when the longitudinal feedback system is not operated) we clearly observed the known synchrotron oscillations of the electron beam, and we could follow these oscillations as a function of beam energy. This proved that the FTIR setup was indeed capable of measuring electron beam motion.

After a presentation given to the Accelerator Physics Group by Michael Martin, John Byrd of that group recognized that the high frequency noise we observed is consistent with a Robinson effect beam motion if something was driving the electron bunches anywhere near these frequencies. A monitoring system in the ALS control room was set up to measure the longitudinal beam motions. Through several comparisons of the spectra versus beam current we showed that this control room measurement was indeed seeing the same beam motion that was

observed with the IR beamline. Now that the beam motion was confirmed and understood to be an instability in the beam, the search turned toward identifying the driving source of the noise.

There are only a few places in which a high-frequency electric field could interact with the beam, namely the 500MHz RF cavities, the longitudinal and transverse feedback systems, and the pinger. The pinger is not used in regular operations, ruling it out. The fact that we did not observe this high-frequency noise in our earlier studies in the fall of 1997, whereas we do observe them in the winter and spring of 1998 indicates that something changed during that time. A new digitally synthesized master oscillator for the RF system was installed in December 1997 replacing an older crystal oscillator. A careful analysis of the noise output from this synthesizer was performed and showed sideband phase noise around the primary 500MHz signal. This was therefore the likely culprit.

A new HP digital synthesizer with a lower noise spec was identified and HP loaned a unit to the ALS for testing purposes during the first week of August 1998. This unit was installed in the RF system and testing was done throughout the week to monitor beam motions. The IR spectra measured with the new oscillator is compared to the previous measurements in Figure 2. The bottom spectrum represents the new measurement and clearly the 2 – 8 kHz noise is way down. Indeed most of the deviations from 100% in the 1000 – 4000 cm^{-1} region are actual changes in the water vapor and CO_2 content in the IR path and therefore are real data. The RMS noise values are seen to decrease throughout the spectral region measured. The noise in the spectroscopically critical 1000 – 4000 cm^{-1} region went from unusable, to nearly the same as in the rest of the spectrum. The high-frequency noise extended even up above 5000 cm^{-1} , where an improvement in the RMS noise of up to a factor of eight was seen. Figure 3 shows the significant reduction in noise power as seen in the control room.

The new lower-noise HP digital synthesizer has been purchased by the ALS and was installed permanently as the master oscillator in the RF system on September 14, 1998. This work has therefore lead to an improved ALS beam for every research project at the ALS.

Figure 2. Comparison of the high frequency noise with the old and new digitally synthesized master oscillators.

Figure 3. Measured power spectrum of synchrotron oscillations with the old and new 500 MHz master oscillators. Harmonics of the klystron power supply are now visible with the reduction in master oscillator phase noise.

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Initial Development of a UV Spectroscopy Endstation on ALS Bend Magnet 1.4 for the Investigation of Wide Bandgap Semiconductors

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INTRODUCTION

This project (duration = 6 months, \$90k funding) encompassed the construction of a new endstation on ALS beamline 1.4 to perform spectroscopy in the ultraviolet (UV) area of the spectrum. By exploiting the high brightness and directionality of the bend magnet radiation, it is possible to make an intense, versatile source for spectroscopic studies in the 180 nm - 350 nm range. The source characteristics were measured and initial spectroscopic experiments were performed with semiconducting films of the III-V nitride family: InN ($E_g = 1.9$ eV), GaN ($E_g = 3.4$ eV), AlN ($E_g = 6.1$ eV) and their alloys. We chose this materials system because there is intense scientific interest in this materials system due to the recent commercialization of high efficiency blue and green LEDs and the demonstration of blue cw laser operation.

RESULTS AND DISCUSSION

Beamline construction and source characterization. A new experimental hutch was constructed (1.4.1) and the requisite laser table and optics were installed. The source strength at the laser table was in good agreement with bend magnet calculations provided by the ALS Systems group. The total cw power at 350 mA ring current is 50 mW broadband at the UHV exit window. After beam shaping and diversion, the power is still 20 mW at the laser table. It was also shown that the beam could be focused without intensity loss to 100 μm and smaller spot sizes; this capability will be useful for studies with small samples. Figure 1 shows the results of a

Fig. 1. Absolute source strength measured at Beamline 1.4.1. UV light was focused by 200 mm fused silica lens onto the entrance slit of a single 0.5 m monochromator (slit width = 350 microns, 1.4 nm bandwidth). The light was detected with PMT and the absolute calibration was performed with a NIST-traceable standard of irradiance. Plotted data is a composite of overlapping scans optimized for maximum throughput at 200, 225, 300, and 500 nm.

Figure 2. Left: absorption spectra of an AlGaIn epitaxial film obtained as function of pressure in a diamond anvil cell. Focused UV light from Beamline 1.4.3 of the Advanced Light Source was used as the UV light source. Bottom: pressure dependence of the fundamental gap of AlGaIn samples obtained from UV absorption measurements at the ALS.

measurement of the absolute source strength measured at the laser table.

Pressure dependence of AlGaIn bandgap. The pressure dependence the band gap of a series of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial films was measured. The bandgap was determined by optical absorption; pressure was applied with a diamond anvil cell (DAC). This experiment is difficult to perform with conventional UV sources because of the small size of the samples (ca. 200 μm in diameter). However, the superior collimation of the ALS source enabled the UV beam to be focused precisely on the sample in the cell. A spectrometer and CCD camera were used to obtain the absorption spectra (Fig. 2, top). The pressure dependence of the band gap of these alloys is being used to understand the band structure of III-V nitrides.

Photoluminescence in InGaIn quantum wells. Photoluminescence (PL) measurements were performed in InGaIn quantum wells at 77 K. A 0.25 m monochromator was used to select the excitation wavelength, which was varied from 300 nm (4.13 eV) to 350 nm (3.54 eV). The

Figure 3. Photoluminescence spectra of $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ quantum wells excited by UV light from Beamline 1.4.3, Advanced Light Source. The peak at 3.05 eV is from the quantum well. The peaks at 3.28 and 3.21 eV are donor-acceptor pair recombination and the LO phonon replica in GaN, respectively. The PL intensity decreases with excitation wavelength due to a reduced absorption depth in the 200 nm GaN cladding layer.

results are shown in Fig. 3. Very little PL was observed for excitation energies below 3.5 eV, the band gap of GaN. This demonstrates that the PL from the InGaN quantum wells originates from electrons diffusing from the GaN cladding layer to the well, rather than from direct excitation of carriers in the quantum well. This experiment demonstrates that Beamline 1.4.1 can generate sufficiently bright, tunable, UV light for investigation of III-V semiconductors.

FUTURE WORK

We are currently constructing an experiment to perform temperature-dependence measurements of absolute reflectivity of manganites in collaboration with J. Orenstein of the Materials Sciences Division.

PUBLICATIONS

J. W. Ager III, W. Shan, K. M. Yu, W. Walukiewicz, E. E. Haller, M.C. Martin, W. McKinney, and W. Yang, "Pressure dependence of the fundamental energy band gap of AlGaIn alloys," *J. Appl. Phys.*, in press.

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Microbial Reduction of Cr⁶⁺ on Mineral Surfaces in Columbia Basalt Rocks: A Synchrotron FTIR Study

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Industrially produced and discharged hexavalent chromium, Cr⁶⁺, occurs in the environment in the highly water soluble forms of the divalent oxyanions chromate (CrO₄)²⁻ and dichromate (Cr₂O₇)²⁻ (1). These compounds readily cross cell membranes mainly *via* the sulfate (SO₄)²⁻ active transport system (2) and are reduced intracellularly to Cr⁵⁺ and Cr⁴⁺, which then mutagenize DNA by disrupting DNA replication (3). When in the environment in the reduced trivalent form (Cr³⁺), they tend to form relatively insoluble compounds that often cannot cross cell membranes and thus become significantly less harmful to the same biological systems (3). These profound changes in physical, chemical, and toxicological properties following reduction have created significant opportunities to detoxify Cr⁶⁺ in geological materials (4).

There are two contradicting views about hexavalent chromium Cr⁶⁺ reduction mechanisms (and polyvalent metal ions as a whole) on mineral surfaces. The “biological mechanism” is based on the presence of Cr⁶⁺-tolerant and Cr⁶⁺-reducing microorganisms detected by conventional microbial techniques in well-sorted and well-mixed geological materials (5). The evidence is corroborated with Cr⁶⁺ reduction to Cr³⁺ measured in batch and flow-through column experiments using similar geologic materials (6-8). Recent research indicates that the role of the microbial mechanism is further enhanced by microbially produced macromolecules (9). Through combinations of carboxyl, phosphoryl, and hydroxyl groups, these macromolecules complex polyvalent metal ions and increase the chromium solubility and thus availability to Cr⁶⁺-tolerant and Cr⁶⁺-reducing microorganisms (9). The alternative “chemical mechanism” suggests that the presence of geological minerals with mixed metal oxides and/or the presence of natural organic molecules can significantly catalyze the redox chemistry of Cr⁶⁺ and other polyvalent metal ions in geological materials (10-12).

In this study, we report systematically observed evidence that provides insight into dominant reduction mechanisms and reduction pathways on mineral surfaces. The microorganisms under study are rock-inhabiting microorganisms in fractured basalt rock systems. They are found in the vadose zone above the rock aquifers within the extensive Columbia basalt flow in the southwestern part of Idaho in the United States. The basalt samples are from the Radioactive Waste Management Complex (RWMC) within the Idaho National Engineering and Environmental Laboratory (INEEL) of the U.S. Department of Energy. This site has been polluted with mixtures of hexavalent chromium, Cr⁶⁺, together with other inorganic ions, radionuclides, petroleum hydrocarbons, and volatile organic compounds (VOCs) from more than 40 years of US nuclear production activity. The samples were collected and sectioned at the site by members of INEEL.

All samples were fine-grained silicate-containing vesicular basalt. Earlier work indicates that although Columbia basalt rocks are generally quite limited in nutrients and organic carbon, there are dense clusters of microorganisms on the vesicles or on the fractured surfaces (14), especially in areas where magnetite is a dominant constituent. Batch studies demonstrated that some of these microorganisms are Cr⁶⁺-tolerant and Cr⁶⁺-reducing microorganisms (15,16). The ability of these rock-inhabiting microorganisms to aerobically reduce Cr⁶⁺ increased significantly during concomitant biodegradation of a volatile organic compound (VOC) (15). Other bacteria with similar abilities to detoxify mixtures of Cr⁶⁺ and VOCs have been reported elsewhere (7).

We used a synchrotron radiation-based (SR) Fourier transform infrared (FTIR) spectromicroscopy beamline (Beamline 1.4.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory) previously described (17) to spectroscopically and spatially document the reduction process as it occurred on the basalt surfaces. All FTIR microspectra were recorded in reflectance mode over the 4000-650 cm⁻¹ infrared region at 4 cm⁻¹ resolution on a Nicolet Magna 760 FTIR-spectrometer coupled to a Nic-Plan IR microscope (18). The SR source is at least 200 times brighter at a 10-μm spatial resolution than a conventional black-body IR source. This makes the technique most useful for examining in real time and at high spatial resolution many compounds and organisms at (dilute) environmental concentrations. The distinct IR absorption bands we used as chemical markers are well known (14, 17, 19-20).

The experiment began with an introduction of 10-ppm (as chromium) chromate solution onto different magnetite surfaces. Fig. 1 shows recorded SR FTIR spectra for chromium on magnetite surfaces shortly after the experiment's beginning and 5 days after exposure. For magnetite surfaces without living *A. oxydans* cells (abiotic), we observed no statistically significant changes in either the IR absorption intensity or characteristic band shapes during the 5-day

Figure 1: SR FTIR spectra of chromate on magnetite surfaces during the 5-day experiment of (left) abiotic reduction, (middle) biotic reduction in the absence of other organic compounds, and (right) biotic reduction in the presence of toluene vapor (as a model volatile organic compound).

period. For magnetite surfaces with living *A. oxydans* cells (biotic) but without the benefit of biodegradation of toluene, the only large change in the spectral region shown was the moderate decrease in the absorption intensity of the Cr^{6+} compound (CrO_4^{2-}) vibrational mode at 846 cm^{-1} (19). A weaker band at 830 cm^{-1} appeared and was accompanied by an even weaker one at 765 cm^{-1} . These bands are reminiscent of either the IR-active stretching frequencies of chromium-oxygen in chromium-carboxylate and chromium-amino acid complexes (21), or the vibrations of oxalate (22) and catecholate (23) anions that both can complex with and/or reduce transition metal ions. All of these organic classes of compounds have been documented (24-25) as being natural products of microbial activities, although it is difficult to establish precisely which complexes are being observed (27).

Magnetite surfaces with living *A. oxydans* cells and the added toluene vapor (biotic + toluene), had all infrared absorption bands in the spectral region displayed significant changes in both intensity and characteristic band shape during the 5-day period. In particular, the absorption intensities of the 846 cm^{-1} and 728 cm^{-1} modes, which are assigned to CrO_4^{2-} and toluene (19), disappeared. At the same time, a new, strong band at 830 cm^{-1} appeared and was accompanied by a sharp but weaker satellite at 765 cm^{-1} . They are again associated with possible intermediate Cr^{5+} . The additional new band at 742 cm^{-1} , accompanied by a sharp and slightly weaker satellite at 770 cm^{-1} , is possibly associated with catechol (28), one of toluene's many biodegradation products (29).

The spatial distributions of IR absorption associated with protein Amide II of *A. oxydans* (1550 cm^{-1}), chromate (846 cm^{-1}), and toluene (728 cm^{-1}) were mapped and are presented in Fig. 2. The close link between the microbial reduction of Cr^{6+} and the biodegradation of toluene is evident. It also reveals that the transformation of chromate and toluene during the 5-day experimental period is controlled spatially by the microorganisms. The lack of significant chromate reduction on surfaces that are free of, or low in, bacterial density supports our thesis that the microbial reduction mechanism is significant even on surfaces of mixed iron oxides.

Similar SR FTIR mapping experiments were conducted on composite mineral surfaces in basalt rocks during four months under conditions typical of the vadose environment at the INEEL site. Spatial distributions of vibrational frequencies associated with intrinsic microorganisms (1550 cm^{-1}), chromate (CrO_4^{2-}) (846 cm^{-1}), reduced Cr^{5+} compounds (830 cm^{-1}), and Cr^{3+} compounds (810 cm^{-1}) were mapped at the end of the second week and the end of the fourth month. At the end of the second week no Cr^{3+} compound was detected. At the end of the fourth month, spatial distributions of the same vibrational frequencies (Fig. 3) demonstrate a correlation between the Cr^{6+} reduction to Cr^{3+} and the distribution of microorganisms. This implies that a four-month incubation time had selectively enriched for the successful growth of Cr^{6+} -tolerant and Cr^{6+} -reducing native microorganisms.

The reduced Cr^{3+} compounds in the present experiments have been confirmed by x-ray absorption fine structure (XAFS) spectroscopy obtained on Beamline 10.3.2 at the Advanced Light Source (30). Measurements done at the same location as the peak in Fig. 3 shows a Cr x-ray absorption edge structure and lack of pre-edge peak that is consistent with Cr^{3+} compounds. All microorganisms on the sample surfaces were killed by the x-ray irradiation during the XAFS experiment. The SR FTIR and the XAFS experiments were repeated after three months and

Figure 2: SR FTIR spectromicroscopy shows the spatial distribution of (top) *A. oxydans*, (middle) chromate, and (bottom) toluene as measured by their spectral signatures.

Figure 3: Distribution of indigenous microorganisms (top) and the Cr^{3+} compounds (bottom) after a 4-months Cr^{6+} -microbe-basalt experiment.

indicated no Cr^{6+} -reoxidation. This implies that the reduced Cr^{3+} is relatively stable under normal atmospheric conditions, which is consistent with results previously reported (1).

Summary

These SR FTIR spectromicroscopic observations have nondestructively monitored and elucidated, for the first time to our knowledge, the transformation and mechanisms of toxic Cr^{6+} on mineral surfaces. It has demonstrated that the microbial reduction of Cr^{6+} is important on magnetite surfaces and on surfaces of Columbia basalt rocks that are rich in magnetite. The Cr^{6+} reduction reaction accelerates during concomitant biodegradation of toluene (a common co-contaminant), which further confirms the significance of biological activities. Our spatially resolved SR FTIR spectromicroscopy further shows that on magnetite, Cr^{6+} is reduced only in the presence of the isolated microorganisms. Time resolved studies indicate that the reduction of Cr^{6+} to Cr^{3+} proceeds at least as a two-step reaction with Cr^{5+} compounds as probable intermediate products. The reduced Cr^{3+} compounds were observed to be stable for many months even after the microorganisms were killed. Thus mutagenic Cr^{6+} pollutants in the environment can be biotransformed into less mobile, less toxic, and stable compounds. One must consider the significant role of microorganisms when designing and implementing new and environmentally benign remediation technologies for the cleanup of mixed waste sites.

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Monitoring individual human cells during exposure to environmental organic toxins: Synchrotron FTIR spectromicroscopy

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) are ubiquitous environmental toxins that are known rodent carcinogens and suspected human carcinogens. Human exposure to these compounds is of great concern and needs to be assessed. Traditional assessment of human exposure and health risk to these toxins relies primarily on animal experiments. A major uncertainty inherent to this approach is the extrapolation from the high-dose animal experiments to the low-dose and long-term human exposure. To overcome this uncertainty, a common strategy is to complement animal experiments with short-term assays that use human cell culture systems and biomarkers that are indicative of exposure. The cytochrome P4501A1, encoded by the gene *CYP1A1*, metabolizes PAHs. *CYP1A1* levels increase as a result of exposure to PAHs or OCs through binding of these compounds to the Ah receptors [1]. Thus the induction of the *CYP1A1* gene expression and/or increase in the associated enzyme activity are selected as global biomarkers for PAH and OC exposure. The increase in *CYP1A1* transcript levels correlates with the levels of the exposure, which can be quantified by reverse transcription-polymerase chain reaction (RT-PCR) [2].

In this study we are developing a faster (than current RT-PCR techniques) and still sensitive method for detecting the exposure of individual human cells to PAHs and OCs. The development involves two key components. First, we identify suitable signals that represent intracellular changes that are specific to PAH and OC exposure. Second, we will construct a device to so guide the biological cell growth that suitable signals from individual cells are consistent and reproducible for a given set of exposure conditions. This paper describes our use of synchrotron-radiation-based (SR) Fourier-transform infrared (FTIR) spectromicroscopy in the mid-IR region (4000-400 cm^{-1}) as a tool to identify IR radiation signals (from individual cells) that are specific to the intracellular response after their exposure to PAHs or OCs. SR FTIR spectromicroscopy was used because it has been proven to be a sensitive analytical technique capable of providing molecular information in a biological system quickly (within minutes) at dilute concentrations and a spatial resolution of 10 microns [3-4]. The potential use of the new method to screen for the exposure to PAHs and OCs at environmentally relevant concentrations was tested using human cells in an environmental medium for which contaminant types and levels are known. In these tests, HepG2 (human hepatoma derived) cells modeled the human epithelial cells that would activate the test compound PAHs and OCs; benzo(a)pyrene (BaP) modeled the PAHs, and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) modeled the OCs. HepG2 cells metabolize PAHs efficiently. They also show *CYP1A1* induction after their treatment with PAHs and OCs. The potential use of our marker signals for detecting intracellular response to mixtures of PAHs was also demonstrated in an

environmental medium with dilute concentrations of coal tar, a complex mixtures of different PAHs.

2. EXPERIMENTAL

The infrared spectromicroscope in conjunction with Beamline 1.4.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory was used to monitor intracellular changes in response to TCDD, BaP, and coal tars exposure. Figure 1 depicts the experimental setup for this direct measurement.

All SR FTIR spectra were recorded in the $4000\text{--}650\text{ cm}^{-1}$ infrared region. This region was selected because it is the region that contains unique molecular fingerprint-exhibiting absorption features of intact biomolecules. For each IR measurement, 128 spectra were co-added at a spectral resolution of 4 cm^{-1} . All spectra were obtained in the reflection geometry and were ratioed to the reflectance spectrum of a gold-coated slide to produce absorbance values (see Figure 1).

Figure 1. Diagram illustrating experimental setup for monitoring intracellular response to polycyclic aromatic hydrocarbons (PAHs) and organochlorine (OCs) exposure. (Note that cells were placed on treated surfaces on a microscope stage. All measurements were made in reflectance mode.)

3. RESULTS AND DISCUSSION

We obtained SR FTIR absorption spectra in the range ($1750\text{--}1000\text{ cm}^{-1}$) of interest at different locations of a randomly selected single HepG2 cell prior to its exposure to the test chemicals. Figure 2 shows a typical absorption spectrum recorded at the proximity of a cell nucleus. The overall spectral characteristics are similar to those reported in [6]. It shows three main informative spectral regions for the architectural details of nucleic acid helices; each corresponds to a molecular subgroup [6]. Absorption bands in Region I ($\sim 1750\text{--}1500\text{ cm}^{-1}$) arise from in-plane vibrations of the bases (in addition to other proteins), and are sensitive to base-pairing and base-stacking effects. Absorption bands in Region II ($\sim 1490\text{--}1230\text{ cm}^{-1}$) arise from base deformation motions coupled through the glycosidic linkage to sugar vibrations. Their spectral characteristics are strongly dependent on the glycosidic torsion angle. Absorption bands in Region III ($\sim 1230\text{--}1000\text{ cm}^{-1}$) arise from phosphate vibrations and sugar vibrations. The absorption band positions and intensities depend strongly on the base-base interactions and the helical geometry in nucleic acids. The architectural structures of nucleic acid helices are extremely sensitive to the surrounding environments. We anticipate that exposing individual cells to the test chemicals, at the appropriate dose and exposure time, will lead to changes in the SR FTIR spectral characteristics in the three regions.

Figure 2. A typical SR FTIR absorption spectrum recorded near/at the nucleus of a single HepG2 cell prior to its exposure to the test chemicals. The spectrum shows three main informative spectral regions. Regions I-III are discussed in text.

Figure 3. Normalized absorbance spectra of individual HepG2 cells after 20-hour exposure to different TCDD concentrations.

To identify spectral signals that were specific to the induction of *CYP1A1*, cells were exposed to TCDD known to interact specifically with the Ah receptor that regulates *CYP1A1* expression. HepG2 cells were treated with different concentrations of TCDD (0, 0.01, 0.1, 0.5, and 1.0 nM) for 20 hours. SR FTIR spectra were measured for randomly selected individual cells, and examined for significant changes in the spectral characteristics as the dose increased. Figure 3 shows the normalized SR FTIR absorption spectra recorded. There are considerable differences in the SR FTIR spectra, with one difference being the increased absorption of the vibration band 1180 - 1160 cm^{-1} , centered at $\sim 1170 \text{ cm}^{-1}$. This systematic spectral change might be related to the alteration in the DNA base structure [7]. This will be the subject of future investigation. For our experimental system, the normalized absorbance intensity for individual cells increased from 0.007 to 0.21 when the TCDD concentration increased from 10^{-11} to 10^{-9} M (Figure 4). The normalized absorbance intensity at $\sim 1170 \text{ cm}^{-1}$ for individual control cells was 0.005. This is a 42-fold increase in the absorbance intensity, which is extremely significant considering the definition of absorbance (see Figure 1).

Figure 4. Dose response in absorption intensity at about 1170 cm^{-1} .

Figure 5. SR FTIR spectromicroscopy versus RT-PCR techniques.

We compared the performance of SR FTIR spectromicroscopy with our current RT-PCR technique. *CYP1A1* expression in HepG2 cells, as measured by RT-PCR, increased 212-fold over the same range of TCDD concentrations used in the SR FTIR study. Relative changes in the absorption intensity at $\sim 1170\text{ cm}^{-1}$ (detected by SR FTIR spectromicroscopy) as compared to the *CYP1A1* expression detected by the RT-PCR techniques are shown in Figure 5. The solid line in Figure 5 is the

least-squares fit to the data. The excellent agreement (with $r^2 = 0.99$) for measurements from the two methods indicates that the fast SR FTIR spectromicroscopy technique is indeed comparable to the RT-PCR technique that specifically measures increases in the *CYP1A1* expression. This demonstrates that SR FTIR spectromicroscopy can be used as a substitute for direct measurements of *CYP1A1* levels.

4. CONCLUSIONS

We have succeeded in using SR FTIR spectromicroscopy to identify specific that represent the intracellular response to PAH and OC exposure. Further development will allow the technique to distinguish biological responses to other different environmental toxins.

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Phyllosphere and Rhizosphere studies using the ALS-IR Beamline 1.4.3

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Scientific goals of Program -- To develop technology for the non-destructive identification, and high-resolution spatial mapping of rhizosphere exudates from intact plant surfaces in response to abiotic stresses, or evolved for microbial recruitment.

Impact of Results -- Considerable land area in the developing world suffers from severe soil acidity (Rao et al. 1993), nutrient deficiencies, while in industrialized countries, metal toxicities are common in soils near former manufacturing sites. IR spectromicroscopy offers an unprecedented glimpse at a significant "sink" for carbon within plants, as well as offering a new screening "tool" with which to evaluate existing germ plasm, or transgenically altered plants. The global importance of root exudates can be appreciated from the following brief examples:

(1) Acid rain, 'Waldsteben' and metal toxicity -- in both the NE United States and Eastern Europe, significant acreage of forests have been weakened or destroyed by acidification of the soil arising from elevated wet/dry deposition of sulfur dioxide and nitric oxides in industrialized areas. At normal soil pH's, aluminum is a very common but insoluble metal in most soils. When the soil pH drops <4 however, its solubility (and hence availability to plants) increases dramatically. One of the principal components of natural waters that limits the bioavailability of Al^{3+} is dissolved organic carbon (Sposito 1989), some of which is derived from root exudation. One key exudate strategy used by Al^{3+} -tolerant plants is malic acid secretion. Using the ALS, we have proposed to set-up a screening program to search for patterns in the distribution of this root-exudation strategy among plant species for use in tropical grassland restoration.

In response to industrial pollution from the transition metal Nickel, researchers have demonstrated that some plants are capable of "detoxifying" high soil burdens by the over-production of histidine-derived non-protein amino acids. In conjunction with the "rhizobox", the IR microscope has the potential has a rapid screening tool for comparison within a phylogenetic group. For plant ecologists, we then have a quantitative tool with which to address evolutionary questions: " How widespread is this mechanism within a plant family? ", or " How many times did this trait arise?" (Monson 1995; Raab et al. 1999).

(2) Nitrogen fixation and nodulation -- Nitrogen is an essential component of healthy soils and plants, and one of the key routes by which nitrogen is introduced into natural ecosystems is through the process of N_2 fixation. In a well-characterized symbiosis between legumes (members of the bean family) and soil bacteria of the genus *Rhizobium*, plants are able to utilize atmospheric N_2 directly for production of amino acids and proteins by forming bacterial "nodules" on the roots. In marginal wet and dry tropical locations, beans are the principal source of protein in human diets (Rao et al. 1993). In the early stages of the nodulation process, unusual flavonoid compounds are excreted from the root zones of legumes (Peters and Long 1988). These "signal" molecules serve as chemo-attractants for soil bacteria participating in the symbiosis. Only a few of the actual signal molecules have been identified, and it is of considerable interest to modern agriculture to identify these "semio-chemicals" in order to "tune" the infecting rhizobial bacteria.

(3) Soil-nutrient mobilization -- A variety of plant species have been demonstrated to excrete significant quantities of low molecular weight organic acids in response to nutrient deficiencies (Lipton et al. 1987; Dinkelaker et al. 1989; Ae et al. 1990). Second only to nitrogen (see above) in its importance to plant and human health, phosphorus is one of the most difficult nutrients for plants to acquire. Taking an evolutionary perspective, botanists now recognize this as a driving force in the creation of plant-fungal symbioses (i.e. mycorrhizae) on several occasions in the evolution of higher plants on Earth. While these fungal symbioses have significantly extended the ecological "latitudes" of higher plants, not all plant families are competent to initiate such symbioses. These plants must devise other methods to (1) increase the specific surface area of their root systems (Schmidt and Stewart 1997), (2) solubilize nutrients within their rhizospheres (Lipton et al. 1987; Dinkelaker et al. 1989; Jones et al. 1994) and (3) change the pH within the root zone (Blanchard and Lipton 1986).

Rationale for using the Synchrotron -- The 10-micron spot-size of the IR microscope at Beamline 1.4.3 allows an order-of-magnitude improvement in the fine-scale mapping of exudate gradients around plant roots. The Nicolet software that governs the collection of IR spectra through the microscope has two modes: i.) a line scan, and a ii.) 2-D array map. It might be appreciated that a linear scan oriented normal to the root surface potentially allows the mapping of gradients of root exudates produced in response to one (or more) of the above abiotic stressors. We have in fact begun collecting such spectral scans from intact roots of the legume *Lens culinaris* L. (mung beans) grown under phosphorus deprivation (Figure 1). The rhizosphere is the area (< 2 mm separation) surrounding the roots where microbes and plant together greatly influence the soil solution chemistry compared to the bulk soil. The fine spatial resolution of the ALS-FTIR allows us to divide this region of influence into smaller parts, and increases the accuracy with which both carbon-sources and -gradients may be delineated.

With line scans oriented perpendicularly to the leaf vasculature, the IR spectra demonstrate strong compositional gradients for leaf protein (Figure 2), based on the intense amide absorptions from 1700 - 1200 cm^{-1} . Depending on the apparent "skin depth" of the IR radiation, we may be sampling to a depth of 10-20 microns into the photosynthetic apparatus. Significant stores of phosphoanhydride absorptions at 2200 cm^{-1} are also seen on the abaxial side of the leaf, whereas, on the adaxial side, no such features are seen, supporting the earlier X-ray studies of Kaiser et al. 1996 that measured P-gradients within leaf tissue.

IR-transmissive windows appropriate for isolating a portion of the root-zone for intense microscopic mapping are rare, but include ZnSe (20,000 - 454 cm^{-1}) and KRS-5 (20,000 - 250 cm^{-1}). Figure 3 shows the latest version of the "rhizobox", with a (50 mm x 20 mm, 2 mm thick) ZnSe window from Spectra-Tech. Deposited on the soil-facing side of the ZnSe window is a vapor-deposited gold spot for use as an internal IR reflection standard. Such a configuration was chosen to overcome any refractive effects from the IR window. A key disadvantage of the IR window materials listed above is their high index of refraction, 2.4 and 2.37 (measured at 2 μm). In the IR wavelength range, uncoated windows will thus lose about 17% of the signal to reflections. While traditional salt-based IR windows have much lower loss figures, it may be appreciated that in the humid environment of roots, these windows would fog quickly. ZnSe and KRS-5 are also translucent in the visible range, which greatly aids in focusing the microscope.

Long-term experiments may include real-time analysis of soil enzymes (Lipson et al. 1998; Raab et al. 1999), and in this case, the discrete time-structure of the ALS beam allows collection of high-resolution FTIR scans of products. Results from this work will contribute substantially to NSF-sponsored soil ecological modeling studies being conducted at CU Boulder and UC

Figure 1.

Figure 2.

Berkeley. These enzymes catalyze a variety of important bio-geochemical transformations of the global Carbon and Nitrogen cycle, and can affect pollution levels in the atmosphere.

Though formal experiments only began in late July of 1998, the support of Drs. Wayne McKinney and Michael Martin greatly accelerated my experiments at Beamline 1.4.3. The selection of IR window materials appropriate for a "rhizobox" (see Figure 3), and "hands-on" training in using the software for the IR microscope has allowed this project to generate the first IR spectral maps from intact plants using a Synchrotron IR facility.

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Figure 3.

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Probing the Photocycle of Bacteriorhodopsin Microcrystals by FTIR Spectroscopy

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INTRODUCTION

Bacteriorhodopsin (bR) is a membrane protein that carries a covalently attached retinal group as a chromophore. Visible light (absorbance max = 568nm) captured by the chromophore provides bR with energy that is ultimately used to pump hydrogen ions out of the cell. The resulting proton-motive force powers ATP synthesis and drives the active transport of ions and nutrients across the cell.

Bacteriorhodopsin undergoes a series of chemical and structural changes as it transforms light energy into chemical energy. The photocycle of bR has been well characterized by both visible and IR spectroscopy. The most important intermediates are identified as K, L, M, N, and O; each has a distinct visible color and a distinct IR spectrum. The photocycle begins with the isomerization of all-trans retinal to 13-cis, followed by deprotonation of the Schiff base that links the protein to the retinal. A series of changes in protein structure subsequently leads to reprotonation followed by reisomerization of 13-cis retinal back to all-trans, and a return of the protein to its resting conformation. Transitions between intermediate states vary in rate from nanosecond to millisecond time scales, and these rates show marked temperature dependence.

High-resolution x-ray diffraction experiments on microcrystals of bR (Fig.1) have recently become possible, through the discovery by Landau and Rosenbusch that bR can be crystallized from the bi-continuous lipid-water gel formed by mono-olein. Consequently, the visualization of the precise structural changes responsible for the conversion of light energy into the proton-motive force is within reach. Members of our group have already collected a complete data set from microcrystals of bR in the resting state, and have begun collection of diffraction data from photocycle intermediates.

It is critical to our goal of obtaining an atomic model of bR in the M state that we confirm that we can trap the desired structural intermediate in the protein microcrystals. Towards this end we have undertaken to use ALS Beamline 1.4.3 to perform FTIR spectroscopy on individual microcrystals under conditions likely to thermally trap bR in the M state.

ACCOMPLISHMENTS

1) Mapping the positions of individual microcrystals -

The IR beam emanating from Beamline 1.4.3 is very bright, and can be focused to a diameter of as little as 10 microns, which is ideal for recording IR spectra from microcrystals whose diameter may not exceed 50 microns. Such a highly collimated beam does, however, require great precision in positioning the crystals that are to be its targets. In-house software has allowed us to easily align the IR beam with a target crystal by displaying spectral properties on a 2-dimensional grid (Fig. 2) whose coordinates correspond to the position of the microscope stage.

2) Recording the IR spectra of individual microcrystals -

Once a microcrystal of bR has been located with respect to the IR beam, we can collect spectra from the crystal itself and from the surrounding mono-olein gel. As expected, peaks signifying the presence of amide bonds appear in the former but not in the latter (Fig. 3).

3) Recording IR spectra at low temperature -

The lifetime of the M state is ~5 ms at ambient temperature, but bR persists in this state for minutes at 220-240K. In order to facilitate accurate cooling of our specimens the ALS purchased a state-of-the-art cryo-chamber that fits on the stage of the microscope through which the crystals are viewed. We have determined that IR spectra of bR microcrystals recorded at temperatures between 298K and 230K are essentially indistinguishable in the region of interest.

GOALS

1) Trapping bR microcrystals in the M state -

We are currently working to demonstrate the transformation of bR microcrystals from the resting state to the M state upon illumination at ~240K. An important step towards this goal was the insertion of a removable thin disk of Si or Ge in the path of the IR beam to absorb contaminating visible light so that the microcrystals remain in the dark as they are cooled.

2) Trapping bR microcrystals in the L state-

A future goal is to work out conditions for trapping an earlier intermediate, the L state, prior to collecting x-ray diffraction data.

FIGURE 1. Hexagonal microcrystals of bR surrounded by mono-olein observed on a gold slide. This image was taken using the microscope at Beamline 1.4.3

FIGURE 2. Three-dimensional representation of absorption at 1546 cm⁻¹, which is diagnostic for protein, in a small area of the specimen. The peak corresponds to a bR microcrystal.

ERNEST ORLANDO LAWRENCE
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Detector MCT/A
Beamsplitter XT KBr
Source External *gel alone (red) and with bR xtal (blue)*

Nicolet Magna 760
Nic-Plan IR Microscope

Number of sample scans 128
Number of background scans 128
Resolution 4.000
Sample gain 1.0
Mirror velocity 1.2659
Aperture 100.00

FIGURE 3. IR spectra of a bR microcrystal embedded in mono-olein (heavy line) and of a neighboring area containing only lipid (light line). The amide I and II bands arise from the peptide bonds of bR.

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Beamline 3.3.2 Abstracts

LIGA Micromachining and Microdevices Using Deep Etch X-ray Lithography at Beamline 3.3.2

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INTRODUCTION

A dedicated LIGA end station was commissioned at the Advanced Light Source (ALS) Beamline 3.3.2 in July, 1998 for exploring the science and technology of high aspect ratio microfabrication. The capabilities at BL3.3.2 have been developed by a Participating Research Team (PRT), named the West Coast LIGA Group, and consisting of Sandia National Laboratories (SNL), the Jet Propulsion Laboratory (JPL), and the Lawrence Berkeley National Laboratory (LBNL). LIGA, an acronym for the German words for lithography, electroforming, and molding is a micromachining technology that uses high energy x-rays from a synchrotron to create high aspect-ratio microdevices having micron to millimeter features [1,2,3].

At the ALS, the LIGA process begins with deep etch x-ray lithography (DXRL) of thick, low stress, photoresists, typically polymethylmethacrylate (PMMA). This is accomplished with the use of a mask patterned with high Z (atomic number) absorbers that prevent penetration of x-rays. The x-ray mask substrate must be made of a material that minimizes the loss of x-rays through absorption, which suggests low Z materials such as silicon and beryllium. The mask absorber material is, conversely, a high Z material corresponding to a high x-ray absorption coefficient material, such as gold or tungsten. In the open areas of the patterned mask radiation passes through the mask substrate and exposes the PMMA resist, which is then chemically developed. The exposed cavities replicate the mask and are used as molds for electroplating. The electroplating step can be the final step in the process or the electroplated part can be used as a mold for replication from another material such as a plastic or ceramic.

ACCOMPLISHMENTS

All three PRT members have used BL3.3.2 extensively since its commissioning in July. Following are summaries of accomplishments in the laboratories individual research areas.

Sandia National Laboratory:

Two major projects were emphasized at the ALS using BL3.3.2 to perform x-ray exposures for the LIGA process. These have included components for a mechanical milliengine design and electrodes for use in electrodischarge machining (EDM). The milliengine consists of a variable reluctance device (Figure 1). Magnetomotive force is created in coils mounted on horseshoe-shaped ferrite pieces attached below the engine substrate. The reluctance in the air gaps dominates the circuit. One air gap varies with position (hence the term variable reluctance device) and the other is constant. All components for this milliengine design were fabricated using LIGA except for the motor coils that were machined from Hiperco. Five different x-ray masks (3 inch Si-wafers with patterned gold) were used to mold thirty different parts including stators, actuators, drive arms, gears and associated connectors. These components have thicknesses ranging from 200 μm to 500 μm and were electroplated from nickel, copper, and permalloy (nickel-iron). The magnetic circuit includes the coil, horseshoe ferrite, the shuttle, the stator, and to air gaps.

The electrode project consisted of components for an AGIE micro sinker electro discharge machine (EDM) used at Sandia, New Mexico. The coupling of the precision of the LIGA technique to the final part and materials that cannot be electroplated, such as Kovar and stainless steel, resulted in the fabrication of copper electrodes for use in the EDM production of a neutron tube screen presently manufactured using chemical milling. 1mm thick PMMA resist was exposed using the pattern of the electrode design to produce molds that were electroplated with Cu-metal (Figures 2 & 3).

Figure 1. Top view of assembled milliengine. The diameter of the output gear is 12 mm

Figure 2. EDM plunge electrode electroplated in copper 1 mm thick X 15 mm diameter. The circular arrangement of pads produces a mesh for the neutron tube design.

Figure 3. Close-up of the EDM electrode showing individual pads that produce screen openings in Kovar sheet for the neutron tube part.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC0494AL85000.

Jet Propulsion Laboratory:

Wave Guides:

JPL has undertaken the task of fabricating wave guides using the LIGA process for high frequency applications ranging from 640 GHz to 4.5 THz. Each application requires high aspect

ratio metal grid structures to be fabricated with active areas ranging from about 0.25 cm² to over 4 cm² with metalized thickness up to about 0.5 mm. The 640 GHz device will be incorporated into NASA's Earth Observing System-Millimeter Limb Sounder (EOS-MLS) which will perform atmospheric spectroscopy. LIGA has proved to be a superior technique for the fabrication of waveguides as it allows very straight sidewalls with high aspect ratios unavailable using other available techniques such as deep trench reactive ion etching or thick film UV photo lithography.

X-ray Collimating Grids:

JPL is fabricating 34 μ m and 58 μ m pitch X-ray collimating grids for the High Energy Solar Spectroscopic Imager (HESSI) to be launched in July 2000 (Figure 4). This instrument is designed to perform imaging of the Sun in the range of soft X-rays through Gamma rays with a spatial resolution of 2 to 10 times better than has previously been available. The technology to fabricate these grids was a direct outgrowth of the X-ray mask process developed to fabricate LIGA masks. Using this technology allowed the mission cost to be reduced by nearly an order of magnitude without significant reduction in the science to be performed.

Figure 4. 34 μ m pitch, 70 μ m thick, Gold X-ray collimating grid mounted on Monel ring with 100 μ m thick Beryllium backing wafer attached

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Modification of the Local Structure of Ga in Amorphous Silicon by Synchrotron X-ray Irradiation

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INTRODUCTION

Achieving high efficiency n- and p-type doping in amorphous silicon materials (a-Si) has been reported to be difficult. According to the “8-N” rule proposed by Mott in 1975, the dopant element in covalent amorphous semiconductors takes on its natural coordination.¹ Consequently group III (B, Ga) and V (P, As) elements will not contribute free holes or electrons in a-Si, suggesting that substitutional doping cannot be realized in covalent amorphous semiconductors.

Experimental evidence for n- and p-type doping (with much lower doping efficiency than crystalline Si) by the incorporation of phosphorus and boron in hydrogenated amorphous silicon (a-Si:H) over a wide resistivity range^{2,3} indicates that at least a small fraction of these impurities are tetrahedrally coordinated in a-Si:H. Street proposed an autocompensation model which suggested that doping in a-Si:H can only occur in the presence of gap states that maintain ionized donor levels.^{4,5}

Recently, we have studied the effects of intense x-ray irradiation on the structure and the crystallization of amorphous Si films.⁶⁻⁹ Our results strongly suggest that a-Si structures are unstable and when irradiated by large x-ray doses, the unstable amorphous network can locally rearrange to a relaxed configuration through the excitation of the sp³ and sp²-like bi-stable dangling bond.¹⁰ In this paper, we report the modification of the local bonding structures, with the aim to increase the doping efficiency of Ga dopants in both hydrogenated (a-Si:H) and hydrogen-free amorphous silicon (a-Si) thin films by exposing the samples to high x-ray doses generated by a synchrotron source.

EXPERIMENT

Hydrogen free and hydrogenated a-Si thin films (~2μm) were deposited on oxidized Si wafers by dc reactive magnetron sputtering of a Si target and plasma enhanced chemical vapor deposition (PECVD) methods, respectively. The hydrogen content in the a-Si:H films was determined to be ~8 at. % by the elastic recoil detection method. Both types of films were grown on thermally oxidized silicon wafers. Ga ions were implanted into the a-Si and a-Si:H thin films with multiple energies (550 keV to 2.1 MeV) creating a relatively uniform Ga distribution of ~1x10²⁰cm⁻³ throughout the 2 μm films.

The Ga implanted samples were irradiated with intense x-rays at beamline 3.3.2 at the Advance Light Source (ALS) at the Lawrence Berkeley National Laboratory. The peak x-ray energy delivered to the beamline was ~4.0 keV. The total x-ray dose was 4.6x10³ mA-min., corresponding roughly to 1 photon/Si atom. It has been concluded from our previous study that this x-ray dose results in a maximum relaxation in a-Si thin film.⁹

EXAFS measurements were carried out at 20K using beamline 4-3 at the Stanford Synchrotron Radiation Laboratory. The Ga K_{α} fluorescence signals from the implanted films were collected by a 13-element Ge x-ray spectrometer. The raw EXAFS data were analyzed by the SPLINE and XFIT code¹¹ using backscattering amplitudes and phase shifts determined from ab-initio calculations (FEFF4.0).¹²

RESULTS AND DISCUSSION

Fig. 1 shows the back-transformed EXAFS isolated for the nearest neighbor (NN) for Ga implanted a-Si and a-Si:H (without x-ray treatment). The difference of the two EXAFS curves as well as the root mean square (RMS) noise of the EXAFS data are also plotted in Fig. 1. Fig. 1 clearly shows that the difference curve exceeds the RMS noise level up to $k = 9 \text{ \AA}^{-1}$ indicating a substantial difference in the structure of the NN around the Ga atoms in the hydrogenated and hydrogen-free samples. Structural parameters obtained by fitting the EXAFS curves using the XFIT code are listed in Table I. The structural parameters for a Ga in c-Si taken from reference 13 are also included in the Table for comparison. The high σ^2 value for the c-Si:Ga is due to thermal vibration since these data were taken at room temperature. We have also performed EXAFS on crystalline GaP standard at 20K and found that the $\sigma^2 = 0.024 \text{ \AA}^2$.

Significant differences in the structural parameters between the Ga impurity in a-Si and a-Si:H are observed. First, we notice that the $R_{\text{Ga-Si}}$ is slightly shorter in the hydrogenated sample (0.8%). The Ga CN in both the a-Si and a-Si:H samples are less than four, indicating only a fraction of the Ga atoms are occupying a tetrahedral doping site while the rest assume threefold alloying sites. Since hydrogen has a negligible scattering cross section, it effectively reduces the Ga CN in the a-Si:H sample. Assuming that the hydrogen in the a-Si:H are randomly distributed, we calculate the fraction of tetrahedral Ga in a-Si and a-Si:H from the Ga CN measured by EXAFS to be 46% and 64%, respectively. Moreover, we observe that the mean square displacement of the bondlength σ^2 for the a-Si:H sample is smaller than that in the a-Si

Fig.2 A comparison between the EXAFS oscillations from the Ga implanted a-Si and a-Si:H thin films. The difference curve between the two EXAFS spectra and the RMS noise level curve are also shown in the figure.

Table I. A summary of the structural parameters, bondlength $R_{\text{Ga-Si}}$, coordination number CN and Debye-Waller factor σ^2 , extracted from the EXAFS data for the Ga implanted a-Si and a-Si:H samples with and without x-ray treatment.

Sample	x-ray treatment	$R_{\text{Ga-Si}}$ (Å)	CN	σ^2 (Å ²)
a-Si	No	2.414 ± 0.002	3.46 ± 0.3	0.0050 ± 0.0009
	Irradiated	2.407 ± 0.003	3.80 ± 0.4	0.0059 ± 0.0012
a-Si:H	No	2.395 ± 0.002	3.35 ± 0.23	0.0041 ± 0.00065
	Irradiated	2.405 ± 0.002	3.82 ± 0.2	0.0054 ± 0.00045
c-Si:Ga	--	2.38 ± 0.01	4.2 ± 0.5	0.004 ± 0.0004

sample suggesting that the hydrogen reduces the static disorder in the amorphous structure. Most obvious is the longer $R_{\text{Ga-Si}}$ and larger σ^2 in a-Si and a-Si:H as compared to c-Si. The longer $R_{\text{Ga-Si}}$ of a-Si results in the lower density of the amorphous material while the larger σ^2 comes from the larger inherent structural disorders incorporated in amorphous structures.

The effects of x-ray irradiation on the local structure of the Ga atoms in a-Si and a-Si:H are shown in Fig. 2. The difference between in the EXAFS of samples with and without x-ray exposure is readily observable. Structural parameters obtained by fitting the EXAFS oscillations listed in Table I show that after x-ray exposure, all of the structural parameters, $R_{\text{Ga-Si}}$, CN and σ^2 for the a-Si sample are similar to those of the a-Si:H. This suggests that while the local structure around the Ga atoms in a-Si:H and a-Si varies substantially, x-ray excitations modified this variation and transforms it into a structurally similar state with $R_{\text{Ga-Si}} \approx 2.405 \text{ \AA}$, $\text{CN} \approx 3.8$ and $\sigma^2 \approx 0.0055 \text{ \AA}^2$.

In particular, the Ga CNs in the a-Si and a-Si:H samples increase by 10 and 14%, respectively after x-ray irradiation. For the a-Si sample, this corresponds to 80% of the Ga atoms in tetrahedral sites, more than a 70% increase in fourfold coordination. In the case of the a-Si:H, the increase in Ga CN due to x-ray excitations is even more pronounced (from 3.35 to 3.82). Such increase four-fold coordination for Ga in a-Si materials suggests that electrical activation can be improved by x-ray exposure.

SUMMARY

In summary we have determined that hydrogen in a-Si reduces the static disorder of the local structures around the Ga atoms. High dose x-ray irradiation modified the Ga local structures in both the a-Si and a-Si:H samples. In particular the Ga coordination increases from <3.5 to ~ 3.80 in both hydrogenated and H-free a-Si, suggesting that x-ray excitation promotes tetrahedral bonding of Ga atoms in a-Si. Moreover we also observed more structural disorder around Ga after x-ray treatment, suggesting that fourfold coordinated Ga is less ordered than Ga on the threefold coordinated sites.

Fig.3 The EXAFS spectra from the Ga implanted a-Si and a-Si:H samples as-implanted and after x-ray treatment. The difference and RMS noise curves are also shown.

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Beamline 4.0.1-2 Abstracts

First Light At Beamline 4.0.1-2, the Elliptically Polarizing Undulator Beamline for Magnetic Spectroscopy

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INTRODUCTION

The Advanced Light Source has designed and is installing a new beamline, Beamline 4.0.1-2, which has been optimized for performing high resolution spectroscopy of magnetic materials. This beamline has an elliptically polarizing undulator (EPU) which can directly produce elliptically polarized x-rays, including both left and right circularly polarized radiation as well as horizontally and vertically linearly polarized x-rays. This undulator source is coupled to a high resolution plane grating monochromator providing a photon source size-limited resolving power of 5000-9000 in the energy range from 100 eV to 1500 eV. Finally, the beamline has a flexible end station system which will accommodate several end stations simultaneously.

BEAMLINE STATUS

Throughout the year significant progress was made in the construction and installation of the beamline. Important milestones, such as the installation of the mirror switchyard (the first beamline optics), were achieved early in the year. The front end was installed in August, and in September the insertion device was installed. On September 29, 1998, we achieved first light, delivering linearly polarized x-rays to a diagnostic chamber between the entrance slit and the main monochromator vessel. All optical elements have been procured and are awaiting installation. The end station system has also been installed. This system features removable experiment carriages which are coupled to a rotating stage. This arrangement will allow experiments to be prepared off-line and quickly attached to the beamline. It also provides for multiple end stations to be attached to the beamline simultaneously, which will enable rapid switchover between experiments.

Figure 1. Schematic diagram of the Beamline 4.0.1-2. This beamline features an elliptically polarizing undulator and a high resolution variable included angle monochromator.

FUTURE WORK

Commissioning and checkout of the beamline has already begun, with preliminary evaluation of the undulator and beamline stability and performance underway. In the coming year we shall complete the installation of the monochromator, which has been delayed due to the manufacturing problems of an outside vendor. However, we anticipate the completion of the beamline in the summer of 1999, with user operations to commence in the fall.

Figure 2. First light at BL4.0.1-2, observed at a diagnostic chamber downstream of the entrance slits.

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Beamline 5.0.2 Abstracts

A Structural Analysis of Directed Evolution Products

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Directed evolution provides a powerful tool to answer biochemical questions involving many aspects of protein stability and function. It allows the experimenter to rapidly and simultaneously screen sequence, structure, and function space for mutant proteins with desired characteristics. Gene shuffling and ensures that all or most silent or deleterious mutations are removed, resulting in mutant proteins where the role of each mutation is, presumably, significant and instructive as a biochemical solution as a defined environment. Rather than relying on sequence or structural alignments of proteins from different species, in which the bulk of the mutations may have arisen from genetic drift and be functionless, directed evolution allows investigation of the minimal sequence change necessary to produce the desired phenotypic change. Additionally, mutations favored in response to multiple different selection pressures can be investigated. This permits a structural view of evolutionary divergence in a setting where the selection pressure, startpoint, pathway, and endpoint are all well defined.

In work recently completed at the ALS, we determined the three dimensional structures of three para-Nitrobenzyl (PNB) esterases that were evolved to possess unique activities and biophysical characteristics. The structures were solved with phases determined from a 3 wavelength mercury MAD experiment performed on crystals of the organophile at the ALS. The MAD data were collected in less than 4 hours. In addition to allowing the experimenter to tailor the activity of an enzyme, directed evolution products present interesting targets for structural study. In this work, the structures of the products of two orthogonal screens, one for thermostability and one for organic activity, were determined. The organophile (56c8) is 100 times more active toward the p-nitrobenzyl ester of the antibiotic loracarbef (pNB-LCN) in 25% dimethylformamide than the wild type enzyme, and the thermophile (8g8) is 17 °C more stable than wild type. Structural analysis reveals these characteristics to be the result of groups of interacting mutations that rigidify surface loops and reshape the active site of the serine hydrolase.

pNB esterase is a 489 amino acid α/β protein of composed of a central 13 stranded Beta sheet surrounded by 15 alpha helices. The evolved proteins are very similar to the wild type with root mean squared deviations of 0.67 Å and 0.44 Å for the organophile and thermophile respectively. The most striking changes occur in four surface loops (66-74, 265-275, 315-324 and 414-420) that form the entrance to the active site as well as forming a face of the active site cavity.

Shown at right is a ribbon diagram of the recently solved pNB esterase. The structure is viewed looking into the active site cavity. The

structure is colored by RMSD showing regions that reorganize substantially in red and regions that are unaffected by the selection pressure in blue. Two loops that are not structured in the wild type but well ordered in 56c8 and 8g8 are shown as dashed lines. The side chains of the catalytic triad are shown in light blue.

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Crystal structure of a repeating superhelix motif in the clathrin triskelion leg

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INTRODUCTION

Clathrin is a triskelion-shaped cytoplasmic protein that polymerizes into a spherical, polyhedral lattice on intracellular membranes (Fig. 1a)[1]. This reversible self-assembly process is required in the formation and turnover of protein-coated vesicles that mediate protein sorting during endocytosis and intracellular organelle biogenesis. The clathrin triskelion is a trimer of three heavy chain subunits (1675 amino acids/subunit), each folding into a filamentous leg and capable of binding a single light chain subunit (Fig. 1b). Polyhedron formation involves interactions over the entire filamentous portions of the clathrin triskelion leg (residues 331-1522). To understand the molecular basis of clathrin self-assembly and its regulation, we have determined the crystal structure of residues 1210-1516 of the clathrin heavy chain to 2.6Å resolution. This segment typifies the structure of the whole triskelion leg and, in addition, comprises an important assembly control region of clathrin.

STRUCTURE DETERMINATION

A 55kDa region of bovine clathrin heavy chain spanning residues 1074-1522 was expressed as a selenomethionine-substituted protein in *E. coli* with an N-terminal polyhistidine tag for purification. The structure was determined by multiwavelength anomalous dispersion (MAD). A 4-wavelength MAD data set was collected from a single crystal (tetragonal space group I4122, one molecule per asymmetric unit) of selenomethionine-substituted clathrin heavy chain fragment (aa1074-1522) on beamline 5.0.2. The crystal was maintained at 100 K using an Oxford Cryostream, and data were collected in 1° oscillations using a 188mm x 188mm

Quantum-4 CCD detector system. 26124 unique reflections were measured, representing 72% completeness in the 30-2.5Å resolution range. The merging R-factor was 5%. Experimental phases produced a high-quality electron density map that was improved by density modification and phase combination. A molecular model of residues 1210-1516 was built into this map and refined to an R-factor of 24% and a free R-factor of 27% at 2.6Å resolution. The N-terminal residues 1074-1209 and C-terminus 1517-1522 are not included in the structural model, due to the

Figure 1. Organization of the clathrin polyhedron and triskelion. A, Portion of the clathrin polyhedron lattice [2], with a triskelion centered at each vertex. Two neighboring triskelions are colored red and blue. Yellow indicates portion of the proximal domain determined in crystal structure. B, Model of a single clathrin triskelion, formed by three heavy chains. Pink, TXD, the trimerization domain; dark gray, globular N-terminal domain.

Figure 2. The three-dimensional structure of residues 1210-1516 in the clathrin heavy chain. Shown in two views related by 90° rotation about the length of the coil. Vertical segments demarcate the regions of clathrin repeats CHCR5, CHCR6 and CHCR7. Top, Ribbon diagram, viewed on the helix face. Yellow and green distinguish helices of separate faces. The "hairpin edge" is along the top of this view. Below, Cylinder representation, viewed on the hairpin edge, showing the relative orientation of individual helices, referred to as labeled. Gray cylinders indicate axes of helices 5c, 5d, and 5e, identified in the electron density map, but whose side chains could not be assigned. Red and blue side chains indicate acidic and basic salt bridge partners, respectively.

absence or poor quality of electron density in these regions of the map. Coordinates for the model have been submitted to the Brookhaven Protein Database (PDB code: 1b89).

A RIGHT-HANDED SUPERHELIX

The structural model of residues 1210-1516 in the clathrin heavy chain reveals a highly elongated structure composed entirely of short α -helices connected into a right-handed superhelix coil (Fig. 2). The α/α coiled fold is generated by stacking fundamental structural units of paired antiparallel α -helices joined by a hairpin turn. The canonical helical hairpin unit (helix-turn-helix-loop-) is 29 residues long, each helix of which averages 11 residues, or 3.5 turns. Ten complete helical hairpins (helices 5g-7f) plus helix 5f comprise the refined model. The electron density map identifies three more helices (5c, 5d, 5e), although this region of the map does not permit more detailed modeling.

Analysis of clathrin heavy chain sequences using the generalized profile method revealed a divergent but statistically significant repeat structure of the distal and proximal leg regions. Seven complete repeats (designated CHCR1-CHCR7) were found over the triskelion leg (residues 537-1566), suggesting a conservation of structural features throughout the leg. CHCR6 plus portions of CHCR5 and CHCR7 are represented in the solved crystal structure.

The organization of the helices within the repeat motif (e.g., CHCR6) may be described as "2+4+4," a single helical hairpin unit (*a* and *b*) followed by two sets of four-helix bundles (*cdef*, *ghij*). Almost all the conserved residues in the clathrin repeat are involved in helix

Figure 3. Ribbon structural model of the clathrin heavy chain leg domains, based on crystallographic identification of a repeated superhelix motif. Each of the seven repeat units is represented in a different color. The region of the solved crystal structure is indicated in space-filled representation.

packing and formation of the hydrophobic core, contributing to stability of the isolated filament. Furthermore, the distribution of conserved residues in helices *c*, *d*, *e*, and *f* suggests that the central helix bundle may be an invariant feature of the clathrin repeat.

Together the structural and sequence alignments predict that the entire filamentous portion of the clathrin triskelion leg is formed by a continuous superhelix comprised of clathrin repeats as defined here. The seven clathrin repeats making up the leg (residues 537-1566) predict that 70 helices fold into a 400Å long superhelix coil, stretching from the linker region at the N-terminal domain to the triskelion vertex (Fig.3). The uniform thickness and linear density of clathrin triskelions observed in electron micrographs [2] also suggest that the superhelix coiling of α -helices extends beyond the region of the seven aligned repeats and in fact may even provide the framework for trimerization interactions.

The distinguishing features of the clathrin superhelix (straightness and generally flat helix faces) likely have a functional impact on assembly. In particular, the superhelix may need to be straight with a slight twist in order to promote face-to-face interaction during self-assembly (Fig. 1a). In continuing studies, we hope to illuminate these and other features of regulated clathrin polymerization.

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Crystal structure of CheA, the histidine kinase central to bacterial chemotaxis.

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INTRODUCTION

CheA, a representative histidine kinase, is a cytoplasmic central component of signal transduction pathways that allow bacteria to sense and respond to their environment [1, 2]. Most bacteria are able to swim by rotating their helical flagella. When the flagellar bundle rotates counterclockwise the bacterium swims smoothly. Switching to clockwise rotation results in a reorientation (tumbling) of the bacterium. The signaling circuit that controls the switching consists of transmembrane chemoreceptors that through an adaptor protein CheW regulate the histidine auto-phosphorylation of the multi-domain CheA protein. CheY obtains the phosphate from CheA and becomes the signal to change the direction of flagellar rotation.

RESULTS AND DISCUSSION

We recombinantly expressed *Thermotoga maritima* CheA Δ 289 [3] (residues 290-671) which lacks the two amino terminal domains, P1 and P2. CheA Δ 289 phosphorylates the fragment composed of *T. maritima* P1 and P2 *in vitro* (data not shown). In solution, CheA Δ 289 forms a complex with recombinant *T. maritima* CheW and the two proteins copurify. Thus, CheA Δ 289 is enzymatically active and retains substrate specificity and binding to CheW.

We determined the crystal structure of CheA Δ 289 at 2.6 Å resolution by combining experimental phases (Table 1 and 2) from multiple isomorphous replacement (MIR) with phases from multiwavelength anomalous diffraction (MAD). Synchrotron radiation was essential to this project as our crystals did not diffract beyond 3.6 Å using a rotating anode as a source of X-rays.

Dimeric recombinant wild type CheA Δ 289 and mercury-modified mutants Q545C and E387C produced crystals suitable for structure determination (Table 1). Crystals of mercury-modified Q545C diffracted better than wild type CheA Δ 289 and were highly isomorphous with unmodified Q545C (Table 1). MAD data collected at ALS beamline 5.0.2 on mercury-modified and seleno-methionine substituted CheA Δ 289 was essential for structure determination. Anomalous diffraction from the seleno-methionine containing protein crystals was used to locate 20 methionines in the electron-density map and aided the definition of the non-crystallographic symmetry and the tracing of the model. Cycles of model-weighted phase combination, manual rebuilding with interactive graphics, and reciprocal space refinement produced the final structure. Our 2.6 Å resolution refined model of mercury modified CheA Δ 289 Q545C (R-factor of 21.3%; R-free 28.5 %) includes a non-symmetric dimer of residues 293-671, 2 mercury atoms, 221 water molecules, and displays reasonable geometry.

Table 1. Native and derivative data statistics.

Data set	Resolution* (Å)	R-sym # (%)	I/σ(I) [‡]	Completeness (%)	Reflections Unique Observed	Wave length (Å)	sites
545Hg	2.6(2.7-2.6)	6.8(34.4)	21.2(3.2)	92.6(79.5)	33278 93352	1.08	2
545	2.5(2.6-2.5)	3.9(28.9)	16.9(2.9)	78.5(67.5)	31655 57757	1.08	2
387Hg	3.2(3.3-3.2)	5.4(26.9)	17.2(4.8)	84.4(78.0)	16572 31820	1.08	2
Hg3	2.7(2.8-2.7)	6.1(31.6)	25.4(7.6)	93.8(97.1)	31863 170975	0.946	2
Seleno 545	2.5(2.6-2.5)	6.2(29.6)	37.2(8.5)	98.2(98.9)	40131 196467	0.979	20
Hg4 peak	2.7(2.8-2.7)	3.9(30.7)	19.4(5.7)	93.2(95.1)	29593 76121	1.001	2
Hg4 inflection	2.6(2.7-2.6)	5.8(28.3)	18.5(5.0)	92.5(95.7)	32719 80860	0.999	2
Hg4 high remote	2.7(2.8-2.7)	5.5(29.1)	17.9(5.5)	92.8(95.0)	29847 73990	0.946	2

545Hg, Hg3, Hg4 represent different data sets of CheAΔ289 Q545C soaked in HgCl₂; 387Hg represents CheAΔ289 E387C co-crystallized with EMTS; and Seleno 545 represents selenomethionine CheA Δ289 Q545C. The crystal Hg4 was used for the collection of MAD data.

*Highest resolution of data set followed by resolution range in highest bin for compiling statistics.

[#]Rsym=ΣΣj |I_j-⟨I⟩|/Σ(I), I=intensity, [‡]I/σ(I)=signal-to-noise. The 3 first data sets were collected at SSRL beamline 7-1 on a 30 cm Mar Research Image plate detector; the others were collected at ALS beamline 5.0.2 on a CCD 2x2 quantum detector.

Table 2. MIR & MAD phasing statistics.

	Resolution (Å)	Phasing power iso* ano**	Riso (%)	Rcen (%)	RK (%)	Anomalous ratio	Dispersive Ratio (vs inflection)	Figure of merit (2.8Å)
545	2.8	2.18	15.8	52.2				MIRAS 0.56
387Hg	3.5	1.03	0.87	39.2	69.3	4.6		
Hg3	2.8		2.30	15.0	16.6	4.8		
545Hg anomalous	3.5		1.59		17.2	4.3		
Hg4 inflection	2.8					4.1		MAD 0.47
Hg4 peak	2.8					4.9	9.8	
Hg4 high remote	2.8					5.1	10.6	
Combined	2.8							0.67

MIR statistics are calculated with 545Hg as the reference data set.

*Phasing power iso = ⟨|FH|⟩/⟨E⟩ where |FH| is the calculated heavy atom structure factor amplitude and E is the lack of closure error. **Phasing power ano = ⟨2|FH''|⟩/⟨E⟩ where |FH''| is the anomalous correction component amplitude. Riso = ΣΣj ||F_j| - ⟨|F|⟩| / Σ⟨|F|⟩. Rcen = Σ||FPH| - |FPI| - |FH|| / Σ||FPH| - |FPI|| for centric reflections of isomorphous derivatives.

RK = Σ||FPH*| - |FPHcalc*|| + ||FPH*| - |FPHcalc|| / ||FPH*| + |FPH| for anomalous scattering.

Anomalous ratio = rms||F*| - |F|| / rms F. Dispersive ratio = rms||F_{λ1}| - |F_{λ2}|| / rms F, rms=root mean square.

The crystal structure of CheA (residues 290-671) histidine kinase reveals a dimer (Figure 1) where the functions of dimerization, ATP-binding, and regulation are segregated into domains. The kinase domain is unlike Ser/Thr/Tyr kinases but resembles three ATPases: GyraseB [4], MutL [5] and Hsp90 [6]. Structural analogies within this superfamily suggest that the P1 domain of CheA provides the nucleophilic histidine and activating glutamate for phosphotransfer. CheA (dimerization and kinase domains) is also topologically similar to the dimeric phosphotransferase Spo0B [7]. However, the kinase-like domain in Spo0B is much shorter than the kinase domain in CheA and lacks all of the residues involved in binding ATP. The topological similarity between CheA and Spo0B shows that signal transduction circuits in bacteria have derived different functions from similar structural modules.

The CheA regulatory domain, which binds the homologous receptor-coupling protein CheW, topologically resembles two SH3 domains and provides different protein recognition surfaces at each end. The CheA dimerization domain forms a central 4-helix bundle about which the kinase and regulatory domains pivot on conserved hinges to modulate trans-phosphorylation. Different subunit conformations suggest that relative domain motions link receptor response to kinase activity.

Figure 1. Overall structure of the CheA₂₈₉ dimer

The 2 subunits (blue for MOL1, gray for MOL2) of the CheA dimer (shown as ribbon diagram) each contain separate dimerization, kinase, and regulatory domains. The dimer associates by a central 4-helix bundle and places the 2 ATP binding sites (located by the G-boxes) 90 Å away from each other.

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Crystal structure of human cytosolic phospholipase A₂ reveals a novel topology and catalytic mechanism

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Cytosolic phospholipase A₂ initiates the biosynthesis of prostaglandins, leukotrienes, and platelet-activating factor (PAF), mediators of the pathophysiology of asthma and arthritis. Here we report the x-ray crystal structure of human cPLA₂ at 2.5 Å solved using multiwavelength anomalous dispersion (MAD) phasing. cPLA₂ consists of an N-terminal calcium-dependent lipid binding/C2 domain and a catalytic unit whose topology is distinct from that of other lipases. An unusual Ser-Asp dyad located in a deep cleft at the center of a predominantly hydrophobic funnel selectively cleaves arachidonyl phospholipids. The structure reveals a flexible lid which must move to allow substrate access to the active site, thus explaining the interfacial activation of this important lipase.

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Crystal structure of NGF in complex with the ligand-binding domain of the TrkA receptor

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INTRODUCTION

Nerve growth factor (NGF) is the best characterized member of the neurotrophin family, which is involved in a variety of signaling events such as cell differentiation and survival, growth cessation, and apoptosis of neurons [1]. These biological functions are mediated through binding to two classes of cell-surface receptors, the Trks and p75 [2]. TrkA is a receptor tyrosine kinase and binds to NGF with high affinity [3]. Of the five domains comprising its extracellular portion, the immunoglobulin-like domain proximal to the membrane (TrkA-d5) is necessary and sufficient for NGF binding [4]. We have determined the crystal structure of human NGF in complex with human TrkA-d5 at 2.2 Å resolution, using data collected at the Berkeley Advanced Light Source.

RESULTS AND DISCUSSION

The asymmetric unit of the crystals contains one complex consisting of two NGF monomers that assemble in a parallel arrangement to form the active dimer and two copies of TrkA-d5. Overall, the NGF dimer is similar to the structure of mouse NGF solved by McDonald *et al.* [5], but the N-terminal segment undergoes a major change upon receptor binding (below). TrkA-d5 folds into an immunoglobulin-like domain of the I-set family [6], consisting of a β -sandwich with two four-stranded β -sheets (ABED and CC'FG). It is noteworthy that this domain has several unexpected structural features, such as an unusual conformation of the AB loop and a disulfide bridge exposed at the surface of the ABED sheet.

Each interface between NGF and TrkA-d5 buries a total of about 2200 Å² of solvent-accessible surface. The interface can be divided into two patches of similar size. One patch involves the central β -sheet that forms the core of the homodimeric NGF molecule and the loops on the C-terminal pole of TrkA-d5, including the unusual AB-loop. The residues comprising this patch are largely conserved, both among the neurotrophin ligands and among their receptors. We believe this patch is utilized for complex formation by all members of the family. The second patch consists of the N-terminal residues of NGF, which were disordered in the previously reported structures of NGF [5] but adopt a helical conformation upon complex formation, packing against the disulfide bond at the surface of the ABED sheet of TrkA-d5. The residues in this patch are poorly conserved among ligands as well as receptors; furthermore, swaps of the N-

terminus of the ligands have resulted in bi-specific neurotrophins able to bind to and signal through several receptors [7]. Therefore, this second patch controls the specificity among the family members. The structure is consistent with the mutagenesis data not only for NGF but also for the other ligands in the neurotrophin family [8,9]. Thus, in contradiction to current belief that these ligands interact with their receptors in different binding modes [10], our structure strongly suggests that the overall manner of binding is conserved throughout the family.

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Crystal Structure of the ATP-binding Subunit of an ABC Transporter

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INTRODUCTION

ATP-binding cassette (ABC) transporters (also known as traffic ATPases) form a large family of proteins responsible for movement of biochemical compounds through cell membranes. Members of the ABC transporter superfamily are widely found in prokaryotes and eukaryotes. Among the eukaryotic members, several are medically important proteins, such as the cystic fibrosis transmembrane conductance regulator (CFTR), the P-glycoprotein (MDR: multi-drug resistance protein), and the transporter associated with antigen processing (Tap1/Tap2). ABC transporters have two highly conserved ATP-binding domains and two transmembrane domains [1]. We report the crystal structure at 1.5 Å resolution of HisP [2], the ATP-binding subunit of the histidine permease, an ABC transporter from *Salmonella typhimurium*, and correlate the crystal structure of HisP with the biochemical, genetic, and biophysical properties of the wild type and of numerous mutant HisP proteins as well as with the properties of mutant CFTR and MDR proteins.

RESULTS AND DISCUSSION

HisP crystallizes in space group P4₃2₁2 with cell parameters 67×67×149 Å. The crystal structure of HisP was determined by four-wavelength Multiple Anomalous Diffraction experiment [3] conducted at ALS beamline 5.0.2. The current model contains residues 5 to 262 of HisP_(his6), one ATP, three possible anions modeled as Cl⁻, and 322 solvent molecules. The overall shape of the crystal structure of the HisP monomer is that of an "L" with two thick arms (arm I and arm II, Fig. 1); the ATP-binding pocket is near the end of arm I (Fig. 2). A six-stranded β-sheet spans both arms of the "L" with a domain of α + β type on one side (within arm I) and a domain of mostly α-helices on the other side (within arm II) of the sheet. The overall fold of the structure is different from that of any known protein. However, the topology of the ATP binding pocket is close to that of RecA [4] and of the α- and β-subunits of bovine F1 ATPase [5]. In agreement with the notion that HisP forms a dimer *in vivo*, a dimer consisting of two monomers related by a two-fold axis is also found in the crystal structure of HisP (Fig.1). All available biochemical data about HisP in the HisQMP₂ complex are compatible with the characteristics of HisP in the crystal structure. The structure of HisP provides a basis for understanding properties those of defective CFTR proteins. This kind of information may eventually lead to a treatment for cystic fibrosis. Moreover, the ability to correlate the

properties of CFTR mutants with the crystal structure of HisP indicates that HisP is a good model for the nucleotide-binding domains of ABC transporters in general.

Figure 1. View of the HisP dimer along an axis perpendicular to its two-fold axis. The thickness of arm II is about 25Å, comparable to that of membrane.

Figure 2. The crystal structure of HisP. This is a view of one monomer from the bottom of arm I, as seen in Figure 1, towards arm II, showing the ATP-binding pocket. The protein and the bound ATP are in "ribbon" and "ball-and-stick" representations, respectively. The N- and C- termini of HisP are indicated.

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Crystal Structure of the Envelope Glycoprotein GP2 from Ebola Virus at 1.9 Å Resolution

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INTRODUCTION

Ebola viruses are nonsegmented, negative-strand RNA viruses which, together with Marburg viruses, constitute the family *Filoviridae*. The most pathogenic subtype (Zaire) of Ebola virus causes a severe form of hemorrhagic fever in humans and nonhuman primates. Ebola virions possess a single surface transmembrane glycoprotein (GP) that plays a central role in entry into target cells by binding to as yet unidentified receptors, and then mediating fusion between the viral and the host cell membranes. GP is expressed as a single chain precursor of 676 amino acids that is posttranslationally processed into the disulfide-linked fragments GP1 and GP2. The first subunit is responsible for binding to cell-surface receptors, while the second subunit is responsible for mediating membrane fusion.

We produced a 95 amino-acid residue fragment of GP2, corresponding to the ectodomain without the amino-terminal fusion-peptide region¹. After establishing the correct disulfide connectivity in the region of the fragment that corresponds to the retroviral immunosuppressive motif (by characterizing disulfide variants of the ectodomain), limited proteolysis experiments were used to identify a proteolytically resistant core of the ectodomain. This 74 amino acid core (referred to as Ebo-74) was crystallized and the X-ray crystal structure was determined at 1.9 Å resolution¹. While our crystal structure was being refined, the structure of a similar fragment of Ebola GP2, fused to a trimeric coiled coil, was reported at 3.0 Å resolution². Our results are in overall agreement with the structure of this fusion protein, and they confirm the remarkable structural similarity between the core of the Ebola GP2 protein and the X-ray crystal structure of the corresponding core from the Mo-MLV TM protein (Mo-55) that had been anticipated earlier³.

MATERIALS AND METHODS

Well-diffracting crystals of Ebo-74 were grown as described¹. Crystals grew as hexagonal bipyramids to a maximum size of 0.1 mm x 0.1 mm x 0.2 mm within 1 - 2 weeks. The crystals belong to the space group P6₂ (or P6₄, a = b = 75.66 Å, c = 67.94 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and contain one trimer in the asymmetric unit, wherein monomers are related by an approximate non-crystallographic three-fold axis¹.

For data collection, crystals were transferred to a drop containing reservoir solution plus 30-40% glycerol, harvested, and flash frozen. Diffraction data were collected at 100 K using a Quantum-4 CCD detector and the 5.0.2 beam line at ALS. The Ebo-74 crystal diffraction limits were improved and the mosaicity was decreased significantly by a cryo-annealing technique in which the crystal was repeatedly thawed for about 30 sec by blocking the cryostream and then frozen again. An elevated concentration of cryoprotectant to prevent ice formation was essential with this technique. Diffraction intensities were integrated using the DENZO and SCALEPACK software⁴, and reduced to structure factors with the program TRUNCATE from the CCP4 program suite⁵. The structure of Ebo-74 was solved by molecular replacement using the program AMoRe⁶. Solvent flattening, histogram matching and three-fold non-crystallographic averaging with the program DM⁷ improved phasing. Crystallographic refinement of the structure (Table 1) was done

Table 1. Data collection and refinement statistics¹

<i>Data collection</i>	
Resolution, Å	20.0 - 1.90
Observed reflections	86,630
Unique reflections	17,326
Completeness, %	98.9 (99.1) ^a
R _{merge} ^b	0.037 (0.309) ^a
<i>Refinement</i>	
Protein nonhydrogen atoms	1806
Water molecules	214
Heteroatoms (Cl ⁻)	1
R _{cryst} ^c	0.205 (0.239) ^a
R _{free} ^c	0.269 (0.319) ^a
RMSD from ideal geometry	
Bond lengths, Å	0.009
Bond angles, °	1.3
Dihedral angles, °	19.8
Average B-factor, Å ²	40.6

^aValues in parentheses correspond to highest resolution shell 1.93 to 1.90 Å.

^bR_{merge} = $\sum_j |I_j(hkl) - \langle I(hkl) \rangle| / \sum_j \langle I(hkl) \rangle$, where I_j is the intensity measurement for reflection j and $\langle I \rangle$ is the mean intensity over j reflections.

^cR_{cryst} (R_{free}) = $\sum |F_{obs}(hkl) - F_{calc}(hkl)| / \sum F_{obs}(hkl)$, where F_{obs} and F_{calc} are observed and calculated structure factors, respectively. No σ -cutoff was applied. 10 % of the reflections were excluded from refinement and used to calculate R_{free}.

terminal helices absent from the trial model. The quality of the map was further improved through noncrystallographic symmetry matrix refinement and solvent mask redefinition with the program NCSMASK⁵. An initial model of Ebo-74 was built based on this map and then refined to convergence¹.

As expected, Ebo-74 forms a homotrimer. Each of the three polypeptide chains folds into a helical-hairpin conformation, in which two antiparallel helices are connected by a loop region (Fig. 1). The N-terminal helices from each monomer form a central, three-stranded coiled coil. This coiled-coil core includes approximately 35 residues from each chain (the two most N-terminal residues are not well defined in the electron density maps and next two are in a random-coil conformation). Shorter C-terminal helices pack in an antiparallel manner into hydrophobic grooves on the surface of the coiled-coil core. In the loop region connecting the N- and C-terminal helices, a disulfide between Cys-601 and Cys-608 links a short α -helix and a short 3_{10} -helix. Additionally, the loop region between the 3_{10} -helix and C-helix are in an extended conformation. Due to asymmetric crystal contacts, the three individual chains in the Ebo-74 structure have slight differences in conformation and degree of order, with the B chain having a higher overall B-factor (43.1 Å²) than the A and C chains (37.7 and 37.1 Å², respectively). The RMSD between the individual chains in the Ebo-74 noncrystallographic trimer vary from 0.74 Å (chains A and C) to 1.31 Å (chains B and C)¹.

with the CNS⁸ and REFMAC⁵ programs. Non-crystallographic symmetry restraints were not used in the final refinement¹.

RESULTS

Although Ebo-74 contains significantly more residues than Mo-55³, and there is only 22% sequence identity between Ebo-74 and Mo-55, the overall similarities of these cores prompted us to attempt to solve the Ebo-74 crystal structure with a molecular replacement approach. A solution was found¹ using a trimeric polyserine model of Mo-55, with the loop regions omitted and a chloride ion retained in the core (i.e., the model contained only 36% of the atoms in the target structure). This solution became apparent after the fitting procedure in AMoRe (final correlation coefficient = 0.431 and R-factor = 0.484 in the resolution shell 10.0 to 4.0 Å), and it also resolved the ambiguity in space group determination in favor of P6₂. Initial phases, calculated from the correctly positioned model, were dramatically improved using three-fold averaging with DM. The initial DM-phased electron density map clearly revealed the structures of the omitted loops and of the C-

Figure 1. Ebo-74 forms a trimer-of-hairpins structure¹. (A) A side view of the Ebo-74 structure. N-helices (dark blue) constitute a central coiled coil and C-helices (red) pack into hydrophobic grooves on the surface of the coiled coil. Disulfides within the loop regions (light blue) are depicted in yellow. (B) Each monomer has an α -helical hairpin conformation.

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In the Ebo-74 structure, a strong X-ray scatterer binds between the adjacent rings of Ser-583 and Asn-586 residues. This density was identified as a chloride ion¹. The individual B-factor refinement of a modeled chloride ion converges at 24.1 Å²; the same value is obtained for the average B-factor of the interacting amide nitrogens of the Asn-586 residues. The average distance between the ion and the interacting nitrogen atoms is 3.28 Å, similar to the distances observed for chloride binding in other coiled coils and close to the sum of the van der Waals radii for NH₄⁺ and Cl⁻ (3.24 Å). If a chloride-binding site is common in other fusion glycoproteins with analogous architectures and can be substituted by bromide, the bromide complex would be an attractive target for MAD phasing experiments when molecular replacement methods fail to permit X-ray structure determination.

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Crystal structures of zinc-free and -bound heme domain of human inducible nitric oxide synthase

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INTRODUCTION

Nitric oxide synthases (NOS) are a family of enzymes that produce nitric oxide (NO) and L-citrulline from L-arginine in the presence of NADPH and O₂. NOS maintains a bi-domain structure with the catalytic center residing in the heme domain utilizing electrons derived from the cytochrome P450 reductase-like biflavin domain. The heme domain also contains the binding site for the enzyme cofactor, tetrahydrobiopterin (H₄B). The NOS family currently consists of three mammalian isoforms. The endothelial (eNOS) and neuronal (nNOS) isoforms are constitutive and are activated by Ca²⁺ - dependent calmodulin binding. The inducible (iNOS) entertains a tightly bound calmodulin subunit and is regulated at the level of transcription.

The structure of the eNOS heme domain revealed a novel zinc tetrathiolate (ZnS₄) at the bottom of the dimer interface [1]. In the structure of the heme domain of murine iNOS [2], a disulfide was identified in the Zn binding site and no Zn was seen in the structure. To understand the structural consequences of the metal center in other NOS isoforms, we have solved the crystal structure of human iNOS in both Zn-free and -bound forms.

METHODS

The human iNOS heme domain (residues 1-504) was cloned and expressed in *E. coli*. The protein sample (residues 74-504) used for crystallization was generated by trypsinolysis upon the purified iNOS heme domain. Rod shaped crystals were obtained using sitting drops in a sandwich box setup at 7°C with a protein concentration of 10 mg/ml. The reservoir solution contained 30 mL of 35% saturated ammonium sulfate, 30% (v/v) glycerol, 50 mM sodium citrate, pH 5.0. The solution used for setting up protein drops is identical to the reservoir solution except that 2.0 mM glutathione (GSH) and 10 mM L-Arg (or 1.0 mM S-ethyl-isothiouraea) were also present. The Zn-containing crystals were grown

with 5.0 mM ZnSO₄ and 2.5 mM tris-(2-carboxyethyl)phosphine added to replace GSH in the Zn-free condition. The same drop setup solution also served as the crystal storage and cryoprotectant reagent.

Crystals were flash cooled under a cold nitrogen stream (100 K) for data collection. The Zn-free data (3.0 Å) were collected using a Mar Research imaging plate on beamline 7-1 at SSRL and the Zn-bound data (2.55 Å) on a Quantum4 CCD detector on beamline 5.0.2 at ALS. Raw data were integrated and scaled with DENZO and SCALEPACK. Crystals were indexed in a primitive tetragonal space group P4₁2₁2 with cell dimensions a=b=187.25 Å, c=227.49 Å. The iNOS heme domain structure was solved by molecular replacement using the dimeric eNOS heme domain as the search model. The Zn-bound structure was refined using X-PLOR with final R = 0.209 and R_{free} = 0.243.

RESULTS AND DISCUSSION

As in the murine iNOS structure [2], the human iNOS structure also reveals a disulfide bond formed between symmetry related Cys 115 residues at the dimer interface. In sharp contrast, eNOS has a Zn ion tetrahedrally coordinated to pairs of symmetry related Cys 96 and Cys 101 residue [1]. The Zn binding motif, Cys-(X)₄-Cys, conserved in all known NOS isoforms to date, suggests that the physiologically relevant NOS structure has the Zn ion bound. The eNOS heme domain, which retains the Zn, was prepared by proteolysis from full-length recombinant eNOS whereas both the murine and human iNOS heme domains were expressed as the heme domain alone. Thus, we postulate that the presence of the reductase domain in the generation of eNOS heme domain may have aided in retaining the bound Zn.

If the Zn site is the "natural" form, then it should be possible to reconstitute the Zn site in iNOS. This was accomplished by simply adding Zn²⁺ in the presence of a strong reducing agent directly to the crystallization cocktail. The topology of the metal binding motif is nearly identical to that found in bovine eNOS. The Zn is located along the dyad axis of symmetry and is tetrahedrally coordinated to pairs of symmetry-related Cys residues. The Zn is equidistant from both H₄B molecules (~12 Å) and both heme iron atoms (21.8 Å). The strategically located metal center underscores its important structural roles that include maintaining the integrity of the pterin-binding pocket and possibly providing a docking surface. The electrostatic potential in the vicinity of the ZnS₄ of iNOS is positive and

similar to that observed in eNOS [1] and could provide a docking site for the negatively charged reductase domain.

A comparison of the Zn-free and -bound iNOS structures also illustrates the interplay between the Zn center and the pterin binding site. In the Zn-free human iNOS heme domain structure the formation of a disulfide between symmetry-related Cys 115 residues causes the peptide flip of Gly 117. This change, in turn, affects H₄B binding by weakening the H-bond between >C=O of Ser 118 and the pterin dihydroxypropyl side chain, which stretches to 3.3 Å from 2.7 Å in the Zn-bound structure. Therefore, it is not too surprising that replacement of the Zn Cys ligands with other residues through site-directed mutagenesis leads to weakened pterin binding as reported in the literature, most likely due to changes in pterin-protein interactions similar to that found by comparing the iNOS Zn-free and -bound structures.

Another role for the ZnS₄ is in maintaining dimer stability. In going from the Zn-free to the -bound state, there is a net gain of eight H-bonds which would contribute favorably to the free energy of dimer stabilization. Even though the Zn-free iNOS heme domain dimer has an intermolecular disulfide bond, the key H-bonds required to stabilize the structural elements in this region are absent. This argues for the inability of a disulfide to substitute for the Zn at the NOS dimer interface. In addition, strongly reducing conditions of the cytosol do not favor disulfide formation, further supporting the view that NOS utilizes Zn binding to amplify the conformational stability of the dimer interface.

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Crystallographic Studies of the Biologically and Medically Important Receptor-ligand and Enzyme-ligand Complexes at Advanced Light Source (ALS)

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INTRODUCTION

Our laboratory is focussed on understanding the structural basis of molecular recognition in the immune system, how cellular receptors interact with their ligands, and inhibition of medically important enzymes. To correlate their structure, function and interactions, we are investigating these molecules by x-ray crystallography. A synchrotron x-ray source at ALS offers an excellent opportunity to use small and weakly diffracting crystals and to obtain data with large unit cells. We have also conducted MAD (multiple anomalous dispersion) phasing experiments on Se-Met proteins or other heavy atom containing crystal samples, that are difficult to study with our in-house rotation anode x-ray source, and extended the resolution of the diffraction data.

EXPERIMENTS CONDUCTED AT ALS

Diffraction data on a chimeric Fab fragment of the decarboxylation catalytic antibody 21D8 in complex with the substrate analog, 5-nitro-3-carboxyindole, have been collected to 2.2Å resolution, with an R_{sym} of 7.6%. The crystal space group is $P2_12_12_1$ with cell dimensions of $a=39.2\text{\AA}$, $b=44.1\text{\AA}$, $c=225.3\text{\AA}$. The structure was determined by molecular replacement with the program AMoRe using the previously determined model of the 21D8-hapten complex structure. Refinement with the program package CNS and manual rebuilding with the program O is in progress. The current R-value and R-free for all data are 24.4% and 29.7%, respectively. A manuscript is under preparation.

A highly active and all purpose aldolase antibody 33F12 Fab was crystallized in space group $P2_12_12_1$ with unit cell dimensions $a=65.5\text{\AA}$, $b=81.8\text{\AA}$, $c=167.3\text{\AA}$, with two molecules in the asymmetric unit. The catalytic antibody crystals were soaked with a sulfonate inhibitor and a data set was collected to 2.0Å resolution with $R_{\text{sym}}=10.7\%$. Molecular replacement and structure determination and refinement are currently underway.

Kaposi's sarcoma (KS) is an angiogenic tumor which is associated with herpesvirus (KSHV or HHV-8). This virus encodes chemokine-like proteins (macrophage inflammatory proteins) vMIP-I and vMIP-II. Both vMIP-I and vMIP-II partially inhibit HIV infection of peripheral blood mononuclear cells. These two viral chemokines may play the roles in the complex pathogenesis of KS. The vMIP-I native protein data were collected at 1.8Å, with the completeness of 99.2% and the R_{sym} of 8.8%. The space group of the crystal is $P1$ with the unit cell dimensions of $a=34.2\text{\AA}$, $b=40.6\text{\AA}$ and $c=54.5\text{\AA}$, $\alpha=83.7^\circ$, $\beta=89.2^\circ$ and $\gamma=79.5^\circ$. The MAD experiment of the Se-Met vMIP-I crystal of the same space group will be conducted in the future.

Diffraction data were collected for crystals containing a complex between Tissue Factor (TF) and deleted Gla construct of Factor VIIa inhibited with EGR-chloromethylketone. The data

indicate either a 500Å long c-axis or some crystal twinning. Since these crystals are difficult to reproduce, we worked at extracting a smaller subcell from the diffraction pattern. A smaller cell in P2₁ space group with dimensions of a=77.7Å b=68.3Å c=70.4Å and beta=110° was found and used to integrate/scale the data, yielding a data set to 3Å with 13% R_{sym}. MR solutions were found using this reduced data set. The model currently has been refined to a R-value of 21.1% and a R-free of 34.7% with a reasonable Ramachandran plot geometry.

A native aldolase DERA that corresponds to our catalytic antibody 33F12, crystallizes in space group P2₁2₁2₁ with cell dimensions of a=50.0Å, b=53.1Å, c=177.1Å, with two molecules in the asymmetric unit. This enzyme consists of 259 residues per monomer; the 6 Met residues were substituted with Se=Met. MAD data for this enzyme were collected at 110°K during two 8-hour shifts. Complete data were collected to 1.8Å at four wavelengths at 0.97946Å 0.97969Å 0.96482Å and 0.99984Å. Ten of the 12 possible Se atom positions were determined and the structure determination is in progress.

A 2.8Å data set was also collected at ALS on a crystal of an intact IgG that is a broad and potent neutralizer of HIV-1. The space group is rhombohedral R32 and the cell dimensions are a=b=c=166.9Å and alpha=beta=gamma=108.5°. Its equivalent trigonal space group with cell dimensions a=b=217.2Å, c=175.1Å, alpha=beta=90.0°, gamma=120° was used for data reduction; the data are 90.9% complete with R_{sym} = 6.5%. A structural understanding of the epitope of this antibody may offer a template for vaccine design. Molecular replacement trials are currently underway.

Out of a series of T-cell receptors reactive against insulin peptide fragments presented by their restricting MHC Class II complex, IA^d, and F₁ of one of these has been crystallized with a long 500Å axis; only 3.8Å data could be collected in house. A data set was collected on this large cell to around 2.3Å at ALS beamline 5.0.2 during January this year, but the resulting R_{sym} is about 20% due to the large mosaicity of the crystal. We have since then improved the quality of crystals and the cryo-conditions. The CCD detectors coupled with the possible two-theta offset at beam line 5.0.2 and the brightest beam will enable us to collect better data at higher resolution in the future.

AICAR Tfase is a folate-dependent enzyme which catalyzes both the penultimate and the last steps in the *de novo* pathway for purine biosynthesis and is thus an attractive chemotherapeutic and anti inflammatory target. The AICAR crystallizes in several different space groups with varying cell dimensions. The Se-Met AICAR crystallizes in space group P2₁ with cell dimensions of a=65.0Å, b=105.7Å, c=103.8Å and beta=108.4°. MAD data were collected at four wavelengths at 0.97946Å 0.97969Å 0.96482Å and 0.99984Å to 2.7Å resolution. Eighteen out of the 24 possible Se atoms in the asymmetric unit of the cell have presently been located, and MAD phasing and structure determination are currently under way.

DISCUSSION

The ALS X-ray beamline 5.0.2 and its macromolecule crystallography facility (MCF) has been a tremendous help in improving the quality and the resolution of diffraction data of our protein crystal samples. In particular, the MAD experiments that we conducted at ALS will result in a faster determination of the *de novo* structures. We are anticipating continued and increase use of the ALS in the future.

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DNA Enzyme Data Collection

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SUMMARY

Progress toward the structure determination of a mechanistically relevant conformation of a DNA enzyme is presented. The structure of a particular RNA:DNA construct of the 10-23 DNA enzyme was determined at 3.0 Å resolution [1]. This structure revealed that the complex had rearranged during crystallization, forming a four-way junction dependent upon a specifically bound metal ion. This result directed the development of a combinatorial crystallization screen designed to capture a functionally relevant conformation of the 10-23 DNA enzyme. This approach has led to ~40 new crystal forms, at least one of which diffracts to 2.8 Å resolution. The research effort is now poised to determine the structure of the active form of the 10-23 DNA enzyme.

In order to capture an active conformation of the DNA enzyme and prevent rearrangement during crystallization, additional experiments were carried out using constructs in which the 5' and 3' stems of the complex were either 8, 9, or 10 base pairs in length. It is expected that the stability of both stems is comparable to, or exceeds that of the 8 base-pair DNA:DNA duplex that forms in the 2:2 complex, thus preventing a significant fraction of the 1:1 complexes from rearranging to the 2:2 form. This is expected to favor the capture of the 1:1 complex within a crystal lattice.

COMBINATORIAL CRYSTALLIZATION SCREEN

For crystallization screening, a combinatorial strategy was used that takes advantage of the bimolecular nature of the RNA:DNA complex [2]. The length of the 5' and 3' arms of both the DNA enzyme and RNA substrate were systematically varied for lengths of 8, 9, or 10 residues, creating $3^4 = 81$ sequence variants. All 9 DNA and 9 RNA molecules were synthesized and used in crystallization trials. For each of the 81 possible DNA:RNA complexes, 48 crystallization conditions were set up, resulting in 3,888 unique combinations. The set of 48 crystallization conditions that was employed was based on previous experiments with the 10-23 DNA enzyme [1].

The concentration of each oligonucleotide in the complex was typically 0.4 mM. 20 nmoles of RNA:DNA complex was the minimal amount required to carry out a screen of 48 crystallization drops. Crystallization trials were carried out by vapor diffusion using the sitting drop method. The optimal volume of the drops was found to be 2 µl. Although the small drop volume increased the rate of nucleation, it allowed more experiments to be conducted with a given sample. 1 µl of nucleic acid solution was mixed with 1 µl of the reservoir solution and placed on a concave plastic pedestal in a 24-well plate. The volume of the reservoir was 1 ml. In order to prevent the evaporation of low molecular weight alcohols present in several of the crystallization solutions, each plate was tightly sealed with clear plastic tape. The plates (162) were maintained at 24.5 °C in a constant temperature incubator for at least two weeks. Molecules with favorable sequences crystallized within ~3 days. The droplets were evaluated using a binocular microscope (40x) equipped with polarizing filters to enable observation of crystal birefringence.

DIFFRACTION QUALITY CRYSTALS

Altogether, 40 new crystal forms were observed [2]. Each of these crystal forms occurred with a unique morphology under a particular set of crystallization conditions and all were large enough for data collection. At least 20 of the 40 forms are birefringent, an indication of their crystalline

order. In addition to these 40 forms, 20 of the complexes yielded small or twinned crystals under one or more of the 48 conditions that were tested.

The diffraction properties of crystals were evaluated at room temperature using CuK α radiation from a Ru200 rotating anode x-ray generator equipped with a graphite monochromator and Siemens multiwire area detector. Crystals that showed the best diffraction with this x-ray source at room temperature (~ 5 Å resolution) were further evaluated at 100 K using synchrotron radiation. Depending on the composition of the crystallization mixture, the crystals were either frozen directly in a stream of cold N₂ gas, or were transferred briefly to a synthetic mother liquor containing increasing concentrations of cryoprotectant, frozen in liquid N₂ and then transferred to the x-ray beam. Typical cryoprotectants employed in the latter method were MPD and glycerol added in 10% increments to the original mother liquor.

Initial evaluation of 12 of the crystal forms, selected on the basis of their size, birefringence, and diffraction properties at room temperature, was carried out on beam line 5.0.2 at the Advanced Light Source (ALS) at Berkeley. There are at least two crystal forms that diffracted to ~ 3 Å resolution. Large rhombic plate crystals of the '99/89' complex showed diffraction to 2.8 Å resolution. The space group of these crystals is I222 or I2₁2₁2₁, with unit cell dimensions $a = 61.3$, $b = 80.5$ and $c = 93.1$ Å, as determined by indexing of both the ALS and room temperature data. For this unit cell the Matthews' coefficient is ~ 3.7 Å³/dalton, assuming one RNA:DNA complex (~ 15 kD) in the asymmetric unit. Large hexagonal crystals of the '910/910' complex also showed diffraction to 2.8 Å resolution. Indexing of images from the ALS and room temperature data indicated that these crystals are orthorhombic. In addition, two crystal forms of the '910/1010' complex diffracted to 3.5–3.6 Å, and a crystal form of the '910/89' complex diffracted to 3.6 Å. In contrast, crystals of the '99/1010' complex, differing by only a single residue from the '910/1010' complex, diffracted to only ~ 10 Å. Because all of the crystal forms contain complexes with at least 8 base pairs in both stems, they are expected to exist as a 1:1 RNA:DNA complex.

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Structural Enzymology on *E. coli* Beta-Galactosidase

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Beta-galactosidase from *E. coli* is a large tetrameric enzyme which carries out two reactions on its disaccharide substrate lactose. The hydrolysis reaction produces the monosaccharides galactose and glucose which then function in various metabolic pathways. The transglycosylation reaction produces the disaccharide allolactose, which acts to induce the production of more beta-galactosidase. In this manner *E. coli* can both respond to and utilize lactose as a food source.

Previous crystallographic studies to a resolution of 2.5 Å in a P2₁ crystal form using data collected at the Photon Factory have shown the beta-galactosidase monomer to be constructed from 5

Figure 1. Ribbon diagram (MOLSCRIPT) of one beta-galactosidase subunit from the tetramer. There are 5 distinct domains formed by a single 1023 residue polypeptide chain. The domain folds are jelly roll (1), immunoglobulin (2&4), (alpha/beta)₈ (3-in black), and supersandwich (5). Domains 1-4 are common folds occurring in a large variety of proteins. The active site is located at one end of domain 3 and includes residues from domains 1&5 and domain 2 from a neighboring subunit.

Based on liganding patterns, several candidate Mg⁺⁺ and Na⁺ binding sites have been identified, including a Na⁺ in the active site which was previously modeled as a water molecule.

Data sets have been collected on various complexes in an effort discern the details of the reaction coordinate. These include both native and mutant enzymes with inhibitors designed to explore ground state, transition state, intermediate, and product state binding interactions. The complexes

distinct domains organized around a central alpha/beta barrel¹ (Figure 1). The active site is shaped from residues of 4 of the domains into a pocket which complements the relatively small size of lactose. Structures of inhibitors bound to the active have suggested a general mode of action consistent with previous biochemical studies. However, the resolution of the complexes (2.6-3.0 Å) has precluded detailed arguments concerning the mechanism.

Use of ALS beamline 5.0.2 has now permitted major progress on the native enzyme and a series of complexes in a new P2₁2₁2₁ crystal form of beta-galactosidase. This form diffracts to higher resolution, allowing the structural studies to be extended to 1.5 Å. The x-ray source and fast CCD detector at beam line 5.0.2 have permitted short collection times of < 2 hours/data set to 1.5 Å, despite the relatively large unit cell dimensions of 201 x 168 x 150 Å.

Refinement of the native structure to 1.7 Å in the P2₁2₁2₁ crystal form has been completed. The model includes 4044 amino acid residues and more than 4200 solvent molecules and has a crystallographic R-factor of 16.2 %.

address questions concerning the decision to follow one reaction path over another, the roles of Mg^{++} and Na^{+} , and the detailed interactions that provide transition state stabilization.

Refinement of these complexes is underway. Figure 2 shows the electron density at 1.7 Å for a 2-deoxy-galactosyl enzyme complex, a reaction coordinate intermediate which has been trapped by flash freezing crystals soaked in galactal. This structure clearly shows a covalent connection to the nucleophile Glu 537 and the normal chair conformation of the sugar. Additionally, noncovalent interactions between the sugar and the enzyme and the sugar and various solvent molecules are clear. It is expected that the higher resolution of these complexes will allow a more detailed description of the reaction coordinate and to answer outstanding questions concerning the mechanism.

Figure 2. Electron density (2Fo-Fo, 1.0 sigma) showing the binding of a trapped reaction coordinate intermediate. There is clearly a covalent connection between the sugar and the nucleophile, Glu 537. The ring pucker is evident suggesting the sugar binds covalently in its relaxed chair conformation. Additionally, the positions of the ring substituents can be clearly seen and their binding interactions to protein and solvent molecules (not shown) accurately determined.

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Structural Genomics of *M. Jannaschii*

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The DNA sequence of a gene does not always yield the cellular function of the protein coded by the gene, but the three-dimensional structure of the protein can be a sensitive indicator of its function. For example, protein structures are classifiable in terms of a finite set of folds associated with a small list of functions. In the early stages of a pilot study of the bacterium *Methanococcus jannaschii*, researchers using protein crystallography at the ALS have determined the structure of a protein of previously unknown function. The structure suggested a small number of possible functions from which biochemical assays were then used to determine the actual function.

The goal of the Human Genome Project is to determine the DNA sequence of the human genome by the year 2005. One of the important objectives of determining the genomic sequences is to understand the cellular and molecular (biochemical and biophysical) functions of all the gene products (i.e., mostly proteins) encoded in the genomes, but the function of a protein cannot be readily inferred from the DNA sequence of a gene unless that sequence is significantly similar to that of a gene whose function is already known. The current estimate of the percentage of genes with gene products of known function varies from approximately 30% to 60%, depending on the genomes sequenced. Furthermore, an even smaller fraction of the genes have gene products with known molecular functions. In structural genomics, we look for clues to the function of a protein in its three-dimensional structure.

Determining the structures of all the gene products of an organism would be an overwhelming task. Fortunately, the current database of protein structures strongly suggests that most proteins are classifiable in terms of a finite set of folds, the “folding basis set,” and that each fold may be represented by a small number of biochemical or biophysical functions. Accordingly, large-scale projects to determine the structures of a few representatives from each fold family can provide a foundation for the functional genomics by identifying molecular functions that can be combined with cellular functions derivable from mutational studies, transcription tracking, translation tracking, and interaction tracking.

To this end, we are using the Macromolecular Crystallography Facility (MCF) at the ALS in a pilot study of the fully sequenced model hyperthermophilic archaeobacterium *Methanococcus jannaschii*. We have chosen several gene products from this organism—some with known cellular functions but without known molecular functions, and some without any known functions—and have begun to determine their structures. The long-term goal of this project is to determine the structures of representative gene products in order to establish a folding basis set for the approximately 1800 gene products expressed in the microbe. The principal focus on finding a large number of new folds makes phase determination by multiple-wavelength anomalous diffraction (MAD) analysis a necessity.

Early results have already allowed the roles of two “hypothetical” proteins (proteins for which there is no other protein in the database with a gene having a similar DNA sequence and a known function) to be tentatively identified from their structure alone. With data gathered at the MCF, for example, we have determined the structure of hypothetical protein MJ0577 from *M. jannaschii*.

Figure 1. Structure of the hypothetical protein MJ0577 in the hyperthermophilic archaebacterium *Methanococcus jannaschii*, solved at the MCF. (Left) Electron-density map derived from MAD experimental phases clearly shows a bound ATP. (Right) The tertiary structure of MJ0577 is a nucleotide binding fold.

The crystal structure was solved and refined within a few days after data collection was completed. The set of high-quality experimental phases from MAD measurements at the MCF has proven to be the key factor for interpreting and modeling the structures of the protein and ligands. For example, MJ0577 was identified as an ATP-binding protein after examination of the electron density map showed bound ATP.

The discovery of the ATP immediately narrows down the possible biochemical function of this protein. Biochemical experiments showed that MJ0577 has no appreciable ATPase activity by itself. However, when *M. jannaschii* cell extract was added to the reaction mixture, 50% of the ATP was hydrolyzed to ADP in 1 hour at 80°C. This result indicates that MJ0577 requires one or more soluble components specific to *M. jannaschii* to stimulate ATP hydrolysis, suggesting that this is an ATP-mediated molecular switch analogous to Ras, a GTP-mediated molecular switch that requires GAP to hydrolyze GTP. In these studies, we have shown that MAD experiments can lead to very rapid protein structure determination. Furthermore, in the case of MJ0577, the three-dimensional structure of an unknown protein has provided direct information for functional (biochemical) assignment.

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Structural Studies of the I-PpoI homing endonuclease

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INTRODUCTION

‘Homing’ is the lateral transfer of an intervening genetic sequence, either an intron or an intein, to a cognate allele that lacks that element [1-5]. The end result of homing is the duplication of the intervening sequence. The process is initiated by site-specific endonucleases that are encoded by open reading frames within the mobile elements. Several features of these proteins make them attractive subjects for structural and functional studies. First, these endonucleases, while unique, may be contrasted with a variety of enzymes involved in nucleic acid strand breakage and rearrangement, particularly restriction endonucleases. Second, because they are encoded within the intervening sequence, there are interesting limitations on the position and length of their open reading frames, and therefore on their structures. Third, these enzymes display a unique strategy of flexible recognition of very long DNA target sites. This strategy allows these sequences to minimize non-specific cleavage within the host genome, while maximizing the ability of the endonuclease to cleave closely related variants of the homing site. Recent studies explain a great deal about the biochemical and genetic mechanisms of homing, and also about the structure and function of several representative members of the homing endonuclease families.

STUDIES CONDUCTED AT THE ADVANCED LIGHT SOURCE AND FHCRC

Conformational changes and DNA target site bending Induced by the His-Cys box homing endonuclease I-PpoI. The homing endonuclease I-PpoI displays a highly extended fold and loosely packed central dimer interface, yet its DNA target site is severely bent in the protein-bound complex, resulting in sharp deformation of minor and major groove dimensions near the scissile phosphates [6]. In order to study the relative role of protein and DNA conformational changes during binding, we have determined the structure of the enzyme in the absence of bound DNA to 2.0 Å resolution, performed a fluorescence transfer analysis of the DNA homing site bending in the presence and absence of bound protein, and have mutagenized a leucine residue that plays a critical role in DNA bending. The structure of this enzyme point mutant has been determined bound to the DNA homing site before and after cleavage to 2.7 Å resolution, and the effect of this mutation on binding affinity and turnover velocity has been measured. The structure of the apo-enzyme displays a small rigid-body rotation of dimer subunits compared to the DNA-bound structure, and the homing site is not significantly bent in the absence of protein, indicating that binding involves a large distortion of the DNA onto a moderately static protein surface. The structure of the L116A enzyme mutant bound to DNA is almost identical to the wild-type apo-enzyme, while the affinity of this complex is reduced by at least 1000-fold. The large energetic cost of binding for this mutated enzyme is reflected in a large decrease in turnover rate. This study provides a direct example of the importance of binding energy for catalytic rate-enhancement.

A novel endonuclease mechanism directly visualized by intermediate trapping. The structure of the I-PpoI endonuclease complexed with its target DNA substrate has been determined in three distinct states on the cleavage pathway: bound in the absence of divalent cations, bound in the presence of magnesium prior to cleavage, and bound to cleaved product with magnesium. Each of these states was trapped by two separate strategies for comparison of the structures. The resulting structures demonstrate that this enzyme follows a single metal mechanism in which the nucleophilic water is activated by a conserved histidine residue, and the bound metal (which is coordinated by a single conserved asparagine residue and two contacts to the DNA) acts to stabilize the phosphoanion transition state and the 3' hydroxyl leaving group. These structures also demonstrate conformational motions of the active site side chains and the scissile phosphate that accompany cleavage, and indicate that a perturbed, high energy enzyme-substrate-metal complex is formed that is relieved upon cleavage. This mechanism appears to be reproduced in a non-specific nuclease and in the T4 endonuclease VII enzyme [7].

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Structural Studies of Neutrophil Gelatinase Associated Lipocalin (NGAL) and the MHC Class I Homolog MIC-A

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INTRODUCTION

Human Neutrophil Gelatinase Associated Lipocalin (NGAL) was originally identified as a component, along with gelatinase (MMP-9), of a disulfide-linked heterodimer secreted by neutrophils [1]. NGAL can also be secreted from neutrophils as both a 25 kD monomer and as a 46 kD disulfide-linked dimer in the absence of associated gelatinase [1, 2]. Neutrophils in the colonic mucosa do not actively synthesize NGAL; rather, the protein is produced in immature neutrophil precursors in the bone marrow and stored in specific granules for subsequent release. Unlike other lipocalins, NGAL shows no affinity for retinoic acid, but does bind the N-formylated tripeptides fMet-Leu-Phe (fMLF) and fNorleucine-Leu-Phe (fNLF) which are active in bacterial chemotaxis [3]. The dissociation constant of NGAL and photo-labeled fMLF is 145 nM; competition assays yield a dissociation constant for fMLF of between 30 and 60 nM [4]. NGAL synthesis is highly induced in epithelial cells in both inflammatory and neoplastic colorectal diseases [5]. Its expression is restricted to the affected tissue only. NGAL may also bind other lipophilic mediators of inflammatory responses, notably platelet activating factor and leukotriene B₄ [5]. The murine analogue of NGAL, 24p3, was originally identified in a screen for genes overexpressed during a SV40-induced mitotic reaction [6]. 24p3 expression is also amplified by an autocrine mechanism in response to dexamethasone or retinoic acid [7]. The synthesis of 24p3 has also been shown to be induced in cultured macrophages by lipopolysaccharide [8]. The rat analogue of NGAL, *neu*-related lipocalin (NRL) is specifically overexpressed in *neu*-initiated rat mammary carcinomas [9].

MIC-A: Responses by the cellular component of the acquired immune system are mediated by the specific recognition of foreign peptides bound to Major Histocompatibility Complex (MHC) proteins by $\alpha\beta$ T cell receptors (TCRs) [10]. A second class of T cells, those bearing $\gamma\delta$ TCRs, are proposed to mediate antimicrobial responses and regulate innate and acquired immunity [11]. The rules governing the interactions between $\gamma\delta$ TCRs and their ligands, while currently undefined, are believed to be distinct from those directing the interaction between $\alpha\beta$ TCRs and their ligands. One subset of $\gamma\delta$ T cells, those expressing V δ 1 TCRs, recognize the distant MHC class I homologs MIC-A and MIC-B [12-16]. Through this interaction, MIC-A is proposed to function as a stress-induced self antigen on gastric epithelial cells [12, 13]. Unlike MHC class I proteins, MIC-A requires neither peptide nor β_2 -microglobulin (β_2 -m) for stability or cell-surface expression [17-19]. We propose to determine the crystal structure of a soluble fragment of human MIC-A in order provide a structural context for understanding $\gamma\delta$ TCR-mediated recognition. The "classical" or class Ia MHC proteins (HLA-A, B and C) are integral-membrane, heterodimeric proteins that are polymorphic and ubiquitously expressed. This sequence polymorphism reflects the ability of class Ia molecules to bind to a variety of antigenic peptides and TCRs. MIC-A and MIC-B, conserved in most mammals except rodents, are homologous to MHC class I proteins.

Unlike MHC class Ia proteins, the expression of MIC proteins is essentially restricted to gut epithelium under the control of heat-shock promoter elements. While MIC-A and MIC-B proteins are quite similar to each other (84% identical), they have diverged significantly from the MHC class I family as a whole [20]. A series of primate MIC sequences is now available [20]. The promiscuous binding of $V_{\delta}1+$ IELs to MIC targets is demonstrated by the uniform cytolytic response of human intestinal epithelial tumor-derived $V_{\delta}1+$ clones (bearing $V_{\gamma}1.8/V_{\delta}1/J_{\delta}1$ $\gamma\delta$ TCRs) to cells transfected with any of these MIC proteins [20]. These results have been interpreted as evidence for a single, conserved recognition site on MIC proteins. This interpretation contrasts the situation in class I proteins, where sequence *polymorphisms* map to peptide and TCR binding sites.

STUDIES CONDUCTED AT THE ADVANCED LIGHT SOURCE AND FHCRC

We have grown crystals of dimeric NGAL at pH = 4.5 (space group: $P4_32_12$) and monomeric NGAL at pH = 7.0 (space group: $P4_12_12$). The dimeric NGAL data were phased with PIP SIRAS phases refined with SHARP/SOLOMON. The monomeric data were phased by molecular replacement with a partial model of an NGAL half-dimer using EPMR. We are currently refining both structures (some loops and side-chains differ in conformation between the various structures). We have also collected data from NGAL co-crystallized with one putative ligand: fMLF. A bound sulphate is seen in the binding site in the monomeric NGAL structure. Interestingly, there is density in the un-soaked NGAL dimer structure that possibly corresponds to a natural ligand carried along during the purification. The density is currently consistent with a partially-occupied fatty acid (most likely palmitate), or possibly some related compound. We are currently conducting a series of mass-spec experiments to further characterize this natural ligand, but several experimental difficulties complicate this analysis. Diffraction data have been collected at ALS with the intent of extending the resolution for NGAL crystallized as is or in the presence of a variety of potential ligands.

We have grown crystals of human MIC-A at low (pH = 5.5) that diffract to a resolution of 2.8Å (space group: $F4_132$). These data were phased by MIR. The initial experimental maps were high quality, likely due to the high solvent content of the crystals ($\approx 78\%$) which aided solvent-flattening. We are currently refining the structure of MIC-A against these data. Preliminary results suggest that the structure of MIC-A is the most highly diverged of the MHC class I family, with many differences in loop structure and the inter-domain relationship. One striking feature is that a stretch of ten residues in the middle of one of the helices that define the peptide-binding groove is completely disordered in our structure. We have been able to transfer crystals of MIC-A grown at pH = 5.5 to pH = 7.0 and pH = 8.0. We have been able to stabilize the crystals at these pH's by rapid cryo-preservation. We have collected diffraction data from these transferred crystals, though the resolution suffers as a result of the transfer. Preliminary results suggest that the loop disordered at pH = 5.5 partially orders progressively at the higher pH's. In solution, the protein is monodisperse at pH's ranging from 5.5 to 7.4, but begins to aggregate at pH = 8.0. Preliminary measurements of the melting temperature (T_m) of MIC-A by CD spectroscopy suggest that MIC-A has an unusually low T_m (48°) that increases to a more reasonable value at pH = 5.5 (56°). The range of this pH change suggests that protonation of histidine residues may play a role in stabilizing MIC-A. Diffraction data have been collected at ALS with the intent of extending the resolution for MIC-A crystals at pH = 5.5, 7.0 and 8.0.

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Structure of Bacteriorhodopsin at 1.55 Angstrom Resolution

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The atomic structure of the light-driven ion pump bacteriorhodopsin and the surrounding lipid matrix was determined by x-ray diffraction of crystals grown in cubic lipid phase. In the extracellular region an extensive 3-dimensional hydrogen-bonded network of protein residues and seven water molecules leads from the buried retinal Schiff base and the proton acceptor Asp 85 to the membrane surface. Near Lys 216 where the retinal binds, transmembrane helix G contains a π -bulge that causes a non-proline kink. The bulge is stabilized by hydrogen-bonding of the main-chain carbonyl groups of Ala 215 and Lys 216 with two buried water molecules located between the Schiff base and the proton donor Asp 96 in the cytoplasmic region. The results indicate extensive involvement of bound water molecules in both the structure and the function of this seven-helical membrane protein. A bilayer of 18 tightly bound lipid chains forms an annulus around the protein in the crystal. Contacts between the trimers in the membrane plane are mediated almost exclusively by lipids.

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Structure of the nNOS-Syntrophin Complex Reveals Unexpected Modes of PDZ Domain-Mediated Assembly

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The PDZ domain of neuronal nitric oxide synthase (nNOS) can specifically heterodimerize with the PDZ domains of PSD-95 and syntrophin via interactions that do not involve typical COOH-terminal motif recognition. The crystal structure of the nNOS-syntrophin PDZ complex reveals that the domains interact in an unusual linear head-to-tail arrangement. The nNOS PDZ domain has two, opposite interaction surfaces — one face has the canonical peptide binding groove, and the other face has a novel beta-hairpin “finger.” This nNOS beta-finger docks in the syntrophin peptide binding groove and mimics a peptide ligand, except that a sharp beta-turn replaces the normally required COOH-terminus. This structure demonstrates that PDZ domains can participate in diverse interactions useful for assembling protein networks: recognition of COOH-terminal motifs, recognition of internal motifs presented within a constrained structure, and formation of head-to-tail oligomers.

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Understanding the basis for RNA folding and molecular recognition: atomic resolution structures of RNA aptamers complexed with their ligands

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INTRODUCTION

Our understanding of the molecular basis for a wide variety of biochemical processes has largely come about through the determination and analysis of macromolecular structure. While more than 5000 atomic-resolution protein structures have been determined by these methods, only a handful of RNAs have been studied at the same resolution. The process of *in vitro* selection (outlined in the inset) has made it possible to evolve many different types of small, well-defined RNA motifs with unique binding activities ('aptamers')^{1,2}. In a typical SELEX experiment, a pool of random sequence molecules (derived from a random chemical DNA synthesis) encounters a selective pressure that physically separates functional from non-functional molecules (e.g., binding to an affinity column). Repeated rounds of selection followed by enzymatic amplification can be used to isolate RNAs that are highly adapted to specific functions. Crystallographic analysis of such RNAs complexed with the small molecules they bind can potentially provide important insights into the basic mechanisms by which RNAs fold into specific three-dimensional structures and the rules that define how RNAs and small molecules interact. X-ray diffraction experiments carried out at ALS beamline 5.0.2 in September, 1999, provide the first high resolution views of RNA aptamer-ligand complexes.

CYANOCOBALAMIN APTAMER

Vitamin B12 and its biologically-active derivatives are large corrin-based cofactors used to catalyze several different classes of enzymatic reactions. Adenosylcobalamin is believed to be one of the most evolutionarily ancient enzyme cofactors³ and its role in extant ribose reductases has led to the postulate that it played a role in the transition from RNA-based biology to modern biology⁴. Given this background and with the goal of identifying RNAs capable of recognizing large, complex ligands, Lorsch and Szostak used SELEX to isolate RNA motifs that specifically recognize cyanocobalamin⁵. A minimal aptamer containing 31 conserved nucleotides was identified that binds the cofactor with high affinity ($K_D \approx 90$ nM) and specificity (distinguishing between different ligands). 1 M lithium chloride was included during the selection experiment with the knowledge that lithium has the potential to form tight complexes with RNA backbone phosphates⁶ in the hope that selected RNAs would be isolated that fold into a highly compact and stabilized structures.

The 3 Å crystal structure of the cyanocobalamin aptamer was determined from a single crystal MAD experiment using the cobalt associated with the corrin ring in the complex as the anomalous scatterer from which crystallographic phases could be deduced. Analysis of the structure reveals that it folds as a pseudoknot whose first helix is embedded within a much larger triplex.

Perpendicular stacking of the triplex and the second helix creates a cleft that functions as the vitamin B12 binding site. Chemical modification studies by Lorsch and Szostak can be interpreted in light of the structure and indicate that the bound and unbound conformations of the aptamer are likely to be fairly similar (most changes in chemical modification upon binding correspond to the protection of residues at the binding interface). Of the 27 nucleotides in the aptamer core (excluding flanking nucleotides required for expression and crystallization), only 4 in helix 2 can be considered to form what would generally be considered conventional secondary structure. The remainder form a variety of interactions that combine to either build the triplex or lock the second helix in position.

The triplex provides a rich set of tertiary interactions for analysis. Five of the seven tiers in the triplex include base triples stabilized by specific hydrogen bonding. The two triples at the bottom of the triplex (i.e. farthest from the vitamin B12 binding site) are defined by nucleotides packing against the minor groove face of Watson-Crick base pairs. Lying above them in the triplex are two Watson-Crick pairs which mediate a switch in base pairing from strands 1-2 to strands 2-3. As a result of this switch, base triples in the top of the triplex are generally arranged with a nucleotide hydrogen bonding instead to the major groove side of a base pair.

Vitamin B12 binds in the cleft formed at the junction between the triplex and the second helix and makes an extensive set of specific interactions. Methyls protruding axially and equatorially from one side of the corrin ring contact either side of the cleft and make van der Waals contacts with the exposed nucleotide faces of the base triple and base pair that cap the triplex and helix respectively. Supplementing these and additional hydrophobic interactions are a set of four specific hydrogen bonds that bridge the amide side chains of the cofactor and the nucleotides of the RNA.

BIOTIN APTAMER

We previously isolated and characterized an RNA motif that specifically recognizes biotin, a ubiquitous carboxylation co-factor used by protein enzymes²⁸. A 31-nucleotide pseudoknot, closely resembling the ribosomal frameshifting elements in retroviral mRNAs, is present in all selected RNAs enriched by affinity chromatography. Independent clones containing the pseudoknot bind biotin with relatively high affinity ($K_D \approx 5 \mu\text{M}$) and high specificity. Binding with this avidity is surprising given the absence of charges and aromatic rings on the ligand, functional groups which often provide the driving force for aptamer binding.

Schematic representations of the cyanocobalamin aptamer illustrating its secondary and tertiary structure.

The 1.5 Å crystal structure of the biotin aptamer was determined by MAD phasing using the selenium of bound selenobiotin as an anomalous scatterer. An anomalous Patterson map (inset) clearly shows a single corresponding to the bound cofactor. The refined structure reveals a coaxially stacked pseudoknot, fitting well with previous models constructed on the basis of biochemical and genetic constraints. The arrangement of helices in the aptamer is similar to that observed by NMR and crystallography for viral pseudoknots that induce ribosomal frameshifting. Biotin binds at the interface between the two helices in a pocket defined by the base pairs capping each helix and by the 3'-end of an A-rich loop running the length of the minor groove of helix 1.

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Beamline 6.1.2 Abstracts

Analysis of engineered mixed culture biofilms: use of soft X-ray microscopy

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INTRODUCTION

Using biofilms for biotechnological applications

Biofilms are frequently studied for the economic damage that they cause. Their impact is felt in diverse areas, from biofouling of oil drilling rigs and heat exchangers to infections in medical implants. However, the attributes of biofilms that are problematic in uncontrolled situations are potentially useful biotechnological features, if the biofilm is populated with beneficial microorganisms. Decontamination of toxic waste using bacteria is an area that could benefit from biofilms. The production of useful bioproducts by metabolically engineered bacteria is another area where biofilms could be valuable.

Using biofilms to enhance bioremediation

Bioremediation is a "green" technology that takes advantage of the enzymatic capabilities of bacteria to decontaminate chemical pollution in the environment. Numerous case studies document the effectiveness of bioremediation for the cleanup of environmental pollutants including crude oil, jet fuel, volatile organic compounds, and chlorinated solvents (Hinchee, 1995a; Hinchee, 1995b). Biofilms are already in use in some wastewater treatment processes, and could play a meaningful role in detoxifying a broad range of industrial and environmental pollutants.

(a)

(b)

Figure 1. (a) Tiled image of *Escherichia coli* biofilm. Bar at top right = 1 micron.
(b) Close-up of biofilm; 2400x magnification.

Features of the XM-1 soft X-ray microscope that benefit biofilm research

Biofilms have a complex three-dimensional structure and are almost always hydrated. It is often difficult to image them at high magnification, for example, by electron microscopy, because the sample preparation dehydrates the biofilm, altering its structure. A unique feature of soft X-ray microscopy that is beneficial for the analysis of biofilms is the ability to image samples while they are still hydrated. Another feature of the XM-1 soft X-ray microscope that is good for biofilm research is its tiling feature. Using this tool, large areas of biofilms can be scanned and regions of special interest can be located for later examination at high magnification (Fig. 1).

CURRENT RESEARCH

Engineered biofilms for bioremediation of mixed wastes.

Industrial wastes sites often contain mixtures of contaminants. For example, trichloroethylene (TCE) and chromium are common contaminants of groundwater that co-occur near former semiconductor manufacturing sites. A separate microorganism may be required to detoxify each component of the waste. Biofilms can help maintain mixed cultures of bacteria with different growth kinetics, since the cells are immobilized (Eliashberg and Keasling, 1998).

We are currently investigating the hypothesis that the distribution of bacteria in engineered biofilms can influence their efficiency for mixed waste detoxification. Recent images of a dual-species biofilm that detoxifies mixed phenol-chromium waste revealed broad areas of surface colonization by the *E. coli*-*Pseudomonas* coculture. An interlocking structure of irreversibly attached cells dominated by *Pseudomonas* was observed (Fig. 2). A notable feature of the colonization was the relatively high percentage of unoccupied area between the cells attached to the substratum.

Figure 2. (a) Dual species biofilm. Note the overlap of cells. (b) *Escherichia coli* 33456 grown in rich media containing $150 \mu\text{g mL}^{-1}$ K_2CrO_4 . 2400x magnification.

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PUBLICATIONS BASED ON DATA COLLECTED AT THE XM-1

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Changes in the Macromolecular Structures of Isolated Humic Substances Under Different Solution Chemical Conditions

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Humic substances (HS) are products of the biochemical transformations of plant and animal residues, and comprise a major fraction of the organic carbon of soil and aquatic systems¹. Their reactivity in the environment is primarily dependent on their functional group chemistry and macromolecular structure (size, shape) induced by the composition of reacting media (solution chemistry, interacting solid matrix)^{2,3}. However, direct (*in-situ*) information on the magnitude of these effects is yet to be documented. Since changes in HS macromolecular structures significantly affect the chemistry of organic coatings on soil mineral surfaces, and modify the retention of pollutants by soils and colloids, information on the magnitude of changes in HS macromolecular structures is essential for understanding the geochemical reactions mediated by natural organic molecules⁴. In this study, we examined the *in-situ* changes in the macromolecular structures of HS as a function of several chemical variables relevant to natural geochemical systems, using the X-ray microscopy facility (BL 6-1-2)⁴. Some of the results of this study are presented here.

EXPERIMENTAL DETAILS

Experiments were conducted on HS fractions (humic and fulvic acids) isolated from river water (Suwannee River, GA, U.S.A), and soil (mollic epipedon, IL, U.S.A) samples. These fulvic and humic acids are isolated at different pH by the International Humic Substance Society. The solution compositions tested were: pH (2-12), ionic strength (0.01-2 M), HS concentration (0.03-10 g C L⁻¹), counter ion composition (1 mM Cu²⁺, Fe³⁺), in the presence of soil minerals (goethite (α -FeOOH); calcite (CaCO₃); clay minerals (kaolinite and montmorillonite)). The macromolecular structures of aqueous HS under these chemical conditions were examined by collecting images at different photon energies.

RESULTS AND DISCUSSION

When examined with the X-ray microscope, the Suwannee River fulvic acid isolates formed aggregates of different shapes and sizes at HS concentrations greater than ~ 1.3 g L⁻¹ (Fig. 1A). In dilute, acidic, high ionic strength NaCl solutions, HS predominantly formed globular aggregates and coils with a small radius of curvature (0.15 - 0.6 μ m; Fig. 1B). As the fulvic acid concentration was increased, large sheet-like structures (2-8 μ m) also formed. Visible coiling was uncommon and the HS dispersed completely into small aggregates (< 0.1 μ m) in solutions of pH > 8.0 (Fig. 1C). Although addition of 1 M NaCl did not favor coiling under these alkaline conditions, concentrated HS solutions formed large globular aggregates bound together with thin films of HS. Additions of di- and trivalent cations to HS solutions promoted their precipitation at low carbon concentration, and displayed macromolecular structures different from those formed in the presence of monovalent ions. Additions of Ca²⁺ to fulvic acid at dilute concentration formed thin thread-, and net-like structures as compared to those formed in the presence of Na⁺ (Fig. 1D, compare with Fig. 1B). Increases in Ca²⁺ and HS concentration caused these structures

to grow larger and denser (Fig. 1 E-F). Coiling was also common in the concentrated Ca^{2+} -fulvic acid solutions (Fig. 1F). Humic solutions reacted with Cu^{2+} and Fe^{3+} also exhibit similar structures, but precipitated HS at a concentration less than those examined in the presence of Na^+ and Ca^{2+} (Fig. 1G). The fluvial humic acids also showed the similar behavior, but the carbon concentration at which a particular structure was formed was smaller for the humic acids, and also globular and rod/lath-like structures were more common in the case of humic acids.

In contrast with the fluvial humics, the low solubility of soil and peat HS promoted their precipitation at much lower HS concentration than the fluvial isolates ($\sim 0.25 \text{ g C L}^{-1}$ for soil fulvic acid in acidic NaCl solutions, and at lower concentration for humic acids and in the presence of complexing cations). Although similar macromolecular structures were noticed for fluvial and soil HS below a pH of 8.0, the latter arranged preferentially in globular, and rod- or thread-like structures in dilute solutions (0.4 g C L^{-1}), and sheet-like structures (occasionally with open holes, which are uncommon for fluvial samples) in concentrated solutions ($> 0.4 \text{ g C L}^{-1}$). In alkaline solutions, soil HS also dispersed at low HS concentration, and formed dense sheet-like structures in concentrated solutions.

The presence of mineral surfaces completely altered HS behavior. The size and structure of organo-mineral aggregates were dependent on the type (fulvic vs. humic acid) and concentration of HS, and the composition of minerals and solutions (pH and cation type and concentration). At low HS concentration ($<$ aqueous saturation), sorption of HS was evident by the formation of thin coatings on the mineral surfaces that could only be resolved with surface-sensitive spectro-microscopy methods. In saturated soil HS solutions of pH 2-10, clay minerals, goethite, and fine-sized calcite formed organo-mineral aggregates with thick HS coatings. Kaolinite and montmorillonite exhibit the same behavior with the majority of their aggregates in the range of 5-35 μm , and HS occurring as cement between the clay platelets. Although, alkaline soil humic acid solutions (pH > 8.0) showed the same behavior as fulvic acids, humic acids formed less dense aggregates with clays than the fulvic acids in the pH range of 2-7. Fine-grained calcite crystals exhibited less dense aggregates than those of clays, and sorbed more HS than the coarse calcite crystals below a pH of 8.0. As the HS concentration was increased well above its aqueous

Fig. 1. Macromolecular structures of fluvial fulvic acid. A: redissolved solid fulvic acid in water, pH 4.0; B: pH 3.0, NaCl = 1.0 M; C: pH 9.0, NaCl = 0.5 M; D: $[\text{C}] \sim 1.0 \text{ g L}^{-1}$, pH 4.0, $\text{CaCl}_2 = 0.018 \text{ M}$; E: $[\text{C}] \sim 1.3 \text{ g L}^{-1}$, pH 4.0, $\text{CaCl}_2 = 0.07 \text{ M}$; F: $[\text{C}] \sim 1.5 \text{ g L}^{-1}$, pH 4.0, $\text{CaCl}_2 = 0.2 \text{ M}$; G: $[\text{C}] \sim 0.1 \text{ g L}^{-1}$, $\text{Fe}^{3+} = 1.0 \text{ mM}$.

saturation, HS formed thick coatings around minerals, irrespective of their composition. All of the mineral samples, excepting those examined in dilute HS solutions, also exhibit separate non-mineralic-HS aggregates in globular and sheet-like forms. Although fluvial HS showed similar behavior with mineral matrices, detectable organo-mineral aggregates formed at high HS concentration ($> 1.5 \text{ g C L}^{-1}$) only.

In summary, these results indicate that the macromolecular structures of HS are highly sensitive to different solution chemical conditions. The commonly held notion that HS form coils at low pH and high ionic strength, and elongated structures in alkaline solutions as the primary structures is too simplistic. However, the following generalizations can be made from this study: 1) HS were found to form globular and thread/net-like structures in dilute HS solutions, and coiled and sheet-like structures in concentrated HS solutions. Dilute alkaline HS solutions always exhibited small aggregates ($< 100 \text{ nm}$) without any discernible structures. Solution pH significantly affected the HS macromolecular structures at low HS concentration, but played a minor role in the case of concentrated HS solutions. Humic and fulvic acid fractions of HS behaved similarly, but the chemical conditions under which transitions in their macromolecular structures occurred were different (more pronounced in the case of soil HS). In addition, humic acids formed globular and lath-shaped structures predominantly under acidic conditions. Although globular, and net-, and sheet-like structures have been reported earlier for dried soil HS on substrate surfaces (e.g. mica, sample mounting stubs for electron microscopes)⁵, a correlation between their solution chemistry and HS structures could not be established. This may be because, chemical changes associated with sample drying (e.g. changes in HS concentration, pH), and sample substrate chemistry can modify the original HS macromolecular structures. 2) The mineral oxides dramatically alter the HS macromolecular structures, which vary depending on the chemistry and grain size of minerals. The chemical differences between fulvic and humic acids (aromaticity, aqueous solubility), notably in the case of soil HS, have caused different interactions with minerals. While soil humic acids predominantly formed structures without mineral oxides at $\text{pH} < 7.0$, soil fulvic acids formed organo-mineral aggregates with HS as cements between the minerals in the pH range of 2-10. 3) The chemical conditions under which soil and fluvial HS assume a particular configuration and interact with minerals are different. Soil HS were found to form globular, thread- and net-like structures in dilute HS solutions, and sheet-like structures in concentrated solutions at $\text{pH} < 8.0$. This behavior is more pronounced in the case of soil HS than the fluvial HS. The macromolecular structures of organo-mineral complexes in soils and those of isolates were similar, which suggests that the results obtained from the latter can be applied to understand the behavior of organic molecules in nature.

The results presented here directly document, for the first time, the variation in aqueous HS macromolecular structures as a function of solution chemical conditions and HS origin. The changes in HS macromolecular structures associated with solution chemical conditions modify the exposed surface area and the functional group chemistry of HS, which may further affect their biotransformation and contaminant sorption⁶. As this study shows, HS form dense structures with low surface area to volume ratio in acidic concentrated electrolyte solutions when compared to high pH solutions. This can significantly inhibit the accessibility of microorganisms into the micropores of dense HS aggregates, and thus prevents the oxidation of organic matter (and also other redox reactions of HS-associated contaminants), and facilitates the stabilization of organic carbon by soils. Differences in the macromolecular structures (e.g. size and C content) of mineral-complexed HS affect the properties of organo-mineral aggregates, and controls the type

of organic carbon retained by different soil minerals. A description of the macromolecular structures of HS together with the associated chemical conditions will help the modeling and understanding the pollutant-particle interactions, and carbon cycling in soils.

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Cryogenic-stage experiments with *Chlamydomonas*

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Introduction

Soft x-ray microscopy has been shown to provide a novel insight into the structure of biological specimens since the images obtained are, unlike transmission electron microscopy where material is chemically fixed, dehydrated, embedded, sectioned and stained, of living hydrated cells (Kirz et al., 1995; Stead et al., 1995). For example, in the unicellular green alga *Chlamydomonas*, there appear to be numerous spherical inclusions which are not seen when transmission electron microscopy is used to study cell ultrastructure (Ford et al., 1994).

To date the main soft x-ray imaging modes have been either contact microscopy using a laser plasma source, or scanning or transmission x-ray microscopy using either a laser plasma or synchrotron source. However, living specimens suffer from radiation damage if the imaging times are too long. For example, measurements of metaphase chromosomes from beans (*Vicia faba*) have shown them to be very radiation sensitive when wet but relatively insensitive when dry (Williams et al., 1993). Viability of yeast cells and functionality of myofibrils were both destroyed by doses of soft x-rays well below the doses used for microscopy (Fujisaki, et al., 1996). Images obtained previously at the ALS have shown not only mass loss but also gross alteration in cellular structures, for example, bacterial spores are damaged by a single short exposure to soft x-rays (2.4nm) but dry spores show little or no sign radiation-induced damage (Stead et al., 1997, 1998). The novel spherical cellular inclusions seen in *Chlamydomonas* are themselves particularly radiation sensitive (Stead et al., 1997). Although images of living *Chlamydomonas* cells have previously been obtained with exposure times of 1-4s some of the initial images still appear to be damaged, that is to say the images appear similar to those which had been irradiated previously. This suggests that the observable damage occurs during the exposure and that any reduction in the exposure time should reduce the likelihood of recording radiation damaged images (Ford et al., 1998). Moreover since damage occurs within this time it is not possible to alter either the field of view or the focus and take a second image. The situation is exacerbated when images are to be recorded at wavelengths other than 2.4nm, as is the case when imaging either side of an absorption edge to determine the elemental composition, because the efficiency of the x-ray optics is diminished therefore the exposure times are greatly increased. In early experiments to determine the oxygen distribution in cells of *Chlamydomonas*, for example, exposure times were often about 30min. and therefore the specimen had to be chemically fixed and/or dried. Such treatment of the specimen negates the very considerable advantage that x-ray microscopy has over conventional electron microscopy as it prevents the imaging of living material. Any increase in the x-ray flux would clearly reduce imaging times and allow hydrated images to be studied without the fear of introducing radiation-induced artefacts. However, the improvements needed to facilitate the recording of two images, each sufficiently short to avoid radiation damage, to give information on elemental distribution in a living specimen are technically too difficult at the present time. Furthermore, during the time it takes to alter the wavelength, any damage caused to the specimen may continue to proliferate even though the specimen is not, at that time, exposed to x-rays.

There is considerable interest, therefore, in treatments which preserve the structural integrity of the tissue and reduce radiation sensitivity. In transmission electron microscopy cryo-fixation, in which the specimen is frozen rapidly and then sectioned and examined whilst remaining frozen, has offered the possibility that chemical fixation could be avoided. Images of cryo-prepared material usually show the cellular structures to be more regular in outline and better preserved. Micrographs, therefore, differ from those of conventionally prepared tissues but cryo-fixation is technically demanding and still only examines a very thin section of the material in question furthermore the material still requires staining to enhance contrast as electrons are scattered, not absorbed as is the case in x-ray imaging.

Several methods are currently employed in electron microscopy which use frozen biological samples (e.g. freeze-fracture; freeze-etching; freeze-substitution) and the cryo-preservation of micro-organisms is routinely used in culture collections. The experience already gained by these

Figure 1 The liquid nitrogen filled dewar through which helium is passed. The specimen holder, onto which the silicon nitride windows are mounted, is placed at the bottom of this assembly. Thermocouples monitor the temperature of the mount in several positions as well as the incoming jet of helium.

techniques needs to be borne in mind when freezing samples for ultrastructural studies using soft x-ray microscopy.

Water can account for 40-90% of a biological sample though micro-organisms such as bacteria, yeast and unicellular algae usually have a much lower water content. When such samples are cooled below zero, ice crystals form which, as they expand, can damage the ultrastructure of cells. Solid water can exist in three main states, hexagonal crystals, cubic crystals and a vitreous or amorphous state. Ultrastructure is preserved best in the vitreous state though this requires rapid freezing at rates of $>2 \times 10^5 \text{ }^\circ\text{C.s}^{-1}$ over the range 20 to -100°C i.e. within a fraction of a ms. In practice, the accepted criterion for freezing speed is that it should reduce ice crystal size to a point where there is no visible structural distortion (which will depend on the resolution of the microscopy). Established freezing methods such as plunge freezing into liquid Freon or propane cooled by liquid nitrogen can produce freezing rates of 10^1 - $10^5 \text{ }^\circ\text{C.s}^{-1}$ though the fastest rates are only achieved with cell monolayers. Liquid nitrogen alone is not satisfactory since it can achieve rates of only $10^3 \text{ }^\circ\text{C.s}^{-1}$ due to an insulating layer of evaporated nitrogen gas. Ultrastructural damage can be reduced by including a cryoprotectant such as glycerol or prior fixation of the sample with glutaraldehyde. However, both of these have the potential for introducing artefacts into the image. Spray or jet freezing using propane cooled with liquid nitrogen is particularly suitable for suspensions of single cells which, due to their low thermal mass, can usually be satisfactorily frozen without using a cryoprotectant.

Cell organelles vary in their sensitivity to ice crystal damage with mitochondria, endoplasmic reticulum and the Golgi apparatus showing best preservation due to their low water content or because of their intra-organelle solute concentration. The nucleus has a relatively high water content and is the most sensitive to ice crystal damage.

The freezing system used for a particular technique will depend of the type of specimen and the constraints of the instrumentation but should aim to freeze within the limits quoted above in order to produce a vitreous state (the ideal) or ice crystals which will not cause damage up to the resolution limit if the microscope. This report relates to the progress made in developing a cryo-stage for soft x-ray microscopy at the ALS and the initial results that have been obtained using this equipment.

Material & methods

Beam line improvements. The use of zone plates to focus the x-rays results in a considerable loss of fluence, since the high resolution zone plates used at XM-1 can only be fabricated with relatively low diffraction efficiency. A new condenser zone plate with an efficiency that was improved by a factor of 15 has now been introduced and thus imaging times are reduced by the same factor.

Cryo-preparation. A monolayer of *Chlamydomonas* cells was sandwiched between two silicon nitride windows, each 50nm thick. This was then frozen by jet-freezing with two jets of helium cooled by passing through liquid nitrogen, one onto each window. The flow rate of the helium could be adjusted to provide different freezing rates. In general, however, rates of cooling of $10^3 \text{ }^\circ\text{C}$ per sec were routinely obtainable with a final temperature of c. -130°C . Throughout the freezing process the frame holding the silicon nitride windows was maintained at 21°C by means of several 'heaters'. Once frozen the complete assembly (Fig. 1) was transferred to the beam line. The flow of liquid nitrogen cooled helium enabled the specimen to be maintained at the desired temperatures whilst the metal frame was kept at 21°C to prevent any thermally induced expansion or contraction of the beamline which would adversely affect the specimen focus.

Results & Discussion

Recently zone plates with a much greater efficiency have been installed on XM-1 and basic imaging times for hydrated *Chlamydomonas* cells have been reduced to approx. 0.2s. This reduction in the exposure time, by more than an order of magnitude, over previous imaging times (Stead et al., 1997) is short enough to prevent radiation-induced structural damage from being evident. However, using a series of very short exposures (ie reduced x-ray dose) it is apparent that radiation-induced specimen damage continues during the intervals between successive images (Fig. 2). Thus there is little damage apparent in either of the initial images (Fig. 2a,c) or in an image taken immediately after the initial image

Figure 2 Images of *Chlamydomonas* showing that radiation damage accumulates within the cells between exposures. Scale bar 1 μm . a) Initial image of a cell, exposure 0.2As. b) Second image taken immediately after the above image, exposure 0.2As. c) Initial image of a cell, exposure 0.1As. d) Second image taken 1min after the above image, exposure 0.1As. e) Initial image of a cell, exposure 0.05As. f) Second image taken 1min after the above image, exposure 0.2As.

(Fig. 2b). However, the damage, especially to the x-ray dense spheres, is very obvious (Fig. 2d) if there is a short interval (eg a few seconds) between recording sequential images. Therefore, whilst the decreased exposure time avoids observable radiation damage when only one image is recorded, sequential imaging of the same cell is still impossible due to radiation damage artefacts. Consequently if the area of interest of a particular cell is not in the field of view, or if it is out of focus, it is not possible to move a few mm and take a second image. If the initial image is very short (Fig. 2e) then it seems that a second image can be obtained (Fig. 2f) without apparent radiation damage even if there is a lag considerable between the images. However, the signal:noise ratio is so poor that it is impossible to ascertain if the image is in focus and unless the object of interest is very distinct it is impossible to be certain that the field of view is appropriate.

The development of the cryo-stage has considerably increased the exposure time that can be used without observable radiation damage (Fig. 3). Indeed even after many exposures totalling in excess of 1.0As subsequent images appear similar, if not identical, to those taken at the very beginning of the sequence (Fig. 3a,b). Because it is possible to increase the exposure time the image quality (signal:noise ratio) can be greatly improved, thus details of the cell structure which were unclear in images of samples held in an aqueous environment become very much more obvious in images of frozen material. For example the flagella are visible and indeed the internal structure (ie microtubules) of these is evident in some images, especially if the exposure time is increased to further improve the signal:noise ratio (Fig. 3c).

The chloroplast and pyrenoid within it are also identifiable (Fig. 3d), but the most striking features are the numerous x-ray absorbing spheres each up to 1µm in diameter. Unlike material held in an aqueous environment (Stead et al., 1997; Ford et al., 1998) the images of the spheres show no sign of radiation damage even after multiple exposures. Such images are very similar to those previously reported by Schneider et al (1995) in which internal cellular details were also visible but in which exposure times of at least 10s were needed because of the lower x-ray fluence that was available.

The greater stability of the specimens has allowed series of images to be taken which cover adjacent areas of the specimen, these can then be tiled together to give an image of the entire cell (Fig. 4). However, in this case the specimen was frozen slowly (a freezing rate of between 10 and 10³°C per sec as opposed to 10³°C per sec for the specimen in Fig. 3) and held at between -50 and -80°C (as opposed to -150°C) to avoid the problems of ice crystal contamination on the window. Under these conditions the cell contents appear somewhat shrunken leaving a clear area around each structure which did not absorb x-rays. More importantly however, is the ability to perform elemental mapping on hydrated, as opposed to dried cells, without any concerns about the introduction of radiation damage. Images taken either side of the oxygen absorption edge (Fig. 5) show that the spherical inclusions are rich in oxygen. The exact function of these structures, however, remains unresolved, in the literature there are only two reports of any structures which initially might be thought to resemble the spheres seen by x-ray microscopy. Wolfe et al. (1997) reported the over production and accumulation of some of the photosynthetic light harvesting proteins in a mutant strain of *Chlamydomonas*. However, all the present images, in which these x-ray absorbing spheres have been observed have been obtained using the wild type of *Chlamydomonas reinhardtii* in

Figure 3: Soft x-ray images of frozen hydrated *Chlamydomonas* cell. a) Exposure 0.02As but had previously been exposed for a total of 0.08As. b) Image of same cell; exposure 0.5As having previously been exposed for 1.5As. c) Anterior part of cell showing flagella and x-ray dense spheres. Exposure 0.5As. d) Posterior of the same cell showing the chloroplast with pyrenoid and the x-ray dense spheres. Exposure 0.2As but by this time the cell had been irradiated for 2.1As. The spheres labelled 1 and 2 and the same on each image. The images show the x-ray absorbing spheres (S), flagella (F), chloroplast (Ch) with pyrenoid (Py). Bar = 1µm.

Figure 4. Composite image comprising 5 individual images tiled together. This was produced directly by the software programme and has not received any further manual adjustments. Several organelles other than the x-ray absorbing spheres (S) are visible, including the nucleus (Nu), chloroplast (Ch) and pyrenoid (Py). This specimen was cooled slowly (10³°C per sec) and whilst radiation damage of the spheres is not obvious there is some shrinkage around each sphere and around the nucleus (arrowed) suggesting that there was shrinkage during the freezing process. Bar = 1µm.

which there is no over production of these proteins. The only other report relates to an accumulation of calcium phosphate at one particular stage of the cell cycle in a related species of *Chlamydomonas* (Siderius et al., 1996), but in the present soft x-ray microscopy study the spheres are not only somewhat larger but they persist throughout the cell cycle. Therefore, neither of these reports seem to be looking at the same structures that we have observed with soft x-ray microscopy. Further work to characterise the composition of these spheres is clearly necessary and this, coupled with biochemical studies, should give a better insight of their possible function.

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Figure 5: Oxygen distribution in a slowly frozen cell. Two images were taken below and at the oxygen K- absorption edge and processed to show the oxygen distribution. Bar = 1µm.

Effect of Chemical Additives on the Alkali-Silica Reaction Product Examined by Transmission Soft X-ray Microscopy

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INTRODUCTION

Worldwide, 104 concrete dams and spillways, massive concrete structures, have been damaged by the alkali-silica reaction (ASR) [1]. Reactive silicates present in some aggregate react with alkalis present in the concrete pore fluid to produce an alkali-silica reaction gel. Overall, two steps comprise the alkali-silica reaction, the dissolution of silica and the formation of a potentially expansive gel product by repolymerization. Swelling of the ASR gel can eventually lead to cracking and overall expansion of the affected structure. As a result of this damage, the structure loses strength, particularly in flexure, stiffness, and impermeability – material properties essential to ensure the integrity and performance of the structure during service. In addition, expansion of the concrete can interfere with clearances required for mechanical elements, such as spillway gates or turbines, in dams. Currently, no practical means exists to arrest ASR once damage is initiated. Reconstruction of affected massive concrete structures, such as dams, is not economically feasible. As a result, structures affected by ASR must be continually monitored so that repair and reinforcement can be performed as needed.

However, research has shown that the introduction of certain chemicals, particularly lithium- and calcium-containing salts and acetone [2], can reduce expansion caused by ASR. Perhaps the most fundamental impedance to the practical use of chemical additives is the lack of knowledge of the mechanisms by which these chemical additives may control expansion. Without understanding the mechanism of control, it is difficult to predict the effectiveness of a chemical additive and to foresee the duration of its control. A more thorough understanding of these mechanisms would aid assessing which chemical are most effective over long periods and which doses are optimal.

OBJECTIVE

The objective was to investigate the mechanisms by which some chemical additives control expansion using transmission soft x-ray microscopy. The reaction of alkali-silicate gel in sodium hydroxide solution in the presence of calcium ions, lithium ions, and acetone was observed using transmission soft x-ray microscopy. These images can be compared to images of the alkali-silicate gel in sodium hydroxide solution, without the chemical additives [3,4], to qualitatively assess the effects of calcium chloride, lithium chloride, and acetone.

EXPERIMENT

Slurries were prepared containing ASR gel and NaOH solutions with $\text{SiO}_2/\text{Na}_2\text{O}=3$, proportions identified [5] to maximize expansion. The ASR gel used in these investigations was obtained from the Furnas Dam located in Minas Gerais, Brazil. The local quartzite aggregate used in the concrete construction was found to be reactive when surface staining, cracking, and the presence of gel were noted in 1995, 32 years after the construction of the dam was completed. To examine the effect of some chemical additives on the ASR gel, the ground gel (~300 sieve) was exposed to four solutions: (a) 0.7M NaOH (control/background), (b) 0.7M NaOH + 0.1M CaCl_2 , (c) 0.7M NaOH + 0.1M LiCl and (d) 0.7M NaOH + 10% (v/v) acetone. The pH of 0.7M NaOH, 0.7M NaOH +

0.1M CaCl_2 , and 0.7M NaOH + 10% (v/v) acetone solutions measured 12.6. The pH of the 0.7M NaOH + 0.1M LiCl measured 12.4.

RESULTS

X-ray images show that the reaction of the ASR gel in 0.7M NaOH + 0.1M CaCl_2 solution produces lath-like structures (Fig.1). The product morphology is very similar to the spherulitic 'sheaf of wheat' structures produced by the reaction of the alkali-silicate gel in saturated $\text{Ca}(\text{OH})_2$ solution [3] and described in the literature as calcium silicate hydrates (C-S-H) or C-S-H precursors [6-8]. It is theorized that the formation of C-S-H or a related compound will decrease the degree of swelling that would otherwise result. The C-S-H-like structure may also contribute strength to the concrete.

X-ray images of alkali-silicate gel in 0.7M NaOH + 0.1M LiCl solution show products of varying morphology (Fig. 2). Small particles ranging from approximately $0.25\mu\text{m}$ to $3\mu\text{m}$ in size are typical of the sample, and repolymerization is evident in some x-ray images. X-ray images show that the repolymerized gel is apparently of decreased density, as compared to the original particles of ASR gel, and is believed to be the source of expansion. However, the volume of repolymerized produce appears to be less than in 0.7M NaOH without the addition of LiCl .

X-ray images of the alkali-silicate gel in 0.7M NaOH + 10% (v/v) acetone are shown in Figure 3. The images show regions of varying density, similar to the repolymerized alkali-silicate product resulting from the reaction of the ASR gel in 0.7M NaOH . The indication of extensive repolymerization suggests that acetone may not be an effective chemical additive for controlling expansion caused by the alkali-silica reaction.

Figure 3. X-ray image of alkali-silicate gel in 0.7M NaOH + 0.1M CaCl_2 . The image was taken with a 14.858 s exposure time with a beam current of 201.3 mA at an original magnification of 2400x, scalebar = $1\mu\text{m}$. 71105101

Figure 2. X-ray image of alkali-silicate gel after 1 week in 0.7M NaOH + 0.1M LiCl . The image was taken with a 11.190 s exposure time with a beam current of 267.5 mA at an original magnification of 2400x, scalebar = $1\mu\text{m}$. 71105101

Figure 3. X-ray image of alkali-silicate gel in 0.7M NaOH + 10% acetone by volume. The image was taken with a 8.978 s exposure time with a beam current of 222.3 mA at an original magnification of 2400x, scalebar = $1\mu\text{m}$. 71105101

CONCLUSIONS

Reaction of the ASR gel in 0.7M NaOH + 0.1M CaCl_2 solution produced spherulitic structures resembling the distinctive 'sheaf of wheat' morphology which is not believed to be expansive. Images of the reaction of the ASR gel in 0.7M NaOH + 0.1M LiCl solution showed that dissolution of the original gel particles had occurred. However, in the presence of lithium chloride, the repolymerization into an expansive gel was decreased as compared to the reaction of the ASR gel in 0.7M NaOH solution. Images of the reaction of the ASR gel in 0.7M NaOH + 10% (v/v) acetone solution showed alkali-silicate gel particles surrounded by repolymerized gel,

indicating that the use of acetone as a chemical additive may not be as effective as once believed in preventing expansion caused by ASR.

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Localization of Nuclear Pore Complex in Hydrated Tumor Mammary Epithelial Cells by High Resolution Transmission X-ray Microscopy

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In order to evaluate the ability for soft x-ray microscopy to reveal well known nuclear structures, we have undertaken a series of immunolabeling experiments for proteins localized in defined nuclear subdomains. Here we present results obtained with staining for nuclear pore complexes, the visualization of which is particularly challenging in conventional electron microscopy. Nuclear pore complex (NPC) is a large (50-100x106 D) collection of proteins which organize the ~9 nm openings in nuclear membranes of eukaryotic cells. NPC immunolabeling was performed in tumor human mammary epithelial (T4) cells followed by imaging of whole hydrated labeled cells with a high resolution transmission x-ray microscope¹ (XM-1) (ALS Beamline 6.1.2). Cells

Figure 1 A. Human tumor mammary epithelial cell (T4) nucleus seen with XM-1. The nuclear pore complex (NPC) was immunolabeled with silver enhanced gold and appears uniformly distributed in a pattern characteristic of NPC.

Figure 1 B: Control image of a cell prepared as for fig. 1 A, but without the primary antibody against NPC, therefore no staining is evident.

were grown on silicon nitrate windows (100 nm thickness), permeabilized with 0.5% triton in cytoskeletal buffer with protease and phosphatase inhibitors, and chemically fixed in 2% paraformaldehyde and 0.1% glutaraldehyde in phosphate buffered saline (PBS). The windows were then preincubated with superbloc in PBS to block nonspecific labeling and incubated with anti-NPC polyclonal antibodies, followed by secondary labeling with a goat anti-rabbit antibody conjugated with fluorescein/nanogold (1:200 dilution). The fluorescein moiety allows imaging by confocal microscopy. Following detection of fluorescent labeling in the confocal microscope, the nanogold particles (1.4 nm diameter) were silver enhanced for viewing with the x-ray

microscope (spatial resolution 43 nm). XM-1 images of cells in an aqueous environment at atmospheric pressure were obtained using a 2.4 nm wavelength (517 eV photon energy level), below the K absorption edge for oxygen (543.1 eV) but above that for carbon (284.2 eV). Under these conditions, water is transparent while cellular structures and metallic labels are not. No staining was evident in control cells labeled with secondary antibody followed by silver enhancement (Fig 1 B). Silver enhanced label revealed numerous and uniformly distributed nuclear dots in cells labeled with both primary and secondary antibodies, a pattern that is characteristic of NPC (Fig 1 A).

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Preliminary Investigation of Molecular Trafficking in Malarial Infected Red Cells

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Investigation of the interactions between the intraerythrocytic malarial parasite *P. falciparum* and the host red blood cell has been the major focus of our biological x-ray effort at LBNL. We published the first extensive study of the development of parasites within normal human erythrocytes, and of the effects on parasite structural integrity of abnormal erythrocyte membranes and protease inhibitors, a class of potential anti-malarials (Magowan 1997). In that study we described newly elaborated carbon dense tubular and sheet-like structures that appeared to surround the parasite and extend into the red cell cytosol. We hypothesized these structures were components of the tubovesicular network (TVN), a network that is thought to be involved in protein and lipid transport. In a more recent study we immunolabeled molecules for x-ray microscopy with silver-enhanced gold-bead conjugated antibodies, demonstrating the success of this technique on both red blood cells and melanoma cells. This technique has enabled us to study the interactions between a parasite induced ligand on the surface of infected erythrocytes, and receptors on endothelial cells which mediate adhesive changes associated with the often fatal syndrome of cerebral malaria (Yeung 1998).

The malaria parasite is a eukaryotic cell that has adapted to a unique environment in which it is surrounded by the red cell plasma membrane and cytosol. The parasite itself has a plasma membrane, and sits within another membrane-bound compartment, the parasitophorous vacuole, enclosed by the parasitophorous vacuolar membrane (PVM). The PVM in turn extends into a series of complex, multicompartimented tubulovacuolar structures in the red cell cytosol known as the tubovesicular network (TVN). Sphingolipid synthesis in the infected red cell has been localized to the TVN which may be analogous to the *cis*-Golgi (Elmendorf and Haldar 1993; Elmendorf and Haldar 1994). While some data strongly suggest that protein transport in infected red cells can proceed via a classical Golgi secretory pathway (Hinterberg et al., 1994) or a functional but reduced Golgi (Ward 1997), other workers hypothesize that a morphologically and biochemically distinct "classical" Golgi complex may not exist (Banting et al., 1995).

Much remains to be learned about the nature of the pathways for trafficking molecules between the parasite and the external milieu. The mechanisms by which parasites transport molecules across the several membrane layers that surround them are of interest because these unique mechanisms may be vulnerable to inhibitors, they may provide information about previously unrecognized eukaryotic transport pathways, and they may provide a means of introducing chemotherapeutic agents directly to the parasite. The physical nature of routes for transport of nutrients, macromolecules and non-metabolized solutes has been debated. There may be a transient or stable parasitophorous duct of 50-70nm diameter which provides direct access between the intraerythrocytic parasite and the external milieu. Its existence was first suggested by the results of a study that used small highly fluorescent

latex spheres to investigate transport of macromolecules (Pouvelle et al., 1991). These results have been contradicted by other studies (Hibbs 1997; Fujioka and Aikawa 1993). A subsequent study hypothesized two distinct macromolecular transport pathways in malaria infected red cells (Goodyer 1997). Transmission EM in that study showed areas of apparent membrane continuity between the erythrocyte membrane and the parasitophorous vacuolar membrane which may constitute the "metabolic window" hypothesized by Elford *et al* to occur at contact sites or regions of close apposition between the host erythrocyte membrane and the PVM (Elford et al., 1995).

The studies currently underway at Beamline 6.1 extend our investigations of subcellular structures and processes that can be imaged using immunogold labeling, and ultimately, the tilt-stage capabilities of the x-ray microscope, to the study of protein trafficking in malarial infected erythrocytes. In the past, transport of proteins to and from parasites has been investigated, for most part, through models based on morphological analyses using fluorescence microscopy. With higher resolution x-ray microscopy and tilt-stage and tomographic reconstruction technology, we will utilize and extend the many tools and techniques that have been developed and tested in fluorescence analyses of malarial protein transport.

To these ends, we obtained two antibodies that are reported to react with the PVM and confirmed that they localize by indirect immunofluorescence with the intracellular parasite. We have acquired the expertise to reproducibly lyse red cells and release parasites using dipeptide induced selective osmotic shock (Elford and Ferguson 1993). We have devised additional steps to overcome the clumping of extruded parasites we encountered. Currently, stereo images can only be collected from dried samples which are manually tilted to gather images from two angles. Difficulties arose when we imaged dried samples of extruded parasites, in that we were unable to obtain the image clarity needed to see the parasites. The implementation of a cryo-tilt stage would eliminate these difficulties. Experiments are continuing to determine whether the extruded parasites can be imaged when they are labeled with antibody-conjugated gold beads enhanced with silver.

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Soft X-ray Microscopy Development at XM-1

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INTRODUCTION

The high resolution soft x-ray microscope XM-1 at beamline 6.1 has been used with applications in biology, environmental sciences, and materials sciences. Instrumental improvements include the development of a cryo-stage, stereo imaging, and a new condenser zone plate lens, which decreased the exposure times at XM-1 by a factor of 15 and also allowed improved spectral resolution ¹.

Biologists utilize both natural (absorption) contrast and specific labeling protocols to study parasites, protein distributions in cells, nuclear structure, algae and bacteria. In collaboration with earth and environmental scientists we study macromolecular structures in humic substances, interactions of microorganisms, and related chemical reactions. Chemical reactions related to cement and concrete, which are important to our infrastructure, are studied in collaboration with civil engineers.

LARGE IMAGE TILES

XM-1 allows us to take thousands of high resolution (43 nm) images a day. The size of each of these images is about 10 μm , larger image fields are now regularly tiled together to provide images of large size. This tiling process utilizes the built in precision and digital control of the XM-1 sample-stages and uses software algorithms originally developed by B. Loo ². Figure 1 shows a tiled image mosaic of a dividing epithelial cell in late anaphase.

Figure 1. Tiled image of epithelial cells in late anaphase. This image was tiled together from 64 individual images (courtesy of Sophie Lelièvre, D. Hamamoto, C. Larabell)

Figure 2 Stereo image of the cell nucleus in an epithelial cell labeled for splicing factor. The sample was fixed by dehydration, which unfortunately does not preserve cell structures. The labeled regions however are clearly visible in 3D, demonstrating the ability to obtain 3D information at high spatial resolution with soft x-rays. Cryo-fixation and observation with a to be developed cryogenic tilt stage would provide the 3D information of the label and the cell structures (courtesy of Sophie Lelièvre, D. Hamamoto, C. Larabell)

3D INFORMATION

Individual x-ray micrographs provide a two-dimensional representation from a three-dimensional sample like a cell. To obtain 3D information, multiple-view images have to be recorded. Two-view images provide stereo sets, and large numbers of views can be used to obtain a full tomographic data set. With a sample tilt stage, XM-1 can be used to take these multiple-view images sequentially. For this to work the sample must not change between the exposures, which cannot be guaranteed with hydrated samples. To demonstrate the 3D capabilities we obtained stereo images of dehydrated cell nuclei that have been labeled with silver-enhanced gold antibodies for RNA splicing factor (Figure 2). To obtain 3D information without dehydration cryo-fixation and observation in a still to be built cryo-tilt stage is needed.

CRYO-STAGE

Cryogenic fixation essentially eliminates structural damage due to the radiation dose needed for multiple high resolution imaging³. We have developed a cryo-stage that uses liquid nitrogen cooled helium jets to maintain the sample at temperatures where vitrified ice is stable (below about 130K). Figure 3 shows a green alga (*Chlamydomonas*) images at a frozen state using

Figure 3 Soft x-ray image of frozen hydrated *Chlamydomonas* cell. The images show the x-ray absorbing spheres (S), flagella (F) (courtesy of A. Stead, T. Ford, J. Judge).

the cryo-stage in XM-1. Plans exist to develop a cryo-tilt stage that allows to obtain multiple view images in a frozen state as well.

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Soft X-Ray Microscopy: A Tool for the Study of Multicellular Organisms

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INTRODUCTION

Electron microscopy is routinely used to study protozoa and small multicellular organisms since conventional light microscopy is inadequate to elucidate their structure. However, each electron microscopy technique has its inherent limitations. Scanning electron microscopy can reveal superficial characteristics of organisms and surfaces of tissue sections. Transmission electron microscopy can provide a wealth of morphological detail, but numerous sections are needed to depict the continuity and interrelationships of internal organs or structures. Confocal microscopy requires fluorescent label to identify the structure of interest. Recent applications¹⁻⁴ of soft X-ray microscopy to study unicellular organisms and the intracellular changes induced by *Plasmodium falciparum* in infected red blood cells yielded results which could not be obtained by other microscopy techniques, suggesting that this technique may have wider applications in biosciences. This study was therefore undertaken to

- 1). - determine whether soft X-ray microscopy could be also be used to elucidate the structure of small multicellular organisms to complement the data obtained by other electron microscopy techniques, and
- 2). - to test the efficacy of selected vital stains to increase the carbon content of biological membranes, thus enhancing the contrast of images obtained.

The results presented are focused on the microfilariae of *Dirofilaria immitis*, the dog heartworm, and on the newborn larvae of *Trichinella spiralis*, a nematode parasite of vertebrates, which is acquired by eating raw or inadequately cooked meat (pork, bear) that contains the encysted, infective larvae. After being ingested, these larvae develop in the upper small intestine. Upon maturation and mating, the females produce newborn larvae which gain access to the circulatory system, become disseminated throughout the body, and infect voluntary muscle cells where they develop to the infective, encysted stage⁵.

MATERIALS AND METHODS

The newborn larvae are approximately 7 x 110 μm in size. They were obtained from in vitro cultures where *T. spiralis* adults, isolated from rats on the sixth day after experimental infection, were maintained. Microfilariae of *D. immitis*, approximately 6 x 310 μm in size, were isolated from the blood of a dog which harbored a naturally acquired infection. All larvae were fixed in 4% glutaraldehyde (Millonig's buffer, pH 7.5); some of the fixed larvae were processed for examination by transmission (Philips 201) and scanning (ETEC) electron microscopy⁶; others were examined by soft X-ray (MX-1) microscopy at the Advanced Light Source of the E. O. Lawrence Berkeley National Laboratory unstained, or after staining with either Methylene Blue, Azure II Blue, Trypan Blue, Crystal Violet or Lugol's Iodine.

RESULTS

The montages prepared from serial X-ray micrographs elucidated the internal structure of both larvae were too large for reproduction in this publication. The following organ systems or structures to be discerned by soft X-ray microscopy within the *T. spiralis* newborn larva body wall, the buccal area with stylet, nerve ring, esophageal thread, stichosome, primordia of the intestine and gonads, rectum and structures hitherto undetected by other techniques, e.g. vaginal primordium (?); nerve cells in the anterior part of the larva which send axonal projections to the cephalic sensory structures, and a ganglion-like structure located in midbody region of the larva.

Transmission electron micrographs were correlated with the montage to elucidate finer morphological details at specific levels of the larva. Longitudinal and oblique sections through the cephalic space reveal a stylet in the buccal capsule and numerous axons converging onto the tip of the cephalic space. An axon bundle is present near the nerve ring. Section through the anterior portion of the stichosome shows prominent triradiate lumen of the esophagus surrounded by the stichocytes. Cytoplasmic granules are prominent within the stichocytes. Sections through the caudal region of the larva show undifferentiated primordia of the intestine and of the gonads, ciliary nerve endings of the caudal sensory organs and the cuticular lining of the rectum.

Three of the five stains tested enhanced the density of structures or components within the larvae. Methylene Blue stained dense material located in the apertures of the anterior sensory organs in *T. spiralis* larvae. Azure II Blue delineated the muscle bands, and Crystal Violet the nuclei in *D. immitis* microfilariae.

DISCUSSION

The combination of microscopy techniques used in this study allowed the elucidation of fine structure of both larvae, although the main emphasis was on elucidation of the structure of *T. spiralis* newborn larva. Data about *D. immitis* microfilaria will be presented in a separate report.

Scanning electron microscopy disclosed that the surface of the newborn larva is similar to that of the adult worms. Despite its small size, the larva has a fully formed body wall consisting of cuticle, muscle cells and hypodermis, and primordia of internal organ systems including the stichosome, intestine, and gonads. Cephalic space contains numerous sense organs which are cilia-like terminations of axons originating from cells located in the anterior portion of the larva. These presumed sensory receptors may function in assisting the larva to locate skeletal muscles. Similar cilia present near the posterior end of the larva, suggest the presence of caudal sensory organs.

A prominent stylet, located in the cuticularized buccal cavity, may be used by the larva to perforate sarcolemma during infection of skeletal muscle cells. Triradiate esophagus, extending from the buccal cavity to the intestine, is enveloped by the primordial stichosome; many stichocytes contain cytoplasmic granules, suggesting that the stichosome may already be functional, secreting products into the esophagus. The granules within the stichocytes, and the granular material within nerve cells in the anterior part of the larva, are autofluorescent and readily detected by confocal microscopy. Intestine appears to be non-patent. Length of the rectum may be used as a characteristic to determine the gender of the larva.

Whereas transmission electron microscopy provided a wealth of morphological detail, soft X-ray microscopy provided an excellent overview of the general structure of the larva, and was the key technique which depicted the location and interrelationship of its internal organs. Such overview is not possible to obtain by scanning nor by transmission electron microscopy. For example, the soft X-ray images strongly suggest that the space between the nerve ring and the cephalic space contains nerve cells, many of which apparently innervate the cephalic sensory structures. In addition, this technique has allowed detection of structures which were hitherto either unknown or were not expected to be present at this stage of development, e.g. the ganglion-like structure located in the mid-body region of the larva, and the lateral thickening of the inner body wall, resembling the vaginal primordium which is more defined in the mature muscle larvae.

These preliminary studies have demonstrated that the unique capabilities of soft X-ray microscopy can be successfully applied to examine the structure of small multicellular specimens, and indicated the potential use of this technology in

biological and biomedical sciences. In addition to providing new information about organization and interrelationship of internal organs, the images obtained by soft X-rays can serve as a valuable reference for interpretation of results obtained by transmission electron microscopy.

Although the images of unstained larvae were very informative, the internal organization of the specimens examined would be depicted more clearly if the contrast of the image could be enhanced. An initial test of five stains, all of which bind to cell membranes and proteinaceous structures, was made to determine whether the increasing the carbon content of the membranes by staining would enhance the contrast of the image obtained. The results suggest that three of the five stains tested, Methylene Blue, Azure II Blue and Crystal Violet, may be useful for contrast enhancement. Methylene Blue rendered visible the dense material, probably glycoprotein in nature, located in the apertures of the anterior sensory organs. Azure II Blue rendered muscle bands of the microfilaria more apparent, and Crystal Violet appeared to have an affinity for the nucleus. Further studies are planned to determine which stain concentration:staining time combination will provide the optimum image contrast.

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Spectromicroscopy at the XM-1

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INTRODUCTION

The XM-1 x-ray microscope has been shown to have a spatial resolution of 43nm¹. In addition to this high spatial resolution, the XM-1 also has a good spectral resolution. Work is underway to characterize the spectral resolution of the XM-1 microscope. The aim is to use the XM-1 to image samples with 43nm spatial resolution and at the same time to use the high spectral resolution to distinguish different elements and even different chemical states within a sample. It has been shown that the energy resolution of the XM-1, $E/\Delta E$, is better than 750. We have shown that with this energy resolution we can distinguish between different chemical states of a particular element. We can see spectra with adequate signal to noise even for individual 42nm pixels. With this, we expect to soon begin work on various experiments in which we will image a sample and distinguish different chemical species of specific elements with 43nm resolution.

EXPERIMENT

The XM-1 X-ray Microscope is a full field imaging microscope using a condenser zone plate to illuminate the sample and objective zone plate to image the sample. The spectral resolution is determined by a linear monochromator which includes the condenser zone plate and a pinhole. The energy is chosen by changing the distance between the condenser zone plate and the pinhole. The bandwidth is determined by the size of the pinhole, which is usually less than 10 microns. To obtain a spectral (energy) scan of a sample, a series of full field images are acquired by the CCD camera, with each image at a different energy. A series of images taken at 100 different energies each covering a field of view of 10 microns and with a spatial resolution of about 43nm takes about 20 minutes.

RESULTS

We have determined the spectral resolution of the XM-1. We scanned the energy of the XM-1 around the L-edge absorption energy of Calcium and measured the absorption in a sample of CaSO₄. The graph of this absorption is shown in Figure 1. The measured width of the absorption peak of Calcium from the XM-1 data is 0.5 eV. For comparison, the absorption in the same sample was measured at the Calibration and Standards Beamline, 6.3.2, which has an energy resolution, $E/\Delta E$, greater than 5000.² The measured width of the absorption peak at that beamline was 0.4 eV. The broadening of the absorption feature is due to the finite spectral width of the XM-1. From this, an early estimate of the spectral resolution of the XM-1 is $E/\Delta E$ greater than 750.

This resolution is fine enough to be able to distinguish between different chemical states of specific elements. The absorption peak energy shift due to the different oxidation states is larger than the broadening due to the finite spectral resolution. We performed spectral scans of Chromium metal, hexavalent Chromium in K₂Cr₂O₇, and trivalent Chromium in CrO₃. The

Figure 1. Absorption of CaSO_4 from the XM-1. The FWHM of the peaks are 0.5eV.

results are shown in Figure 2. It is clear that the different oxidation states of the Chromium cause a shift in the absorption spectra that is large enough for us to distinguish the different states.

Figure 2. Absorption of Chromium in three different oxidation states.

In order to reap the full benefits of this spectral resolution on the XM-1 microscope, the spectral resolution must be available on the microscopic scale approaching the 43nm resolution of the microscope. Since there are fewer photons passing through small areas on the sample, the photon noise is larger and the spectra have decreased signal to noise. With reasonable exposure times which do not destroy the sample, at least for a dry sample, then the signal to noise is clearly good enough that shifts in absorption peaks of a few eV corresponding to oxidation state changes would clearly be visible. Figure 3 shows sample spectra from four single 42nm by 42nm pixels.

Figure 3. Absorption spectra for four different single 42nm pixels from a sample of CaSO_4 .

CONCLUSIONS

With this ability to distinguish between different elements and different chemical states of these elements on a 43nm scale, a variety of interesting experiments are now accessible for future research at the XM-1. One interesting experiment that has been started looks at bacteria that are known to reduce hexavalent Chromium into trivalent Chromium. It is important to understand the mechanism by which these bacteria reduce the Chromium. We hope to be able to map the distribution of the different Chromium species within and around the bacteria.

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Beamline 6.3.2 Abstracts

A comparison of mechanically ruled versus holographic varied line spacing gratings for a soft X-ray flat field spectrograph

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INTRODUCTION

Soft X-ray flat field grazing spectrographs are widely applied for plasma diagnostics¹. These spectrographs take advantage of the recent significant progress of 2-D detectors. In 1982, Fonck et al² developed a near grazing-incidence ($\alpha = 70.6^\circ$) spectrograph which uses an aberration corrected holographic grating. The grating was recorded by a system consisting of two coherent point sources. This spectrograph has a quasi-flat focal curve and a flat focal field in the wavelength range of 10-17 nm. With the advent of the modern numerical-controlled ruling engine³ it became possible to fabricate a wide variety of varied-line-spacing (VLS) gratings. Taking advantage of this, Nakano et al⁴ developed a compact flat-field grazing incidence soft X-ray spectrograph working in the 0.5-40 nm region. In this spectrograph, the focal plane is almost perpendicular to the diffracted rays, an advantage for the use of 2-D detectors.

Recently laminar-type holographic gratings have been revived in the soft X-ray region. The advantages of laminar-type holographic gratings over mechanically ruled gratings are: 1) the suppression of overlapping higher orders; 2) reduced scattered or stray-light^{5,6}; 3) durability to higher heat loads.⁷ The purpose of this note is to present measurements of the diffraction efficiency and resolution of a laminar-type holographic grating recorded by aspheric wave-fronts⁸ and a blazed-type aberration corrected ruled grating.

SPECTROGRAPH AND GRATING DESIGN

A schematic diagram of the soft X-ray flat field spectrograph⁴ is shown in Fig.1. A spherical holographic grating G accepts light emerging through an entrance slit E. Diffracted light is focused on an image plane Σ that makes an angle ϕ with the plane Σ_0 that is perpendicular to the diffracted principal ray OB_0 . The angle ϕ is positive when measured counterclockwise from Σ_0 toward Σ and $|\phi| \leq \pi/2$. The basic design parameters are as follows.

The radius of curvature of the grating $R = 5606$ mm; effective grating constant $\sigma = 1/1200$ mm; ruled width $W = 50$ mm; ruled height $L = 30$ mm; slit height $H = 1$ mm; wavelength of the recording laser $\lambda_0 = 441.6$ nm; spectral order $m = +1$; distance from slit to the grating center, $r = 237.0$ mm; incidence angle $\alpha = 87.0^\circ$; distance from the focal plane perpendicular to the y-

Figure 1. Schematic diagram of the soft X-ray flat field spectrograph.

axis to the grating center $D = -235$ mm; and wavelength range of a 5-20 nm. Therefore, the distance from grating center to the image plane $r' = 235 / \cos(\pi/2 + \beta_0)$, and $\phi = -\beta_0 - \pi/2$.

We used an aspheric wave-front resulting from the reflection of a spherical wave-front from a spherical mirror to record a holographic grating. The design parameters were determined by the analytical design method⁸ are given below: $r_c = 1890.99$ mm, $R_s = 570.00$ mm, $p_p = 546.13$ mm, $q_c = 498.60$ mm, $\gamma = -60.0002^\circ$, $\delta = -19.6399^\circ$, $\eta_p = 50.1400^\circ$, $\lambda_0 = 441.6$ nm. For the definition of the parameters refer to Ref. 8. The substrate of the holographic grating was SiO_2 with a RMS roughness of 1 nm. The photoresist, OFPR5000, was used as an etching mask. The sinusoidal grooves of the holographic grating thus recorded were processed into laminar grooves by reactive ion beam etching in CHF_3 . The groove depth of 10 nm and the groove width to groove spacing ratio of 0.34 were etched on the blank. After making the grooves the surface was coated with Au of a 100 nm thickness.

As a reference, we also measured a blazed-type mechanically ruled VLS grating³. The radius of curvature R and groove parameters n_{20} , n_{30} , and n_{40} for this grating are: $R = 5649$ mm, $n_{20} = -7.08090 \times 10^{-3} \text{ mm}^{-1}$, $n_{30} = 2.85666 \times 10^{-6} \text{ mm}^{-2}$, $n_{40} = -5.25446 \times 10^{-7} \text{ mm}^{-3}$. The blaze angle is 3.2° and the coating material is Au. The blaze wavelength at the incidence angle $\alpha = 87^\circ$ is 10 nm.

EXPERIMENT

The absolute efficiency of both the holographic and the ruled VLS gratings were measured at the standards and calibrations beamline 6.3.2, built and operated by Center for X-ray Optics at the Advanced Light Source (ALS),

Lawrence Berkeley National Laboratory.

The measurements were performed at a fixed incident angle $\alpha = 87^\circ$ just as the gratings are used in the spectrograph. The results are shown in Fig. 2 for spectral orders $m=0, 1, 2$. For the $m = +1$ order, as expected, the ruled grating has a higher efficiency than the holographic grating except for wavelengths shorter than 6.5 nm. An essential difference can be seen in the higher orders, between the two gratings. For the holographic grating, the ratio of the second order to the first order efficiency is about 10% and is independent of wavelength. Whereas for the ruled grating, the second order to first order ratio varies from $\sim 300\%$ at 4.5 nm to $\sim 10\%$ at

20 nm. The cross point of the efficiency curves for the first and second order lights is 6.5 nm, and below this wavelength the second order is stronger than the first order.

A measurement of the spectral resolution was performed using a spectrograph with a laboratory X-ray source at Research Institute for Scientific Measurements at Tohoku University. This system consists of the soft X-ray generator (The Manson model 2 mini-focus ultra-soft X-ray source), a vacuum spectrograph having the correct mounting parameters assumed at design stage of the gratings, and a microchannel plate with a 1-D photodiode array as a focal plane detector (Hamamatsu Photonics C2321-01). The emission band of C-K (4.4 nm) generated at a power of 4 kV and 0.035 mA was observed for a 10 min. exposure time (refer to Fig.3). The intensity was normalized to the intensity of the first diffraction order. For the ruled grating,

Figure 2. Efficiency measurements for the holographic and mechanically ruled gratings versus wavelength.

relative intensity of the second (or third) order light to the first order light is about 95% (or 80%), and up to sixth order is observed. On the other hand, for the holographic grating the relative intensity of the second (or third) order is less than 10% (or 5%). This result also confirms the character of extremely lower higher order lights of the holographic grating than the ruled grating.

The FWHM of the first order is about three times worse (4 Å) for holographic grating as compared to (1.5 Å) the ruled grating. In addition, the dispersion of the holographic grating is slightly smaller than that of the ruled grating. It is likely that these are the result of alignment errors in the recording system of the holographic grating. Actually, for a small change of the incident beam direction, the best image point of the first order light was shifted. Therefore it is possible that a small correction of the recording system or an adjustment of the focal curve to the detector plane could improve the FWHM value for the holographic grating.

Figure 3. The normalized spectrum of 4.4 nm C-K band. The full and dotted lines show the intensity of the holographic grating and ruled grating, respectively.

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Characterization of Multilayer Reflective Coatings for Extreme Ultraviolet Lithography

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INTRODUCTION

The synchrotron-based reflectometer at beamline 6.3.2 is an important metrology tool within the current Extreme Ultraviolet Lithography (EUVL) program. The EUVL program is a joint activity of three National Laboratories and a consortium of leading semiconductor manufacturers. Its goal is the development of a technology for routine production of sub-100 nm feature sizes for microelectronic circuits. Multilayer-coated normal-incidence optical surfaces reflecting in the Extreme Ultraviolet (EUV) spectral range near 13 nm are the basis for this emerging technology. All optical components of existing and currently manufactured prototype EUV lithographic steppers need to be characterized for their at-wavelength reflectance during their development and manufacturing process. Multilayer coating uniformity and gradient, accurate wavelength matching and high peak reflectances are the main parameters to be optimized. The mechanical and optical properties of beamline 6.3.2 proved to be well suited for the needs of the current EUVL program. In particular this beamline is highly precise in its wavelength calibration and the determination of absolute EUV reflectivity. Beamline 6.3.2 as well as reference multilayer coatings proved to be stable over a period of more than two years within 0.2 % for reflectivity and 0.002 nm for wavelength.

MULTILAYER DEVELOPMENT

Molybdenum/Silicon (Mo/Si) multilayer coatings with 40 periods, a peak reflectance near 67 %, a centroid position near 13 nm and a bandwidth of about 0.6 nm (Fig. 1) are the current standard for EUV reflective coatings fabricated at the Lawrence Livermore National Laboratory (LLNL)[1]. These coatings are routinely deposited with alternating 2.8 nm thick layers of Mo and 4.1 nm thick layers of Si (Fig. 2). Magnetron sputter film deposition is performed either on Si wafers or polished glass substrates. In order to achieve the above mentioned reflectivity, the high spatial frequency roughness (HSFR) needs to be in the order of 0.1 nm as measured with an atomic force microscope (AFM). An alternative multilayer material combination is Molybdenum/Beryllium (Mo/Be). For this multilayer system a reflectivity of 70% has been demonstrated at a slightly lower wavelength near 11 nm (Fig.1). At this wavelength the spectral match with the laser-plasma EUV source currently under development at Sandia National Laboratories (SNL) would improve the optical throughput of the overall system by a factor of 5. In general there is still a potential for further improvement of Mo/Si as well as Mo/Be multilayers. In particular the stability of multilayers under atmospheric as well as under EUV exposure at realistic EUVL vacuum conditions is currently under investigation. These activities focus on deeper understanding of the top layer interactions under different environmental conditions. Preliminary observations indicate no change in the resonant wavelength, but a loss of reflectivity on the order of a few percent depending on the experimental conditions.

Figure 1 Mo/Be and Mo/Si multilayer reflectance curves

Figure 2 TEM cross section of a Mo/Si multilayer

COATING OF EUVL OPTICS

Coatings for the 10x Microstepper

Two EUV lithography systems at SNL were recently upgraded with new projection optics. These optics replaced cameras coated earlier [2]. Each new camera consists of two multilayer coated spherical mirrors in a Schwarzschild configuration with greatly improved optical performance. First, better figure and finish of the mirror substrates reduced the wavefront error and the flare of the final optics. Second, the precisely graded multilayer coatings (Fig.3 a, b) increased the wavefront error only by a small amount, well within the error budget. Together with improvements on EUV masks and EUV photoresist, high quality prints of 80 nm 'elbows' were achieved (Fig.4) [3]. Multilayer deposition on the 10x Microstepper projection optics was performed at LLNL. Mirror substrates were spun under a shadow mask during the deposition in order to precisely grade the multilayer thickness along the radius of the mirrors. In an iterative approach several surrogates were coated at LLNL and characterized at beamline 6.3.2. The results were then used for improvements of the mask shape for the next coating run. The goal was to achieve a gradient such that the peak wavelength is matched on all locations of the mirrors for the illumination angles in the Schwarzschild arrangement. Wavelength mismatch would result in throughput losses as well as phase errors, which would lead to decreased image quality.

Figure 3a Grading of the Mo/Si coating on the small 10x mirror

Figure 3b Grading of the Mo/Si coating on the big 10x mirror

Figure 4: 80 nm 'elbows' printed with a multilayer-coated Schwarzschild camera with numerical aperture 0.088 [3].

Coatings for the Engineering Test Stand

Mirror M3 for the Engineering Test Stand (ETS) projection optics was coated recently. The ETS represents an early prototype EUVL stepper, which will allow printing 100-nm features. Four projection mirrors and four condenser mirrors will be used in the ETS. Along one diameter of projection mirror M3 a uniform coating is needed on its convex spherical surface (Fig. 5a). Along the perpendicular diameter a slight linear grading is necessary in order to compensate for the slightly different angles of illumination (Fig. 5b). The atomic level control of coating uniformity and gradient was possible because of the accurate and precise features of beamline 6.3.2. Long-term high accuracy is needed for wavelength matching all ETS mirrors, while even higher precision is necessary for the determination of the gradient/uniformity of the multilayer coatings.

Figure 5a: Normalized multilayer d-spacing variation for the M3 mirror along the uniform diameter.

Figure 5b: Normalized multilayer d-spacing variation for the M3 mirror along the graded diameter.

EUVL MASK DEVELOPMENT

Another important task within the EUVL program is the development of multilayer reflective masks for lithographic printing. Low defect density multilayer-coated mask blanks are produced at LLNL for subsequent patterning at the semiconductor companies. The ultra-low defect density deposition of multilayer films on silicon wafers is the critical first step in the manufacturing process of EUVL masks. Mask blanks as well as patterned masks are routinely characterized at beamline 6.3.2 in order to assure wavelength matching, spatial uniformity and sufficient EUV reflectivity throughout the entire mask before and after patterning. Mask patterning requires chemical and thermal treatment, which may influence the multilayer performance dramatically. Absorber covered areas ideally should not reflect at all in the EUV spectral range, while open areas should maintain their full reflectivity.

OTHER EUVL RELATED ACTIVITIES

Other activities, which involve the use of the reflectometer at Beamline 6.3.2 include the development of multilayer stress reduction strategies and substrate recovery techniques.

CONCLUSION

Beamline 6.3.2 is an important tool for the development of Extreme Ultraviolet Lithography. It provides the necessary accuracy for wavelength matching the multilayer coatings in EUV optical systems with several resonantly reflecting surfaces. Furthermore, it provides the necessary precision in order to measure the uniformity or the gradient of multilayer coatings. Finally, it is instrumental in the further development of multilayers by enabling reliable absolute reflectivity measurements. Its precision was determined to be 0.2% for absolute reflectivity and 0.002 nm for wavelength over a long period of time. Multilayer d-spacing uniformity control in the order of 1 part in 1000 allows us to minimize wavefront distortion in EUV optical systems, permitting image patterns such as in Fig. 4 to be obtained.

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Element-specific photo-breakdown studies of environment-relevant molecules in the VUV to soft X-ray region at Beamline 6.3.2 and Beamline 9.3.1

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The large-scale industrial consumption of chlorofluorocarbons (CFCs) has attracted a lot of attention due to their destructive effects on atmospheric ozone and global change. Since the Montreal Protocol¹ a decade ago, there is now a serious effort made by many industries to replace their traditional CFC-based products (involving the so-called Annex A and B controlled substances), including refrigerants, aerosol propellants, plasma etchants, etc., with the more environment-friendly substitutes, which consist primarily of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and their derivatives. Many of the photochemical properties and electronic structures of these replacement molecules are, however, not known, which creates an unsettling potentiality that heavy commercial usage of these replacement molecules may in turn generate unforeseen adverse effects on the environment. Recently, we have begun a systematic study to examine the photoexcitation of a series of common substitutes, including HCFCs² and HFCs. In particular, a comprehensive data base of precise photoabsorption and photofragmentation cross sections (and branching ratios) of these industrially relevant molecules is being determined in the VUV to soft-X-ray region by using time-of-flight and photoion double or triple coincidence techniques.³ The characteristic photoion-photoion coincidence (PIPICO) spectra not only give a detailed picture of the dissociation dynamics following photoexcitation,^{4,5,6} but also provide an element-specific fingerprint of the target of interest if the excitation photon energy is tuned to specific ionization edges. This type of photodissociation information may be used ultimately for diagnostic purposes of unknown waste emission and for other smog analysis.

In addition to the obvious practical relevance, the measurements of photoabsorption and photofragmentation cross sections of HCFCs and HFCs can be used to provide important insight to shape resonance phenomena and non-Franck-Condon behaviour^{7,8} and to critically evaluate modern photoionization theories and electronic structure calculations. In particular, the presence of resonances (usually manifested as broad, intense features) in the photoabsorption and photoionization cross section profiles of small molecules has already attracted a lot of recent attention.^{4,7} The interplay between shape resonances (a resonant transition to a quasibound state that couples to the continuum) and autoionizing resonances (a multielectron discrete transition to an excited state that decays by ejection of one or more electrons) is believed to play a key role in molecular photoionization dynamics. The $\text{CF}_n\text{Cl}_{4-n}$ ($n=0-4$) and $\text{HCF}_m\text{Cl}_{3-m}$ ($m=0-3$) series provide an interesting variety of benchmark systems for investigating the geometry effect on the nature of the observed shape resonances. The devolution of molecular symmetry from $\text{CF}_n\text{Cl}_{4-n}$ ($n=0-4$) to its monohydride homologs, $\text{HCF}_m\text{Cl}_{3-m}$ ($m=0-3$), would clearly reduce the hypothesized “centrifugal potential barrier” that leads to the shape resonance effect. The increasing chlorination in these two series may also produce interesting effects due to expansion of the diffuse bonding region (and the size of the molecule). Furthermore, atom-specific effects involving different “localized” inner shells [e.g., C-K, F-K, and Cl-L shells of $\text{CF}_n\text{Cl}_{4-n}$ ($n=0-4$)⁹ and $\text{HCF}_m\text{Cl}_{3-m}$ ($m=0-3$)]¹⁰ would be of particular interest to differentiate contributions from the so-

called inner-well and outer-well states in the observed resonance features. The cage and partial-cage structures of these molecules represent model systems to investigate the fine-structure phenomena near the absorption edge (XANES) as well as diffraction-related effects (such as EXAFS). Moreover, the studies of photofragmentation cross section profiles will further elucidate the interplay between electronic structure and geometry in cation chemistry and spectroscopy. Of particular interest is the change in the electronic structure of the cation and the subsequent breakup dynamics as a result of photoexcitation at different sub-shells localized at specific sites of the molecule. Finally, although most of the photochemical atmospheric processes were found to occur below 5 eV, these valence and inner shell studies offer new information about the excited (final) states, which are important to quantum mechanical modelling of the potential curves involved in the photodissociation dynamics of these atmospheric processes.

The significantly improved brightness available at the Advanced Light Source makes it possible to determine the photoabsorption and photofragmentation cross sections in these large molecular systems with unprecedented resolution, precision and speed. The markedly improved signal-to-noise also makes viable the previously challenging experiments involving low signal rates (e.g., the non-dipole states) and coincidence detection. In a series of photodissociation studies on the common CFC and HCFC series at different ionization edges of Cl, F and C by using photon-triggered PIPICO techniques at Beamline 6.3.2 and Beamline 9.3.1, we have demonstrated the unprecedented timing (energy) resolution achievable at the ALS, which allowed us to resolve and identify, for the first time, many of the photofragments resulting from photodissociation of these large, complex molecules. Other photofragmentation and photoabsorption experiments of the so-called Annex-C controlled substances (in particular, fluorocarbons)¹ also demonstrate the enormous potential of using the PIPICO spectra for element-specific

chemical analysis and for probing changes in the photo-breakdown behaviour across different ionization edges. The wavelength tunability of the synchrotron beamlines (appropriate for different inner-shell ionization edges) offers a powerful means to investigate near-resonance effects localized at specific elements (Cl, F, or C) in the photo-breakdown process. In-situ formation of some rather unexpected (short-lived) species from the photofragments has been observed. The presence of these exotic species suggests the viability of using these core-specific techniques as a means to study ultra-fast photo-induced radical and gas-phase ion chemistry. Finally, the intense

A typical charge separation spectrum of selected ions produced during double photoionization of Freon 22 (HCF_2Cl) at a Cl 2p resonance. Data collected at Beamline 6.3.2.

brightness deliverable at the interaction region offers an unique opportunity to investigate “new” decay processes resulting from not just the dications, but also for the first time triply and other multiply charged photoions by using triple and multiple photoion coincidence techniques. Together these experiments at the ALS offer the first comprehensive research program on the photodissociation phenomena of complex molecular systems (of technological interest) over a wide energy range from the VUV to soft X-ray region and are expected to have a wide impact on areas such as environmental research, radiation and space sciences, fusion, lasers, aeronomy and astrophysics.

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Generation of Femtosecond Synchrotron Pulses from the Advanced Light Source

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INTRODUCTION

The application of x-ray techniques to understand fundamental atomic motion in condensed matter is a rapidly emerging area of research in chemistry, solid-state physics, and biology. The dynamic properties of materials are governed by atomic motion which occurs on the fundamental time scale of a vibrational period, ~100 fs. This is the time scale of interest for ultrafast chemical reactions, non-equilibrium phase transitions, vibrational energy transfer, surface desorption and reconstruction, and coherent phonon dynamics. To date, our understanding of these processes has been limited by lack of appropriate tools for probing the atomic structure on an ultrafast time scale. X-ray techniques such as diffraction and EXAFS yield detailed information about “static” atomic structure. However, the time resolution of high-brightness synchrotron x-ray sources such as the Advanced Light Source (~30 ps) is nearly three orders of magnitude too slow to directly observe fundamental atomic motion. Conversely, femtosecond lasers measure transient changes in optical properties of materials on a 10 fs time scale, but optical properties are only indirect indicators of atomic structure.

We report our first results using a novel scheme[1] to generate femtosecond pulses of synchrotron radiation. We directly measure femtosecond pulses in the visible synchrotron emission from bend-magnet beamline 6.3.2 at the ALS. This work is a first step toward developing a synchrotron-based source for ultrafast x-ray spectroscopy.

EXPERIMENTAL METHODS

The temporal duration of the synchrotron light pulses at the ALS is determined by the duration of the stored electron bunches, ~30 ps FWHM. The duration of the x-ray pulses may be reduced by more than two orders of magnitude by selecting radiation which originates from only a thin (~100 fs) temporal slice of an electron bunch[1]. Such a slice can be created through the interaction of a femtosecond laser pulse co-propagating with an electron bunch in an appropriate wiggler (Figure 1a). The high electric field present in the femtosecond laser pulse produces an energy modulation in the electrons as they traverse the wiggler (some electrons are accelerated and some are decelerated depending on the optical phase, ϕ). The optimal interaction occurs when the wiggler period λ_w satisfies the resonance condition $\lambda_x = \lambda_w (1 + K^2/2) / 2\gamma^2$ where γ is the Lorentz factor, K is the deflection parameter, and λ_x is the laser wavelength[1]. In addition, the far field laser radiation must overlap with the far field spontaneous radiation from the electron passing through the wiggler, and the laser spectral bandwidth (number of optical cycles per

pulse, M_l) must match the spectrum of the fundamental wiggler radiation (determined by the number of wiggler periods, M_w). Under these conditions, the energy absorbed by the electron from the laser field (or transferred to the laser field), ΔE , is calculated by considering the superposition of the laser radiation and the spontaneous electron wiggler radiation[1]:

$$(\Delta E)^2 = 4\pi\alpha\hbar\omega_l \frac{K^2/2}{1 + K^2/2} \frac{M_w}{M_l} A_l \cos^2 \phi$$

where A_l is the laser pulse energy and ω_l is the laser frequency. We estimate that a 35 fs laser pulse with a photon energy of 1.55 eV, and a pulse energy $A_l=100 \mu\text{J}$ will produce an energy modulation amplitude $\Delta E \sim 10 \text{ MeV}$, using the protein-crystallography wiggler, W16 (19 periods, $\lambda_w=16 \text{ cm}$) at the ALS.

Figure 1. Schematic illustration of the technique for generating femtosecond synchrotron pulses. (a) laser/electron beam interaction in resonantly-tuned wiggler. (b) separation of accelerated femtosecond electron slice in a dispersive (bend) section, (c) generation of femtosecond x-rays at a band-magnet beamline.

The laser-induced energy modulation is several times larger than the rms beam energy spread at the ALS (1.2 MeV), and only a thin slice of the electron bunch (the portion which is temporally overlapped with the laser pulse) experiences this modulation. The accelerated and decelerated electrons are then spatially separated from the rest of the electron bunch (in a dispersive bend of the storage ring) by a transverse distance that is several times larger than the rms transverse size of the electron beam (Figure 1b). Finally, by imaging the displaced beam slice to the experimental area, and by placing an aperture radially offset from the focus of the beam core, we will be able to separate out the radiation from the offset electrons (Figure 1c). Since the spatially offset electrons result from interaction with the laser pulse, the duration of the synchrotron radiation produced by these electrons will be approximately the same as the duration of the laser pulse, and will be absolutely synchronized. Furthermore, the extraction of an ultrashort slice of electrons leaves behind an ultrashort hole or dark pulse in the core of the electron bunch (Figure 1c). This time structure will be reflected in the generated x-rays, and can also be used for time-resolved spectroscopy.

The average flux of the femtosecond radiation is defined by three factors: $\eta_1 = \tau_L/\tau_e = 35 \text{ fs}/30 \text{ ps}$, $\eta_2 = f_L/f_{synch} = 10 \text{ kHz}/500 \text{ MHz}$, and $\eta_3 = 0.2$, where τ_L and τ_e are the laser pulse and electron bunch durations, f_L and f_{synch} are the laser and synchrotron repetition rates, and η_3 accounts for the fraction of electrons that are in the proper phase of the laser pulse to get the maximum energy exchange suitable for creating the large transverse separation. Accounting for the above factors, we estimate a femtosecond x-ray flux of $\sim 3 \times 10^5$ photons/sec/0.1% BW at 2 keV (5×10^4 photons/sec/0.1% BW at 10 keV) from a bend-magnet beamline at the ALS with a 3 mrad x 0.4 mrad collection optic.

Synchrotron radiation damping provides for recovery of the electron beam between interactions. Since the laser interacts sequentially with each bunch, the interaction time is given by n/f_L where n is number of bunches in the storage ring. Furthermore, the bunch slice is only a small fraction of the total bunch. Thus, the storage ring damping time is more than sufficient to allow recovery of the electron beam between laser interactions (even for laser repetition rates as high as 100 kHz [1]) and other beamlines at the ALS can be operated at the same time without adverse effects.

A Ti:sapphire femtosecond laser system is located near beamline 6.3.2, and the laser pulses ($\sim 500 \text{ }\mu\text{J}$, 60 fs pulse duration, 1 kHz repetition rate) are projected across the storage ring roof blocks to sector 5, where they enter the main vacuum chamber through a back-tangent optical port. Amplified femtosecond pulses co-propagate with the electron beam through wiggler W16 in sector 5. A photon stop/mirror following the wiggler reflects the laser light and the visible wiggler emission out of the vacuum chamber for diagnostic purposes. Images of the near field and far field wiggler emission are observed on a CCD camera, and the near and far field modes of the laser propagating through the wiggler are matched using a remotely adjustable telescope at the back tangent port. Timing between the laser pulse and the electron bunch is synchronized to better than 2 ps by phase-locking the laser-cavity repetition rate to the RF master oscillator for the storage ring. The spectrum of the laser is also matched to the fundamental wiggler emission spectrum. The efficiency of the laser/e-beam interaction is tested by measuring the gain experienced by the laser beam passing with the electron beam through the wiggler. The gain is a direct indication of the energy exchange, ΔE , between the laser and the electron beam and is equivalent to the gain that occurs in a free electron laser.

RESULTS

Femtosecond duration synchrotron pulses are directly measured by cross-correlating the visible light from bend-magnet beamline 6.3.2 at the ALS with the synchronized laser pulses in the nonlinear crystal, BBO. Figure 2a shows a laser synchrotron cross-correlation measurement on a long time scale. The measured pulse duration, $\sigma=16 \text{ ps}$, corresponds to the overall electron bunch duration. Measurement with higher time resolution (Fig. 2b) shows the femtosecond “dark” pulse (264 fs FWHM, $\sigma=112 \text{ fs}$) which appears as a narrow hole in the main pulse, and originates from the central core of the sliced electron bunch. Figure 2c shows a measurement of the femtosecond pulse (379 fs FWHM, $\sigma=161 \text{ fs}$) originating from the spatial wings of the sliced electron bunch. An important point is that the femtosecond time structure will be invariant over the entire spectral range of bend-magnet emission from the near infrared to the x-ray regime, making this a very powerful tool for femtosecond spectroscopy.

Figure 2. Cross correlation of visible synchrotron pulse with femtosecond laser pulse (and schematic illustration of the corresponding region of the electron bunch): (a) overall synchrotron pulse, (b) femtosecond dark pulse from on-axis radiation, (c) femtosecond pulse from off-axis radiation.

In conclusion, femtosecond x-ray pulses are generated from the ALS using a novel laser slicing technique. A pulse duration of ~ 300 fs is measured in the visible using cross-correlation techniques. The pulse duration is determined by the storage ring dispersion integrated from sector 5 (wiggler location) to the center bend magnet in sector 6. The limit on the pulse duration that could be generated from a bend-magnet in sector 5 is less than 100 fs. This technique also generates complementary "dark" femtosecond x-ray pulses, and is the first step toward development of a high-brightness femtosecond source for ultrafast x-ray spectroscopy.

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High-resolution electron time-of-flight apparatus for the soft x-ray region

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INTRODUCTION

The pulsed nature of synchrotron radiation (SR) emitted from electron or positron storage rings provided the basis for the development, about 25 years ago, of electron-TOF spectroscopy as an efficient, but relatively low resolution alternative to electrostatic or magnetostatic analysis. In the TOF technique, kinetic energies are determined by measuring flight times, typically up to several hundred nanoseconds, of electrons traveling a fixed distance between an interaction region and a detector. The method inherently relies on a coincidence between a timing pulse and an electron signal; background noise is suppressed and evenly distributed over the entire time spectrum, greatly simplifying data analysis. Another advantage of the TOF technique is that an entire electron spectrum can be collected simultaneously. In comparison, electrostatic analyzers, even with modern multichannel detection, collect only a portion of an electron spectrum at one time, which in some circumstances renders them susceptible to fluctuations in beam intensity and, in the gas phase, sample pressure. Simultaneous collection of an entire spectrum obviates these fluctuation effects and can increase the measurement efficiency of the electron-TOF method by a significant factor (up to 10^3 in the best of cases) relative to electrostatic analysis. A gas-phase time-of-flight (TOF) apparatus, capable of supporting as many as six electron-TOF analyzers viewing the same interaction region, has been developed to measure energy- and angle-resolved electrons with kinetic energies up to 5 keV. Each analyzer includes a newly designed lens system that can retard electrons to about 2% of their initial kinetic energy without significant loss of transmission; the analyzers can thus achieve a resolving power ($E/\Delta E$) greater than 10^4 over a wide kinetic-energy range. Such high resolving power is comparable to the photon energy resolution of state-of-the-art synchrotron-radiation beamlines in the soft x-ray range at the ALS, opening the TOF technique to numerous high-resolution applications. In addition, the angular placement of the analyzers, by design, permits detailed studies of nondipolar angular-distribution effects in gas-phase photoemission.

APPARATUS

A schematic of the experimental setup is shown in Fig. 1. An integral part of the apparatus is a differential-pumping section adapting the beamline pressure of less than 10^{-6} Pa to the chamber pressure during data collection of 4×10^{-3} Pa.

The vacuum chamber supporting the analyzers can be rotated about the x-ray beam (x axis) by $\pm 90^\circ$, permitting collection of spectra at many different angles and thereby improving the precision and accuracy of angular-distribution measurements. An in-line rotational feedthrough decouples the chamber rotation from the differential-pumping section while the apparatus is under vacuum. Two gravitational sensors with an operating range of $\pm 45.0^\circ$ each

Figure 1. Experimental schematic of the electron time-of-flight system. Light from the ALS storage ring passes through beamline optics into a differential-pumping section. The chamber and analyzers can rotate around the photon beam for more accurate electron angular-distribution measurements.

determine the chamber rotation angle. The chamber is aligned with the x-ray beam along its rotational axis in order to avoid movement of the analyzers relative to the interaction region while rotating. A needle (30 mm long, 50 μm inner diameter, positioned less than 1 mm from the photon beam) directs an effusive jet of sample gas perpendicular to the x-ray beam. The interaction region viewed by the TOF analyzers runs about 3 mm along the x-ray beam and is defined by the beam size in the other dimensions. Sample gas enters the gas-inlet assembly through a manual leak valve. A 1000 l/s turbomolecular pump maintains the background pressure, with no sample gas flowing, of less than 10^{-4} Pa.

Figure 2. Cross section of an electron time-of-flight analyzer.

TOF ANALYZERS

Figure 2 shows a cross section of the electron-TOF analyzers. All analyzers are differentially pumped by a 50 or 80 l/s turbo pump to avoid pressure buildup near the MCPs, which have a recommended operating pressure of 10^{-4} Pa, significantly less than the chamber pressure during data collection. A straight electron flight path provides fundamental simplicity to the TOF technique, especially in analyzer design. The cylindrically symmetrical analyzers view the same interaction region with the 2 mm entrance apertures at a distance of about 20 mm. The apertures and needle are electrically grounded to maintain a field-free interaction region, an essential attribute for electron angular-distribution measurements. To optimize alignment to a common interaction region, the entrance aperture of each analyzer can be moved *in situ* ± 3 mm along two axes perpendicular to the electron flight path, and the length of each analyzer can be adjusted *ex situ* +28 mm/-11 mm from its nominal length. A total flight path of 437.5 mm and minimum active areas on the MCPs of 41.9 mm diameter yields an angular acceptance of $\pm 2.7^\circ$. This corresponds to a solid angle of 1/1800. Typical flight times are 738 and 73.8 ns for 1 and 100 eV electrons, respectively. With the time window of 328 ns between pulses in ALS two-bunch mode, a minimum kinetic energy of 5 eV is required for electrons to arrive at the detector before the next x-ray pulse reaches the interaction region. Electrons slower than 5 eV overlap with fast electrons created by the following bunch and complicate the spectra. If desired, the lens system can accelerate electrons to avoid these overlaps.

Figure 3 shows the front end of an analyzer, its lens system, and electron trajectories determined by ray tracing using SIMION software. In this simulation, the electrons begin in the interaction region with a kinetic energy of 505 eV, pass through the entrance aperture, then about 4.0 mm further pass through a second aperture with a diameter of 4.0 mm. The second aperture is usually at ground potential but can be biased with a negative 1–2 V to repel thermal electrons created in experiments with metal-vapor targets. Directly behind the second aperture is the first retardation element of the lens system at a potential of 80% (400 V) of the total retardation voltage of 500 V.

The next three elements have 91.5%, 97%, and 100% of the total voltage, respectively. The voltages are applied using a resistor cascade with the following approximate values: 15, 2.2, 1.0, and 0.56 M Ω , totaling 18.76 M Ω . After passing through the lens system, the electrons enter a field-free drift tube with a final kinetic energy of 5 eV. The drift tube extends to the MCP mounting. A coaxial magnetic-shield cylinder made of a Co-Netic AA alloy with a wall thickness of 0.76 mm surrounds the drift tube and reduces the magnetic field inside by a factor of up to 100, typically to about 4 mG. The shielding effect is less near the tube ends.

Figure 4 shows a neon spectrum taken at the $1s \rightarrow 3p$ resonance (867.1 eV) with flight time on the x axis and total counts on the y axis. The spectrum was collected for 200 s with a ring current of 20 mA. The entrance and exit slits were set at 50 μm , and the monochromator grating provided a bandpass of 650 meV, corresponding to a photon resolution of 1350. The analyzer was positioned parallel to the plane of the storage ring ($\theta = 0^\circ$) and perpendicular to the photon beam ($\phi = 90^\circ$). A retarding voltage of -750 V was applied to reduce the initial electron kinetic energies by 89%–97%. The fastest signal, at channel number 3930, is the prompt, created by fluorescent and scattered light, which indicates a timing resolution of 255 ps.

APPLICATIONS

With this apparatus, angular distributions of valence photoelectrons showing effects due to higher-multipole interactions have been measured for the first time.^{1,2} The experiments were performed on Ne $2s$ and $2p$ throughout the 250–1200 eV photon-energy range. Furthermore, it was possible to prove the breakdown of the independent-particle approximation throughout the same range.³ Other measurements include the photon-energy dependence of ionization excitation in helium at medium energies (90–900 eV),⁴ where we measured the photoionization-excitation-to-photoionization ratio for He⁺ nl ($n=2-6$) and determined asymptotic high-energy ratios for He⁺ nl ($n=2-5$). Current research projects include nondipole angular-distribution measurements in Xe and small molecules such as N₂. We have observed a strong resonance-like increase in the value of the γ parameter about 60 eV above the N₂ $1s$ ionization threshold, which causes an angular-distribution effect about 20 times more pronounced than predicted by theory for atomic nitrogen. Other projects include electron angular-distribution measurements of the Ar $2s$ satellite lines as well as the Ne valence lines in the Ne $1s \rightarrow 3p$ resonance region.

In conclusion, we have described the development of significantly improved electron-TOF analyzers for gas-phase samples and the design of an apparatus for angle-resolved-photoemission experiments to study dipole and nondipole angular-distribution effects. The new retarding-lens system increases the resolving power to up to 10^4 for high-kinetic-energy electrons. These improved electron-TOF analyzers are an alternative to electrostatic analyzers while maintaining the advantages of electron-TOF spectroscopy: constant background, large energy window, and independence of varying gas-target pressures and fluctuations in the beam intensity. A high-brilliance light source like the ALS with submillimeter beam sizes, combined

Figure 3. Cross section of the electron lens system right behind the entrance aperture of the analyzer. The trajectories of electrons with an initial kinetic energy of 505 eV passing through the retarding-lens system were calculated using SIMION software. An applied voltage of -500 V slows the electrons down to a final kinetic energy of 5 eV or about 1% of their initial kinetic energy.

with this type of electron-TOF analyzer, provides state-of-the-art instrumentation for high-resolution angle-resolved photoelectron spectroscopy.

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FIG. 4. Electron time-of-flight spectrum taken on the Ne 1s → 3p resonance at 867.1 eV. The FWHM of the "prompt" (255 ps) determines the total timing resolution of the analyzer and electronics.

***In situ* characterization of EUV multilayer mirrors deposited by UHV magnetron sputtering**

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INTRODUCTION

Mirrors with a high reflectance at normal incidence in the extreme-ultraviolet (EUV) wavelength region are useful in a number of applications, including EUV lithography, astronomy and microscopy. To date, the best results were obtained with Mo/Si and Mo/Be multilayers with measured peak reflectances of ~67.5% and ~70.2% in the 13.0–13.5 nm and 11.1–11.8 nm wavelength regions, respectively.¹ However, a critical limitation to achieving the maximum theoretical peak reflectance is the oxidation and corrosion of the top layers, which both increase the absorption and degrade the phase coherence of the reflection from these layers.² Preliminary studies of the effect of surface oxidation on the reflectance of Mo/Si multilayers were performed.

EXPERIMENT

A unique deposition-reflectometer system, constructed at the National Research Council of Canada, was used for those experiments.³ This system was designed to deposit single or multilayer coatings and then to measure their reflectance *in situ* without exposure to ambient air. Two Mo/Si multilayers were fabricated and near normal incidence (5°) reflectances of 66.7% around 13.5 nm were measured for both samples, immediately after deposition (Fig. 1). This is comparable to the best reflectances reported to date and represent an achievement for the type of system we used for the deposition.

Fig. 1 Peak reflectances near 67% were measured for two Mo/Si multilayers around 13.5 nm at 5°.

Preliminary experiments where the reflectance of the samples is measured at regular intervals of exposure to air were performed. Surprisingly, the reflectance of both samples remained stable over the 48-hours period they were monitored. A rapid decrease of the reflectance with the oxidation of the top Si layer was expected. More extensive experiments are required to confirm and explain this result.

SUMMARY

Excellent Mo/Si multilayer mirrors were deposited and characterized with a new hybrid deposition-reflectometer system. Two samples with reflectances comparable to the best obtained to date were achieved and were monitored over a period of 48 hours. The results are still pre-

liminary and more extensive studies are required to understand the oxidation process of the Mo/Si multilayer surfaces.

These experiments were made on well-known and stable Mo/Si multilayer mirrors. Future work with this deposition-reflectometer system will involve more exotic material pairs where the unique capability of the system can be exploited. For example, Mo/Y and Mo/Sr multilayers, which are known to be much less stable in air, will soon be investigated.

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Magnetic Properties of Fe/V(001) Superlattices Studied by Resonant Scattering of Polarized X-Rays

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The magnetic properties of artificially structured devices can be tailored to specific needs using appropriate elements, growth modes or periodic structures. Metallic multilayers, featuring oscillating magnetic coupling and giant magnetoresistance effects, are preeminent among such devices. Fe/V superlattices are a good example of how a multilayer device can present a whole variety of magnetic behavior, depending on the layer thicknesses t_{Fe} and t_{V} , and on the crystal orientation [1]. Until recently, the magnetic properties of V in these layers have been subject to controversy, since it is difficult to investigate the weak magnetism of V in a superstructure containing a large amount of Fe. The only studies of the V magnetism in multilayers have been performed by circular dichroism at the 2p absorption edge [2], detecting the sample drain current or, equivalently, the total electron yield (TEY). Circular dichroism in x-ray absorption spectroscopy (XAS) is a powerful technique because of its element selectivity and the access it gives to a quantitative evaluation of magnetic moments via the application of sum rules, but the TEY detection mode has several drawbacks that have been discussed in the past [3]. We have adopted a different experimental approach, based on x-ray resonant magnetic scattering (XRMS), which takes full advantage of all aspects of dichroism in x-ray absorption, along with some additional technical and conceptual points of interest. As in XAS, we use photons tuned to core excitation resonances, obtaining element selectivity, and we can excite the $2p \rightarrow 3d$ dipole transitions that directly probe the 3d magnetic orbitals. In addition, soft x-ray wavelengths match the typical spacings of metallic multilayers, so Bragg diffraction experiments under resonant conditions may be performed. Another relevant aspect of XRMS, when dealing with magnetic multilayers, is that it is a photon-in / photon-out experiment which means that the presence of applied magnetic fields does not affect the measurements. Moreover the probing depth is only limited by the photon path within the sample and no saturation effects need to be accounted for. The large probing depth is very important if we wish to extract bulk properties from capped multilayer samples (i.e., not those just related to the topmost layers).

The superlattices were epitaxially grown by sputter deposition of the metallic layers on MgO(001) single-crystal substrates. Their final structure is $(\text{Fe } 5 \text{ ML} / \text{V } n \text{ ML})_m$, where ML means monolayers, with $(n = 1, m = 80)$, $(n = 2, m = 60)$, and $(n = 5, m = 40)$. Their structural properties have been described previously [1]. The easy axes of magnetization are always along the [110] axes of the substrate, i.e. [100] in-plane directions of the superlattice. XRMS measurements were performed at the Fe and V 2p edges on beamline 6.3.2 at ALS [4] using elliptically polarized light (40 % circular polarization rate). The external magnetic field, applied along an easy axis, in the sample surface and in the scattering plane, was reversed after each energy scan. We also measured the absorption spectra and circular dichroism under the same experimental conditions by the drain current detection method. As implicitly suggested

above, the probing depth is small (about 15 Å in Fe): this implies that we are only measuring a few layers of our sample. Moreover, only the outermost layers are probed which are more likely to be affected by inhomogeneities, contamination or by the presence of the capping layer (Pd, in our case).

We needed the absorption lineshapes to build up the dielectric tensor for Fe and V employed in the analysis of XRMS data, leaving as a free parameter a multiplication factor on the magnetization dependent part of the optical constants. Using the computational method described in a previous paper [5], we were thus able to fit the magnetization dependent part of the optical constants to the ensemble of the energy and angle dependent scattering curves, including resonant Bragg diffraction spectra.

All resonant spectra showed magnetization dependence. Fig. 1, for instance, shows the energy dependent reflectivity curves for the $n=1$ sample: the left panels refer to the V and Fe 2p edges, measured at $\theta=10$ degrees. Full and dashed lines are the sum and the difference of reflectivity curves obtained for opposite magnetizations. In the right panel, the corresponding asymmetry ratios are presented. We have drawn them on different energy scales so as to give a visual match of the 2p spin-orbit separations for Fe and V.

Figure 1. Resonant reflectivity at the V and Fe 2p edges for the $n=1$ sample and corresponding magnetic signals. Right panel : asymmetry ratio curves on an arbitrary energy scale in order to visually match the spin-orbit splitting of the 2p core hole for Fe and V.

Fitting the XRMS spectra at the Fe 2p edge gave optical constants such that the dichroism curves in absorption did not deviate appreciably from that of a bulk Fe reference. Applying sum rules, we obtained values of the magnetic moment per Fe atom between 2.1 and 2.3 μ_B , depending on

choices made in the data reduction. We conclude that for these multilayers there is no measurable change in the Fe average magnetic moment as a function of V thickness. This also implies a ferromagnetic alignment of all the Fe layers in the superstructure.

Fig. 2 compares experimental asymmetry ratio curves at the V 2p edges with best fit calculations. Only one scattering angle per sample is shown, but the fitting procedure included at least five different angles per sample. For a more quantitative analysis, we have applied sum rules to the V 2p absorption spectra corresponding to the optical constants derived from the fit.

Figure 2. Experimental asymmetry ratio curves at the V 2p edges for $n=1, 2$ and 5 . Lines are best fits obtained varying the magnetisation dependent part of the optical constants.

The main qualitative and quantitative results of our XRMS experiment on $(\text{Fe } 5 / \text{V } n)_m (001)$ superlattices can be summarized as follows:

- i) the magnetic moment of iron does not change with respect to its bulk value, regardless of the V thickness, at least to within the sensitivity of the method;
- ii) the coupling between Fe layers is ferromagnetic for V spacers up to 5 ML;
- iii) for all the samples under study, the V 3d band carries a magnetic moment and its coupling to Fe is always antiferromagnetic;
- iv) for $n=1$, the orbital moment is of the order of $-0.08 \mu_B$ and the spin moment $0.37 \mu_B$, giving an average total magnetic moment of $0.66 \mu_B$ per vanadium atom;
- v) this value reduces to $0.40 \mu_B$ and $0.26 \mu_B$ for $n=2$ and $n=5$, respectively.

In conclusion, XRMS has a large probing depth, it is not affected by applied magnetic fields, and it provides spectroscopic as well as structural information. These characteristics make it an interesting complement to dichroism in absorption. We have shown that sum rules developed for

x-ray absorption may also be applied to resonant scattering data to extract quantitative information. Moreover, XRMS may be used to distinguish magnetic arrangements with different magnetization profiles, even when they have the same average properties. Together with its intrinsic element selectivity, this opens the way to interesting future applications in the field of magnetic multilayers.

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Micro – ESCA/NEXAFS at Beamline 6.3.2

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INTRODUCTION

We have developed a micro-ESCA/NEXAFS end station for CXRO beam line 6.3.2 at the ALS. Initial experiments were performed in the total yield mode for micro-NEXAFS. The beam line 6.3.2 allows tunability of the EUV/soft x-ray energy between 50 –1300 eV region with high spectral resolution, high flux and accurate wavelength/energy calibration. The system achieves a spatial resolution approaching 1 μm coupled with the chemical specificity of the NEXAFS technique. This high spatial resolution was achieved using an x-ray microfocusing system based on a Kirkpatrick-Baez mirror optical system made by elastically bending a pair of side profiled silicon mirrors. Samples are mounted on an X-Y stage, which allows 2D micro-ESCA/NEXAFS images of samples to be obtained by scanning, with sub- μm precision. Some representative results are presented.

BACKGROUND - ESCA ANALYSIS

Electron Spectroscopy for Chemical Analysis (ESCA) is a widely-used analytical technique for investigating the chemical composition of solid surfaces. The technique is a basic tool in a wide variety of materials science related fields such as metallurgy, corrosion, contamination, tribology, plastics, polymers and ceramics, and is proving useful in geochemistry, environmental sciences, and in fact in any field in which requires chemical analysis of a surface that can be maintained in ultra-high vacuum. Surface analysis by ESCA is accomplished by illuminating the solid, under UHV conditions, with soft x-rays of a single energy. The spectrum of the emitted photoelectrons is then analyzed with an appropriate electron spectrometer. Since the mean free path of the electrons is very small, the detected electrons originate from the topmost few atomic layers (20-30 Å); hence ESCA is a *surface*, rather than a *bulk*, analysis technique although greater depths can be investigated through ion etching. Each element has a unique photoemission spectrum, and the spectrum of a mixture or compound of elements is approximately the sum of the spectral peaks from the individual elements. Quantitative data can be obtained from the peak heights (or areas) and identification of the chemical states (e.g. valence) can be made from the exact peak positions and spectral line shapes. This information allows the identification of functional groups and molecular types. For example, ESCA can readily distinguish between the ionic and covalent forms of fluorine. For most metals, ESCA can distinguish between oxidized and reduced species. ESCA is sensitive to as low as 0.1 atom percent and detects elements except H and He. It can be applied to all solid materials, including insulators such as polymers and glasses. With the addition of auxiliary sample preparation facilities the technique becomes more powerful. For example an ion gun for sputtering enables compositional depth profiling to be carried out to sub-nanometer spatial resolution.

MICRO-ESCA WITH SYNCHROTRON RADIATION

The lateral spatial resolution of ESCA is determined by the size of the x-ray spot on the sample. In commercial ESCA machines, this spot is produced by a more or less conventional x-ray tube (usually with an aluminum or magnesium anode to give Al K or Mg K x-rays). These spots are characteristically of the order of a few hundred μm to a millimeter in diameter. Hence commercial ESCA machines are incapable of resolving the microstructure of an inhomogeneous material. A number of "Small-spot ESCA" machines have been developed. These machines still employ conventional x-ray tubes, using focusing or collimating optics to achieve an x-ray spot of the order of tens of μm . Thus the range of lateral structures that can be investigated with commercial ESCA machines ranges from 10 μm to 2 mm. A summary chart of Detection Limits vs. Probe Size for analytical techniques published by Charles Evans Associates shows that at 10 μm resolution the detection limit for commercial ESCA machines is about 10^{20} atoms/cc or a fraction of 1%.

It is clear that even a bending magnet source on a third generation storage ring such as the ALS is many orders of magnitude brighter than the conventional hot-cathode x-ray tubes used in commercial ESCA machines. Thus the possibility exists for improving the resolution and sensitivity by orders of magnitude. Improvement of the spatial resolution to the order of 1 μm would enable chemical mapping on a scale appropriate to the study of grain boundaries of alloys, ceramics, rocks or minerals, of corrosion-induced cracks, wear tracks in bearings or on magnetic recording media, contamination of optical surfaces...etc. In addition the higher brightness of the ALS should allow the lowering of the detectivity limit by an order of magnitude to the order of 0.1%, thus allowing the study of subtle phenomena.

MICRO-ESCA/NEXAFS AT BEAMLINE 6.3.2

NEXAFS (Near-Edge X-ray Absorption Fine Structure) spectroscopy is another spectroscopic method for determining the electronic and structural properties of molecules in solid state systems. The "total yield" method, in which the electron current from the sample is measured directly (as the sample drain current) or with an auxiliary electron detector such as a channeltron is simple to implement. An advantage of the NEXAFS over the ESCA technique is that it does not require ultra-high vacuum. The high flux, high spectral resolution, accurate energy calibration, and ease of use have made beamline 6.3.2 popular for NEXAFS spectroscopy. A wide range of measurements primarily using the total yield technique, have been carried out on the beamline since its commissioning in 1995. It soon became evident that reduction of the x-ray spot size to $\sim 1 \mu\text{m}$ would have the same advantages for the NEXAFS technique as for ESCA, i.e. would allow solid state chemical analysis to be performed at microstructural scales.

On beamline 6.3.2, this small x-ray spot is obtained by using a Kirkpatrick-Baez (K-B) optical system to demagnify a pinhole positioned at the center of the reflectometer chamber. The desired elliptical figure of the K-B optics is obtained elastic bending of profiled mirrors bent with unequal end couples. This technique has been developed and refined by CXRO personnel over the course of many years [1,2] to the point where spot sizes of $\sim 1 \mu\text{m}$ are routinely achieved [3].

Figure 1. Schematic of micro-ESCA/NEXAFS end station as installed on beamline 6.3.2

The layout of the of the micro-ESCA/NEXAFS end station is shown in Figure 1. A new UHV tank and stand was built to house the a refurbished SPECS EA 10 plus analyzer, the sputtering gun from a Leybold-Heraeus ESCA system (both obtained from another DoE laboratory on surplus) and a vacuum new transfer stage. This tank also houses the K-B optical, system including a visible alignment and focusing microscope. The sample puck is carried on a scanning x-y stage designed and built by CXRO personnel. The scanning and data acquisition are controlled by the same LABVIEW software that runs the 6.3.2 beamline. The system has been installed on beamline 6.3.2 several times and has been fully exercised (except as noted below). A spot size in the range of 1-2 μm has been demonstrated with the mirror system and the scanning stage has been shown capable of sub-micron accuracy.

RESULTS

A wide variety of samples has been scanned and some representative results are shown below. Figure 2. shows the visualization of standing waves on the surface of a Mo/Be multilayer reflector. The lozenge shape outlines a crater in the surface of the multilayer produced by sputter etching. The fringes around the border represent contours of photoelectron emission intensity obtained by scanning the surface of the multilayer with the monochromator wavelength set at the Bragg peak, approximately 11.5 nm. These variations map the intersections of the nodes and antinodes of the multilayer standing wave with the sloping sides of the sputter crater.

Figure 3 is a scan of a sample of the hexagonal form of boron nitride (hBN) deposited on a silicon wafer. By treatment with an ion beam, the region at the left of the frame has been partially converted to the cubic form of BN. The scan was made with the monochromator tuned to the π^* resonance of hBN at 191.8 eV. This resonance disappears in cubic BN; thus the areas that have been converted to cubic BN appear darker. In this scan one can clearly see the microstructure, including cracking, of the cubic BN region.

Figure 2. Visualization of standing waves on the surface of a Mo/Be multilayer reflector at a wavelength of 11.5 nm. The fringes surrounding the "lozenge" shape represent regions of high and low photoelectron emission resulting from the intersection of the standing wave in the multilayer with the sloping edges of the crater.

Figure 3. High resolution scan of an hBN film deposited on a silicon wafer. The region at the left of the frame has been partially converted to the cubic form of BN. The scan was made at the energy of the π^* resonance of hBN, which disappears in the cubic form. Hence the region at the left appears darker. (Sample provided courtesy of L. Terminello, LLNL).

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Resonant Magnetic Scattering Study of Iron Oxide Layers on Alumina

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INTRODUCTION

Magnetic oxides, particularly in the form of thin films, are of considerable technological as well as fundamental interest and are the subject of intense research [1]. The epitaxial growth of iron oxides on single crystal oxide substrates leads to the preparation of thin films of high quality. The use of magnetic iron oxides in multilayers opens up new possibilities for the development of spin-polarized tunneling devices [2]. They can also be used as a reference for the investigation of the electronic and magnetic properties of these systems, covering the thicknesses from a single atomic layer to bulk [1,3,4]. Here we describe a resonant scattering experiment of polarized soft x-rays applied to the study of iron oxide epitaxial layers (α -Fe₂O₃ and Fe₃O₄) grown on α -Al₂O₃. This technique combines the advantages of absorption spectroscopy (this is the *resonant* aspect) with the structural sensitivity of X-ray scattering. Ferromagnetic ordering can be studied in resonant scattering using either linearly or circularly polarized light on the same footing [5,6], and spectroscopic details can be enhanced selectively by the interplay of the real and imaginary parts of the optical index at resonance [6]. Combined spectroscopic and microstructural studies have been performed on metallic multilayers [7,8], and used to determine the magnetization dependent optical constants [8]. The photon-only aspect of the scattering process is a major advantage for studying insulating samples. We take full advantage of this in our study of magnetic oxide layers in the presence of a magnetic field.

EXPERIMENTAL

Fe₃O₄ (111) and α -Fe₂O₃ (0001) films were prepared by molecular beam epitaxy assisted by an atomic oxygen source, using alumina (0001) single crystals as substrates. The growth procedure and structural characterization have been described elsewhere [3,9].

Measurements were performed at the *Soft X-ray Metrology* beamline 6.3.2 [10] of the Advanced Light Source storage ring in Berkeley, using the reflectometer endstation. A 70% circular polarisation rate was obtained by asymmetrically positioning the jaws which set the accepted beam divergence. The resolving power at the Fe 2p edges (700-730 eV) was set to 2000. The external magnetic field (about 1 kG) was applied along the intersection between the sample surface and the scattering plane using a permanent magnet. The direction of the field was reversed at each acquisition point by rotating the magnet via a computer controlled in-vacuum stepper motor.

RESULTS AND DISCUSSION

Fig. 1 shows a series of reflectivity curves measured on an 80 Å thick Fe₃O₄ film grown on Al₂O₃(0001), for several photon energies around the iron 2p edges. The magnetization averaged intensity is reported in the bottom panel, on a semilogarithmic scale. The oscillations of the intensity as a function of θ come from the interference between the beams reflected at the vacuum / Fe₃O₄ and Fe₃O₄ / Al₂O₃ interfaces, and indicate a total thickness of the film of 85 Å, in

excellent agreement with RHEED and RBS results [11]. The corresponding magnetic signal is reported in the top panel, expressed as the asymmetry ratio $(I^+ - I^-) / (I^+ + I^-)$ between the scattered intensities for the two opposite magnetization/helicity orientations. The different behaviour of the asymmetry ratio curves for different photon energies is related to the energy dependence of the dichroism (see, e.g., Fig. 2) : when going from 709.5 eV to 710.5 eV, for example, the sign of the magnetic signal is reversed, leading to mirror image asymmetry curves in the reflectivity (Fig. 1, top panel).

Figure 1. $\theta/2\theta$ reflectivity scans at three photon energies around the Fe L_1 edge for an Fe_3O_4 thin film. Bottom: magnetization averaged scattered intensity. Top: asymmetry ratio curves, defined as the difference divided by the sum of the scattered intensity for opposite magnetization / helicity orientations.

We have also investigated thin $\alpha\text{-Fe}_2\text{O}_3$ films on $\text{Al}_2\text{O}_3(0001)$, using both linearly and circularly polarized light. Structural analysis of these samples indicates the formation of a non standard Fe oxide phase during the growth of the first 15-20 Å. Various observations (RHEED, LEED, XPS) suggest that this phase has a 14% lattice expansion with respect to alumina, has an fcc structure like FeO, but contains Fe^{3+} ions [11]. For films thicker than 20 Å only the $\alpha\text{-Fe}_2\text{O}_3$ phase, of high crystalline quality, is detected. $\alpha\text{-Fe}_2\text{O}_3$ is an antiferromagnet, so we do not expect to observe magnetic circular dichroism. We have tested this point on an $\alpha\text{-Fe}_2\text{O}_3(0001)$ single crystal: no magnetic signal was detected above a noise level of 10^{-4} . On the contrary, reflectivity

measurements on an 80 Å α -Fe₂O₃ / Al₂O₃(0001) film indicate a weak (1%) but measurable magnetization dependence.

Fig. 2 compares the energy dependent reflectivity at $\theta=10^\circ$ for two 80 Å thick oxide layers, one of composition Fe₃O₄ (top panel), the other Fe₂O₃ (bottom panel). The magnetic signal is much weaker for Fe₂O₃ (note the multiplication factor of 20 on the difference curve), but its shape agrees very well with the one measured for Fe₃O₄.

Figure 2. Comparison between $\theta = 10^\circ$ reflectivity curves for Fe₃O₄ (top) and Fe₂O₃ (bottom) films on Al₂O₃.

Our data indicate that :

- i) the non standard phase observed at the early stage of α -Fe₂O₃ growth on alumina is not transitory, but remains in the final sample as a sort of naturally formed buffer layer
- ii) iron ions contained in this buffer layer carry a net average magnetic moment.

The similarity between dichroism spectra shown in Fig.2 suggests an analogy between the magnetic behaviour of Fe₃O₄ and that of the buffer layer, but we cannot conclude, on the basis of this observation only, that Fe₃O₄ is present in the α -Fe₂O₃ thin films, especially because the 2+ valence of iron has never been detected by in situ XPS on thinner films (between 4 and 80 Å). The buffer layer might be γ -Fe₂O₃ like, a ferrimagnetic phase that exhibits nearly the same

inverse spinel structure as Fe_3O_4 but contains only ferric ions. Simulations based on atomic calculations including magnetic and crystal field parameters [12] are in progress, in order to determine the local iron environment giving rise to the observed magnetic signals.

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Resonant Reflectivity and Bragg Diffraction in Metal / Oxide Magnetic Multilayers

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Spin-polarized tunneling in thin multilayers alternating ferromagnetic (FM) and insulating (I) components (usually called magnetic tunnel junctions) are currently the focus of considerable interest in the field of artificially structured magnetic materials. These systems display large tunnel magnetoresistance (TMR) [1], that can be exploited in devices such as magnetic sensors, read heads for magnetic recording and non-volatile magnetic memories [2].

The overall magnetic behavior is controlled by several parameters, notably the spin polarization near the Fermi level of the conduction electrons in the metal, changes in the dielectric constant at interfaces, and interlayer magnetic coupling. The role of the ferromagnetic layer is obviously very important, since it acts as the source of spin polarized electrons. For this reason, ferromagnetic materials with a high spin polarization, such as Co, Fe or their alloys, are usually employed. The *active layer* for the injection of polarized electrons through the insulating barrier is of very limited thickness and in contact with the insulator (Al_2O_3 in the present case). As a consequence, spin polarized tunneling will be strongly affected by structural and magnetic roughness, as well as by the oxidation of the active layer that might take place during the formation of the insulating barrier [3]. The characterization of the active layer requires an element selective and non-destructive technique, capable of probing the magnetism of buried layers in realistic structures (i.e. the ones expected to be used in devices).

In recent experiments performed at ALS, we have shown that the resonant magnetic scattering of circularly polarized soft x-rays (XRMS) can yield information about several interesting properties of magnetic multilayers [4]. X-ray scattering from a layered material is sensitive to changes in the optical constants along the normal to the layers. Since magnetic properties affect the optical constants at core excitations, resonant scattering of polarized x-rays can provide information about magnetic ordering of the layers, as well as about the magnetization depth profile within each layer of a given element.

We have started XRMS studies on metal/oxide magnetic structures using $\text{Co}/\text{Al}_2\text{O}_3$ and permalloy/ Al_2O_3 multilayers as model systems. The samples were prepared by radiofrequency sputter deposition, and their characterization will be described elsewhere [5].

Measurements were performed at beamline 6.3.2 of the Advanced Light Source [6], using the high precision $\theta/2\theta$ high-vacuum reflectometer. The circular polarisation rate was set to 70 % by moving the vertical jaws defining the beam divergence accepted by the monochromator. The external magnetic field (1 kG) was applied along the intersection between the sample surface and the scattering plane using a permanent magnet. The direction of the field was reversed at each acquisition point by rotating the magnet via a computer controlled in-vacuum stepper motor.

Figure 1. Magnetization averaged scattered intensity on a semilog scale (bottom) and magnetic asymmetry ratio (top) for a $(50 \text{ \AA} \text{ Al}_2\text{O}_3 / 50 \text{ \AA} \text{ Co})_{15}$ multilayer. Filled squares refer to spectra collected for a photon energy corresponding to the Co L_{α} absorption edge (on resonance), open circles to an energy of 650 eV (off resonance).

Fig. 1 shows the result of a $\theta/2\theta$ scan on and off resonance for a $(50 \text{ \AA} \text{ Al}_2\text{O}_3 / 50 \text{ \AA} \text{ Co})_{15}$ multilayer of 15 periods grown on silicon. The resonant scattering spectrum is taken at a photon energy (778.5 eV) corresponding to the Co L_{α} edge. The bottom panel reports the magnetization averaged scattered intensity, while the magnetic signal at resonance is shown in the top panel as the ratio between the difference and the sum of spectra obtained for opposite orientations of sample magnetization and photon helicity. The off resonance curve shows the Bragg peaks of 1st, 2nd and 3rd order related to the multilayer periodicity. The corresponding d value is 101 Å, which agrees well with the nominal periodicity of 100 Å. Between the 1st and 2nd order Bragg peaks one can also observe the oscillations related to the total number of periods in the superstructure. At 778.5 eV, we observe a much higher scattered intensity (about 2 orders of magnitude above 12 degrees) coming from the resonant contribution to the charge scattering amplitude, which is weakly dependent on the angle over the measured range. At the same time, the strong absorption of the photons at the L_{α} Co edge broadens the Bragg peaks and smears out the fine oscillations related to the number of periods. The top panel shows that large variations in the magnetic signal occurs under Bragg conditions. The observed oscillations versus angle do not

lie either side of a zero value, but rather a line shifted by - 6 % (thin dotted line). This is due to the fact that at resonance the scattering amplitude of the elliptically polarised photons is affected by the term $(\mathbf{e}_i^* \times \mathbf{e}_f) \cdot \mathbf{m} (F_{+1} - F_{-1})$, where $\mathbf{e}_i$ and $\mathbf{e}_f$ are the polarization vectors of the incoming and outgoing photons, $\mathbf{m}$ is the unit vector in the direction of the magnetization, and $(F_{+1} - F_{-1})$ is related to circular magnetic dichroism in absorption.

In general, working under resonant Bragg conditions enhances the magnitude of the magnetic effects. This can be very important when one wants to use the dichroism on the scattered intensity as a measure of magnetization related properties, such as drawing element specific hysteresis curves, imaging magnetic domains, or defining critical values of temperature and applied magnetic field. For such applications, the sensitivity is directly related to the maximum observable magnetic contrast. Fig. 2 shows the result of an energy scan at the Co 2p edges for a scattering angle that fulfills resonant Bragg conditions for the (50 Å Al_2O_3 / 50 Å Co) multilayer: an asymmetry ratio in excess of 60 % is observed at 776.4 eV, meaning that a change by a factor of four in the scattered intensity is obtained upon magnetization reversal.

Figure 2. Scattered intensity over the photon energy range including the Co 2p edges, for a grazing angle of 13 degrees satisfying resonant Bragg conditions. The vertical dotted line indicates the photon energy giving an asymmetry ratio in excess of 60%

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Scattering and Flare of 10x Projection Cameras for EUV Lithography

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INTRODUCTION

Scattering becomes increasingly important as the wavelength of light is reduced. For a reflective optic the total integrated scatter increases roughly as $1/\lambda^2$. The detrimental effects of scattering are: 1) a reduction in throughput due to light being lost from the camera; 2) a reduction in the image contrast by light which is redirected from bright regions of the imaged pattern into otherwise dark regions. A loss in throughput may be compensated, for example by increased exposure time. However, a reduction in the contrast degrades the image quality and is a more serious problem. The level of the scattered light in an otherwise dark region we refer to as flare. Flare reduces the exposure latitude. In addition, flare may cause the contrast to vary over the field of view if the pattern density varies, or as the edge of the field is approached. In turn, a variation in contrast will result in a variation in the printed line width.

Optical substrates for two Schwarzschild cameras have been fabricated with extremely strict tolerances on both figure and finish errors. These cameras are representative of the current state-of-the-art in optical fabrication. The substrates were coated and assembled into cameras. The characterization of the scattering from the individual mirrors is described here along with the determination of the flare level in the assembled cameras.

THEORY

The scattering from a multilayer can be rather complex; however, for small scattering angles the multilayer may be regarded as a single reflecting surface. This approximation is valid for the small angles corresponding to the field of view (0.1 deg) of the Schwarzschild camera being discussed here. The scattering from a single surface may be calculated according to¹

$$\frac{1}{I_0} \frac{dI}{d\Omega} = \frac{16\pi^2}{\lambda^4} R \cdot S \cdot \text{PSD}(f) \quad (1)$$

where R is the reflectivity of the smooth surface and $S = \exp[-(4\pi\sigma/\lambda)^2]$ is the Strehl ratio. The two dimensional power spectral density (PSD) describes the surface roughness, which is assumed to be isotropic and is a function of the radial spatial frequency, $f = \sin \theta/\lambda$, where θ is the scattering angle measured from the specularly reflected beam. This expression assumes that the incident and scattered angles are small (close to the normal) and the scattering is rotationally symmetric about the reflected beam.

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The effect of scattering on the image produced by a camera may be described by a scattering point spread function (PSF_s). The image is calculated by convolving the PSF with the aerial image intensity calculated without scattering, but including the effects of the figure errors of the optics and the coherence of the illumination. For a single mirror, the PSF_s is proportional to the angular distribution of scattering,

$$PSF_s(r) = \frac{1}{\rho^2} \frac{1}{I_0 R} \frac{dI}{d\Omega} \quad (2)$$

where ρ is the distance between the mirror surface and the image plane.

Figure 1. The 10x Schwarzschild camera.

For the Schwarzschild 10x camera consisting of two mirrors, shown in Fig. 1, the scattering point spread function is given by²

$$PSF_s(r) = S\delta(r) + \frac{16\pi^2 S}{\lambda^4 \rho_2^2} \left(PSD_2\left(\frac{r}{\lambda \rho_2}\right) + \alpha^2 PSD_1\left(\frac{\alpha r}{\lambda \rho_2}\right) \right) \quad (3)$$

where the delta function which accounts for the specular image has been explicitly included. The first term with the brackets describes the scattering from the secondary (final) mirror with PSD_2 at a spatial frequency of $f = r/\lambda \rho_2$. The distance from the secondary mirror to the image plane is $\rho_2 = 137.7 \text{ mm}$. The second term describes the scattering from the primary mirror at a spatial frequency which is scaled by $\alpha = M\rho_2/\rho_1 = 5.48$ relative to that of the secondary, where $M = 10$ is the camera magnification and $\rho_1 = 251.3 \text{ mm}$ is the object to primary mirror distance.

The reduction of image contrast by scattering may be seen by considering the intensity in an isolated dark line within a bright field. The aerial image intensity may be calculated by convolving the image produced in the absence of scattering with the PSF given above. The intensity in the center of the line is increased due to the tail of the PSF which extends from the bright regions of the field into the dark line. As the width of the line is reduced the intensity in the center of the line increases because of the contribution from nearby bright points. Since it is

convenient to describe the effects of scattering on the image contrast by a single number, *flare* is often defined as the intensity in the center of a dark line of a specified width in a uniformly bright field.

SCATTERING FROM THE INDIVIDUAL MIRRORS

EUV scattering was measured for each of the two secondary mirrors after they were multilayer coated. The measurements were performed at the reflectometry and scattering beamline (6.3.2) operated by the Center for X-ray Optics at the Advanced Light Source (ALS) in Berkeley. EUV synchrotron light, at a wavelength of 13.4 nm, was used to illuminate a pinhole at a distance of 110 mm from the mirror. The pinhole was re-imaged with a magnification of unity into a channeltron detector which could be scanned in angle. The angular distribution of scattering for the S2 mirror is shown in Fig. 2. The calculated angular distribution is also shown and was obtained from Eq. (1) and the measured PSDs of the coated surfaces. The single surface scattering approximation is not expected to hold for large angles and indeed the calculated curves deviate from the measurements above about 15 deg.

Figure 2. EUV scattering from the secondary mirrors. The solid lines are the calculated scattering for a single surface with the PSD measured for the top (coated) surface of each of the mirrors.

FLARE OF THE CAMERA

The mirrors were assembled into cameras and aligned. The flare of the assembled camera 1 (consisting of the P3 and S2 mirrors) was determined in three different ways. In the first test the camera was used to image a 750-nm pinhole which was illuminated with synchrotron light at the EUV Interferometry beamline (12.0) at the ALS. The light passing through a 0.5-mm square aperture in the image plane was detected with a photodiode. The size of the aperture was chosen to match the field of view of the camera. With the aperture centered on the image of the pinhole, the intensity of light measured by the photodiode is the sum of the specular and scattered light. The amount of light contained in the specular image can be determined by using the edge of the aperture as a knife-edge to scan through the image of the pinhole. The results of such a scan are shown in Fig. 3 where the photodiode signal was normalized to that obtained when the aperture was centered on the image. The flare can be directly obtained from the measured scan. Choosing to specify the flare for a 4 micron line, the width of the scan in Fig. 3, the measured flare is 4.5%. This is in good

Figure 3. Knife-edge scan through the image of a 750 nm pinhole produced with camera 1. The flare is the amount of light scattered outside the image. For a 4 micron line, the width of the scan, the flare level is 4.5%. The solid line was calculated from the surface profile measurements on the individual optics of camera 1.

agreement with calculations based on the measured surface roughness of the individual optics, shown as a solid line in Fig. 3, which would predict a flare of 4% for a 4-micron line.

Two additional independent measurements have been performed which also put the flare level in the 4-5% range. One uses the wavefront errors determined by EUV interferometry¹ to determine the point spread function (PSF) of the camera. The wings of the PSF, which describe the level of scattering, are determined from the high frequency wavefront errors. The PSF obtained from the Fourier transform of the measured wavefront, both phase and amplitude, is shown in Fig. 4. Finally, the flare was measured lithographically with camera 1 installed in the Sandia 10x1 system. In this measurement, 4 micron lines were printed and it was found that an overexposure of 20x did not quite clear the line. This puts the flare level at somewhat less than 5%.

Figure 4. The Point Spread Function of camera 1 as measured by EUV interferometry is compared to that calculated from Equation (3) and the measured PSDs of the individual mirrors.

CONCLUSIONS

The relationship between the optical finish of the mirror substrates and the flare of an assembled EUV camera is clearly demonstrated. The improvements made in mirror finishing translate directly into a reduced level of flare compared with previous cameras⁴. These results are very encouraging for the success of the next generation of EUV imaging optics which will have more mirrors and an increased field of view, both of which tend to increase the level of flare.

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Surface induced structural disorder in semiconductor nanocrystals observed by XANES

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INTRODUCTION

The emergence of colloidal methods to prepare high quality inorganic nanocrystals has led to an increasing number of studies of size dependent scaling laws. Due to the finite size of nanocrystals, the structure and composition of their surface may have particular significance for their chemical and physical properties [1]. Nanocrystals have a high surface to volume ratio (a 28Å diameter CdSe particle has 37% of its atoms on the surface), and their thermodynamic, electronic, and chemical properties are influenced by the surface [2, 3]. Thus, in order to comprehend fully the size dependent properties of nanocrystals, it is necessary to determine the structure of the surface. However, the surface structure of semiconductor nanocrystals is not well understood. Techniques such as x-ray diffraction (XRD) and transmission electron microscopy (TEM) that yield much information about the shape and interior structure of nanocrystals are insensitive to the atomic configuration at the surface [4-6]. The TEM image in Fig. 1 shows evidence that nanocrystals are crystalline and faceted, but information about the surface is limited. Furthermore, methods that are used to measure the surface structure for two-dimensional surfaces such as low energy electron diffraction require long-range order.

Fig. 1. High resolution TEM image of a CdSe nanocrystal. The scale bar is 50Å.

We use x-ray absorption spectroscopy (XAS) to measure surface atom configurations in nanocrystals. Due to the local nature of the absorption process, XAS does not rely on any long-range order in a sample. The spectrum within 50 eV above the absorption edge (x-ray absorption near edge structure, XANES) is sensitive to the relative arrangement of multiple atoms due to the contribution of multiple scattering effects [7, 8]. From the absorption spectrum one can extract complex information such as bond angles. Here we report that XANES spectra at the In and Cd $M_{4,5}$ edges of InAs and CdSe nanocrystals show a size dependent broadening which can be interpreted the presence of reconstructions at the surfaces of the nanocrystals.

EXPERIMENT

CdSe and InAs nanocrystals with a mean diameter ranging from 17-80Å were synthesized according to literature methods [9, 10]. The particles are capped with an organic ligand. High-resolution TEM show crystalline, well separated CdSe (Fig.1) and InAs particles with wurtzite and zincblende lattice fringes, respectively, in agreement with corresponding XRD patterns. Sub-monolayers of particles were deposited onto HF etched Si wafers from toluene solutions. The XANES spectra of the $M_{4,5}$ edge at 405eV (Cd) and 445eV (In) were measured in total current yield on beamline 6.3.2. The photon energy was calibrated to the F 1s line in MgF_2 (690eV). The linewidth for the 3d core level of both In and Cd is estimated at ~300meV [11] which is the limiting factor in the resolution of the experiment. Note that since we are exciting 3d core

electrons we are mapping the local partial density of states with p-character in the spectra. Therefore, we are *not* exciting into states located at the conduction band edge which are mainly derived from the metal 5s-states, but into higher p-bands that are 2-6eV above the conduction band minimum.

Fig. 2. XANES $M_{4,5}$ spectra of Cd (a) and In (b) in CdSe and InAs nanocrystals and the bulk materials. nanocrystal diameter in Å. (c) XPS of In 3d core in InAs nanocrystals and bulk.

Fig. 2 shows the absorption edge of the a) Cd and b) In $M_{4,5}$ edges as a function of size of CdSe and InAs nanocrystals as well as the respective bulk spectra (bottom). As the size of the particle decreases, the spectral features broaden significantly to the point that for the smallest particle (17 Å for InAs) no splitting within spectra is visible anymore. X-ray photoelectron spectroscopy (XPS) of the Cd and In 3d (Fig. 2c) core levels show a slight size-dependent shift to higher binding energies and an increase of the spectral linewidth due to decreased core-hole screening in nanocrystals [12]. However, the magnitude of this effect is negligible compared to the effects seen in the XAS spectra. Therefore, the smearing of the XANES spectrum is not due to

the core level from which the electron is ejected but the environment of the photoelectron in the crystal.

To understand the spectral behavior, we have simulated the In $M_{4,5}$ edge absorption spectra using a multiple scattering model for XANES spectra, FEFF7 [13]. The particles are modeled as spherical with a layer of In atoms terminating the surface, in accordance with results from XPS [14]. In the simulations, the two outermost layers of In and As atoms are distinguished from those in the interior of the particle by separate calculation of their muffin-tin potential [15]. The absolute energy of the simulated spectra was shifted to match the data at the first spectral feature of bulk (446.5 eV), and the calculation included a broadening of 100 meV to account for the finite experimental resolution and a factor of 300 meV for core hole broadening. Fig. 3 shows simulations (lines) and spectra (dots) of a) InAs bulk, as well as b) 28 Å (441 atoms) and c) 17 Å (99 atoms) diameter InAs nanocrystals using bulk lattice parameters. In agreement with the experiment, the simulated bulk spectrum shows features at 446.5 eV and 449 eV, though it introduces a spurious peak around 460 eV. For the nanocrystals, the simulation predicts similar results with

a slight broadening of the features at 446.5 eV and 449 eV as the size of the nanocrystal is decreased. However, the degree of broadening in the calculated spectra is much smaller than observed in the experimental data. Apparently, if the nanocrystal has uniform bulk bond lengths, the spectra of the

Fig. 3. In $M_{4,5}$ spectra of InAs nanocrystals and bulk (dots) with FEFF7 simulations (lines) for nanocrystals assuming bulk lattice constants.

Fig. 4. $M_{4,5}$ spectra for 17Å and 28Å nanocrystals (dots) and FEFF7 simulations including a surface reconstruction.

smaller particles is not reproduced. Thus, the observed broadening does not arise solely from the finite number of coherent scatterers.

When a reconstruction of the surface into the calculation for spherical 17Å and 28Å InAs nanocrystals (Fig. 4) we observe a broadening of the simulated spectrum comparable to the experiment. We assume a relaxation of the outermost In layer by -0.85Å (inwards) and the next As layer by +0.39Å (outwards). This is similar to results from calculations for III-V bulk semiconductors [16]. For the (110) surface of zincblende III-V and $(10\bar{1}0)$ surface of (II-VI) wurtzite semiconductors this type of reconstructions conserves the nearest neighbor bond length but changes angles [17]. Note that in nanocrystals this surface relaxation changes the bond lengths at the outermost surface layers. This increases the number of distinct photoelectron scattering paths in a nanocrystal, yielding a broadening of the XANES spectra in the simulations. However, the experimental broadening may not only be due to a structural

rearrangement of exclusively the two outermost layers as assumed here. It is very probable that the reconstruction is quite complex, where geometries deviate from the bulk values throughout the particle, the largest displacements at the surface. However, lacking an appropriate model to account for such rearrangements, we only state here that the observed broadening of XANES spectra can be related to structural disorder within the nanocrystals, which is believed to be largely due to atomic displacements at the surface.

Other possible sources for the broadening effects have been systematically studied. We simulated spectra for an unreconstructed 17Å nanocrystal with a) a capping of the outermost In layer with P atoms and b) a slightly elliptical shape shown in Fig. 5. The surface capping with P atoms models the experimental situation that the outermost In layer is covered by a disordered layer of ligands (tri-n-octylphosphine) as confirmed by XPS [14]. Since scattering scales as Z^2 (the atomic number) the P atoms are a negligible contribution to the spectrum compared to As or In. An elliptical particle shape (aspect ratio 1.1) which has been observed [3, 6] increases the number of scattering paths due to the symmetry reduction from a sphere, which should in principle lead to a broadening of the XANES spectra. However, this contribution is insignificant compared to the experimental result. Quantum size effects convoluted with the finite size distribution of the nanocrystals can also be excluded. We simulated the effects of a size distribution with 10% width on the x-ray absorption spectrum of 17Å InAs nanocrystals [18]. The bulk spectrum was convoluted with a Gaussian of a width of 100 meV representing the conduction band shifts corresponding to the size distribution. The result (not shown) exhibits an insignificant amount of broadening of the spectrum relative to the experiment. We conclude that structural disorder in small InAs and CdSe nanocrystals is the major factor in the broadening of the XANES spectra at the In and Cd $M_{4,5}$ edge.

Fig. 5. FEFF7 simulations of an unreconstructed 17Å nanocrystal with (a) P on the surface and (b) an aspect ratio of 1.1.

However, as may be expected for a single bulk-derived reconstruction of the outermost surface layers, it is still not in quantitative agreement with the experiment. The simulation of XANES in larger nanocrystals requires substantial improvement of the multiple scattering calculations. Also, the simultaneous presence of multiple faces, each with different reconstructions, must be accounted for in the models. Further experiments for nanocrystals with different surface stabilizations might provide enough information on the nature of the reconstruction. The nanocrystals can be stripped of their surfactant and epitaxial shells of related semiconductors can be grown onto the cores (e.g. InAs coated with CdS). These surface modifications will provide additional checks on the complex surface reconstructions of the semiconductor nanocrystals.

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Beamline 7.0.1 Abstracts

A Direct Probe to the Electronic Structure of Interfaces in Heterostructure Semiconductors

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INTRODUCTION

The characterization of interfaces is a key concept for understanding the properties of semiconductor devices. The large penetration length and site selectivity of soft-x-ray-emission (SXE) spectroscopy offer the possibilities of investigating the electronic structure of buried layers and their interfaces of heterostructure semiconductors.

Nilsson *et al.* measured Si *L* emission spectra of 1 and 3 ML thin Si buried under 100 thick GaAs (100) at the excitation energy of 120 eV. [1]

In the case of Si *L* SXE of Si/GaAs, the Si *L* and Ga *M* levels have almost same binding energy and thus the emission from two different atom sites overlaps in the same energy region. In order to draw out the information about Si layer, we subtracted a scaled Ga *M* SXE spectrum of bulk GaAs from Si/GaAs spectra. Figure 1 displays the difference spectra.

Figure 1. The Si *L* soft-x-ray-emission spectra subtracted by the Ga *M* spectrum of bulk GaAs from the 1- and 3-ML Si/GaAs buried under 100 GaAs(100) compared with bulk Si *L* emission spectrum. Photons of 120 eV were used for excitation.

The 1 ML spectrum shows bigger energy separation of main peaks than others and has humps around 86 and 95 eV at the both side of the main peaks. These features doesn't appear clearly in the 3 ML spectrum. These features are associated with a hybridising effect between the Si *s* states with the As *s* states.

We have measured Al *L* emission from 1, 2, 5 and 20 ML AlAs layers buried under 100 thick GaAs (100) capping layer. [2] Because the energy ranges of Al *L* emission and Ga *M* emission are separated, one can see the layer thickness effect for AlAs layers directly.

EXPERIMENTAL

The soft-x-ray-emission spectra were recorded using a high-resolution grazing incidence x-ray fluorescence spectrometer [3] at beamline 7.0.

During the Al *L* SXE measurements, the resolution of the beamline was 0.12 eV and the resolution of the fluorescence spectrometer was set to 0.22 eV. The incidence angle of the photon beam was about 20 degree to the sample surface.

The heterostructures were grown by solid source molecule-beam epitaxy on GaAs (100) substrates and thin 1, 2, 5, and 20 ML AlAs layers were finally capped by a 100 Å thick GaAs layer. Because Al, like Ga, is a III-valued atom and AlAs has a similar lattice constant to that of GaAs, we have assumed that Al only occupies Ga-site.

Figure 2. A schematic geometry from 2 ML-AlAs (100)-layers. Two unit cells side by side are displayed.

Figure 2 shows a schematic atomic geometry two unit cells side by side of 2 ML-AlAs (100)-layers. Al state of AlAs could be strongly effected the neighbour GaAs in the case of ultra thin AlAs layers and in the central layer in the thick layers Al should be like bulk state.

RESULTS

Thick curves in Fig. 3 show the smoothed Al *L* SXE spectra of AlAs buried under the 100Å thick GaAs(100) capping layer form heterostructures with 1-, 2-, 5-, and 20-ML-AlAs thin layers. Photons of 80 eV were used for excitation. Since AlAs layers were ultra thin, the Al *L* emission intensity was very weak. The error bars are shown on the left.

The 20-ML-spectrum is identical to a bulk spectrum [4], however thinner layers spectra show a dip at around 68.5 eV and the peak at 67.3 eV becomes broader. In the case of the 1 ML case, a hump appears at 66 eV (A). These distinct difference must be caused by interface effect between AlAs and GaAs. Thin curves show the *ab initio* theoretical calculations spectra. The top theoretical spectrum is calculated for bulk. The tendency of change of spectra shape depending layer thickness is well reproduced.

The spectral broadening is caused by appearing of B, and small peak A appears clearly only in the case of monolayer (1 ML) AlAs, this is expected to be effected form the neighbour Ga state through the As state. We interpret these features as a hybridized states at the interface. Peak A intermixed states are not found in 2 ML spectrum, thus this is a character of monolayer in the heterostructure. Hump B is observed in 2 ML spectrum as well. This is also assumed to be from hybridization effect with the surrounding.

In the thicker layers the Al *L* SXE spectra show bulk like spectra. The electronic structure is fully bulk like in the centre layer, Only at the interface the Al states strongly mix into the neighbour GaAs.

CONCLUSION

This investigation demonstrates that it is feasible to study details of the electronic structure of internal ultra thin layers using soft x-ray emission spectroscopy. For the 1 ML case monolayer states are found to mix strongly into surrounding GaAs. Because the object to investigate is ultra thin and is buried under thick capping layers, the intensity of SXE spectrum is very weak. The high brilliant synchrotron is necessary for this kind of measurements.

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Figure 3. The smoothed Al *L* soft-x-ray-emission spectra under 100 Å GaAs(100) with various thickness of AlAs layers. Photons of 80 eV were used for excitation. The error bars are shown on the left.

A Study of the Electronic Structure of V_xC_{60} Complex Films by XES and XAS

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V_xC_{60} co-deposited films have been studied by X-ray absorption and emission spectroscopies (XAS and XES) at different V content x ($x=1.0, 4.4$ and 5.4) in the films with respect to possible V_xC_{60} compound formation. In addition, pristine C_{60} and vanadium carbide spectra were recorded for comparison. In the absorption spectra the same peaks are observed as in pure C_{60} up to vanadium content $x=5.5$, which was the highest used in our experiments. However, the decreasing relative π^* absorption intensity (with respect to the σ^* energy region) can suggest partial charge transfer from the metal 3d states to the lowest unoccupied molecular orbital (LUMO) of C_{60} with π^* symmetry. The detuned XES spectra, excited slightly (1.6 eV) under the 1s - LUMO absorption resonant peak indicates a partial symmetry breaking from the interaction between C_{60} and vanadium.

Introduction

Fullerene chemistry has been a very active field since the advent of buckminster fullerene in 1990¹. In metal-fullerene compounds it has been found out that the metal atoms can be bonded in different geometries. The alkaline and alkaline earth metals and mercury are the only metals that have proved to make stable compounds with C_{60} (also predicted theoretically as long as the ionic model can be applied). More recently, some evidence indicating a compound

formation for transition metals has been published^{2, 3}. We tried to study the electronic structure of vanadium fulleride films.

Experimental

The films were produced by co-evaporating C_{60} and on a Si substrate in a UHV-grade vacuum system. The XAS spectra were recorded in total electron yield (TEY) mode, with a 0.3 eV resolution, measuring the sample current. The XES spectra were taken using a grazing incidence spectrometer using spherical grating (5 m radius, 400 lines/mm) grazing incidence x-ray spectrometer with a 2D detector. The spectrometer as well as the monochromator resolution was set to about 0.6 eV during the carbon K emission measurements.

Results and discussion

The XAS spectra show differences in the σ^* absorption region with varying V content in the films; higher V content gives stronger σ^* absorption. (with electron transfer from the metal (3d levels), the LUMO π^* orbitals (t_{1u}) are being partially filled. This does not directly lead to symmetry breaking, but it leads to changes in certain bond lengths⁴. The non-resonant XES spectra (Fig. 2) of $V_{1.0}C_{60}$ is almost identical to that measured for the pristine C_{60} sample. Slight depletion of the E_5 spectral feature which consists mainly of ungerade states which are

spectroscopically allowed to fill the (gerade) core hole (for assignment of the E_{1-5} see, e.g. ref. 5, or a related abstract⁶ in this volume). The emission spectra with detuned excitation (1.6 eV below the π^* absorption resonance), however, indicate considerably larger intensity outside the E_5 feature, which is dominant in the respective pristine C_{60} spectrum. This can be

Figure 1 XAS spectra of the V_xC_{60}

Figure 2 The a) non-resonantly and (C $1s$ -LUMO) resonantly excited X-ray emission spectra of C_{60} , $V_{10}C_{60}$ and VC. Excitation energies resp. 284.5 eV and 295 eV. Features E_{1-5} are explained in the text (e is elastic peak).

interpreted as a result of symmetry breaking, as E_5 is dominant in C_{60} due to symmetry reasons. The C_{60} emission bandwidth of the V_xC_{60} films is preserved throughout the excitation energy range, and the changes in spectra do not indicate uniquely carbide-like bond formation, i.e. C_{60} cage breaking (the $V_{1.0}C_{60}$ spectrum is not a composite of C_{60} and VC spectra). This can be interpreted as an indication of V_xC_{60} compound formation, with partial charge transfer towards the C_{60} - cage.

Further experiments are planned with emission spectroscopy over a larger vanadium concentration range, to gain more understanding of the bonding mechanisms.

Figure 3 X-ray emission spectra, excited 1.3 eV below π^* absorption threshold (at 282.9 eV)

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B K and C K emission studies of superconductors: YNi₂B₂C and LuNiBC

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INTRODUCTION

Bulk superconductivity has been observed in Ni- and Pb-based rare-earth borocarbides [1, 2] with critical temperatures T_c up to 23 K. This has raised questions about the understanding of the origin of superconductivity. One of which concerns the role of the transition metal nickel: if the Ni 3*d* electrons are involved in the conductivity the electron-electron correlation (due to the presence of a partially filled 3*d* band) may play a significant role in the determination of properties. Superconductivity has also been observed [2, 3] in the closely related RE-Ni-B-C system (RE = Y, Tm, Er, Ho, and Lu) with a maximum critical temperature of 16.6 K in non-magnetic LuNi₂B₂C and 15.6 K for YNi₂B₂C.

The crystal structure for LuNi₂B₂C and YNi₂B₂C is a body centered tetragonal (bct) structure similar to the ThCr₂Si₂-type system with an additional carbon atom in lanthanide layer [4]. Local density approximation (LDA) band structure calculations [5, 6] have shown that, although Ni 3*d* dominates near the Fermi Level (E_F), all four atoms are involved in the bands at E_F and above. The states at Fermi level consist primarily of Ni *d*, B *p*, C *p*, and Lu *d*. The dispersion of the bands (with Lu *d* and Ni *d* + B *p* characters) along the *c* direction is comparable to that in the plane, giving a strongly three-dimensional (3D) character. Photoemission studies of YNi₂B₂C [7, 8] show that Ni 3*d* emission is expected at 1.5 eV below E_F , and that the structures at ~6, ~10, and ~14 eV have significant B and/or C 2*sp* character.

Soft x-ray emission spectroscopy (SXES), probing the occupied part of the 2*p* derived partial density of states (DOS), has been used in previous studies of the electronic structures of high temperature superconductors [9,10]. Here we report the SXES studies of the electronic structure of quaternary intermetallic compounds YNi₂B₂C and LuNiBC and a comparison of the results to the calculated DOS of LuNi₂B₂C and LuNiBC.

EXPERIMENT

The samples were prepared by arc-melting and annealing. The starting materials are lanthanide (Y, Lu) shavings, pure Ni, B, and C powders. The phase purity of the samples was detected by x-ray powder diffraction. Both samples, YNi₂B₂C and LuNiBC, were found to be phase pure within the resolution of the x-ray diffraction system. The YNi₂B₂C and LuNiBC compounds are superconductors with $T_c \approx 16$ K and $T_c \approx 2.9$ K, respectively.

The experiments were performed at Beamline 7.0 of the Advanced Light Source (ALS) [11], Lawrence Berkeley Laboratory (LBL). This Beamline is comprised of a 5-meter, 5-cm-period undulator and a 10,000-resolving-power spherical grating monochromator (SGM) covering the spectral range from 100 to 1300 eV. The soft x-ray emission spectra was recorded using a high-resolution grazing-incidence grating spectrometer with two-dimensional detection [12].

In the SXES measurements the bandpass of the incoming photon beam was set to about 0.2 and 0.3 eV for boron and carbon, respectively. The spectrometer resolution was 0.25 eV and 0.45 eV for B and C *K*-emission measurements, respectively.

RESULTS AND DISCUSSION

The B *Kα* spectra of YNi₂B₂C and LuNiBC with excitation energy above ionization threshold is shown in Figure 1. Although the B *Kα* spectra of YNi₂B₂C and LuNiBC show some differences on spectral profile in detail, both have a sharp edge at the high energy side. The B *Kα* emission of YNi₂B₂C exhibits a double-structure band with a 4.0 eV full width at half maximum (FWHM). The peak maximum and the high-energy shoulder are located at about 181.2 eV and 182.4 eV, respectively. The high-energy edge cut off at about 186.1 eV. In contrast, the B *Kα* emission of LuNiBC exhibits a single-band dominant structure with a 2.7 eV FWHM, and peak maximum locates at about 182.0 eV. The high-energy edge cut off at about 186.0 eV.

The calculated boron partial density of states of LuNi₂B₂C and LuNiBC, obtained from LDA band structure calculation [5], are displayed in Figure 1. Because we are not aware of the calculated boron partial DOS of YNi₂B₂C at present, the B *Kα* emission spectrum of YNi₂B₂C is compared with the boron partial DOS of LuNi₂B₂C since the boron partial DOS of YNi₂B₂C is very similar to that of LuNi₂B₂C. The energy scale of the calculated partial DOS was obtained by aligning the Fermi level, as indicated in the Figure 1, to the cut-off edge in the experimental spectrum of YNi₂B₂C. Both calculation results agree well with the B *K* emission spectra of YNi₂B₂C and LuNiBC.

X-ray diffraction results showed that the crystal structure of YNi₂B₂C and LuNiBC is a three-dimensionally connected framework [4], and it may be viewed as a layered system, reminiscent of the high-*T_c* oxide superconductors. LuC, NaCl-type layers alternate with Ni₂B₂ layers, with a stoichiometry of 1:1 for YNi₂B₂C (or 1:2 for LuNiBC). The Ni₂B₂ layers are two-dimensional networks of the inverse PbO-type, with nickel being tetrahedral-coordinated by four boron atoms. The Ni₂B₂ layers contain a square-planar Ni₂ array sandwiched between the boron planes. The tetrahedral-coordinated Ni produces Ni-B bonds that are relatively weak, and this leads to Ni-B hybridization effects that are moderate in strength.

Figure 1: The B *K* x-ray emission of YNi₂B₂C and LuNiBC with photon-excitation energy above the ionization threshold (open circles). The calculated B *p*-DOS of LuNi₂B₂C and LuNiBC, obtained from an LDA band structure calculation [5], are displayed (solid curves). The calculated *p*-DOS was shifted so that the *E_F* level is in accordance with the cut-off edge in the XES spectrum of YNi₂B₂C.

B $2p$ states mix with the Ni $4sp$ band and form occupied bonding states $2p-4sp$ with main $2p$ character. The interaction between B $2p$ and Ni $3d$ electrons results in bonding and antibonding $2p-3d$ states close to the Fermi level. The splitting between bonding and antibonding states is small since the interaction between the $2p$ and $3d$ states is weaker. In Ni the $3d$ band in the formation of chemical bonds is positioned near the Fermi level, and there are empty states above the Fermi level. In this energy region, the B $2p$ partial DOS is expected to be very low, as it was pointed out in the calculated B $2p$ partial DOS of $\text{LuNi}_2\text{B}_2\text{C}$ [5, 6].

The predominant feature in the B $K\alpha$ emission spectrum of $\text{YNi}_2\text{B}_2\text{C}$, appearing at about 181.2 eV, has mainly pure B $2p$ character. At higher emission energy in the B $K\alpha$ spectrum of $\text{YNi}_2\text{B}_2\text{C}$, a plateau of intensity appears which ends with a sharp edge at about 186.1 eV. The intensity at the Fermi level in B K -emission spectrum from $\text{YNi}_2\text{B}_2\text{C}$ is due to B $2p$ - Ni $3d$ hybridization with main $3d$ character. The observed cut-off edge at the Fermi level in the XES spectrum indicates that the antibonding $2p-3d$ states are partly occupied.

The C $K\alpha$ emission of $\text{YNi}_2\text{B}_2\text{C}$ and LuNiBC with photon-excitation energy above the ionization threshold are shown in Figure 2. The C $K\alpha$ emission of $\text{YNi}_2\text{B}_2\text{C}$ exhibits a double-band structure with a 6.1 eV FWHM. The peak maximum and the high-energy shoulder are located at about 276.6 eV and 279.59 eV, respectively. The C $K\alpha$ spectrum of LuNiBC also exhibits a double-band structure with a 5.4 eV FWHM and peak maximum located at about 278.4 and 280.5 eV, respectively.

The calculated carbon partial DOS of $\text{LuNi}_2\text{B}_2\text{C}$ and LuNiBC , obtained from the LDA band structure calculation [5], are displayed in Figure 2. The energy scale of calculated partial DOS was obtained by aligning the dominant features with respect to the same features in the experimental spectrum of $\text{YNi}_2\text{B}_2\text{C}$. The contributions from the lowest partial DOS bands, which have carbon $2s$ character, are absent in the XES spectra due to their dipole forbidden nature. Both calculated carbon partial DOS are in very good agreements with the C $K\alpha$ spectra of $\text{YNi}_2\text{B}_2\text{C}$ and LuNiBC .

Figure 2: The C K x-ray emission of $\text{YNi}_2\text{B}_2\text{C}$ and LuNiBC with photon-excitation energy above the ionization threshold (open circles). The calculated C p -DOS of $\text{LuNi}_2\text{B}_2\text{C}$ and LuNiBC , obtained from an LDA band structure calculation [5], are displayed (solid curves). The calculated p -DOS was shifted to align the dominant features with respect to the same features in the XES spectrum of $\text{YNi}_2\text{B}_2\text{C}$.

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Decay and dissociation of core-excited OCS studied by X-ray scattering

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Introduction

The rapid advancement in synchrotron radiation instrumentation in the last few years has led to much progress in the field of molecular core-level spectroscopies. The energy selectivity, which is obtained using monochromatic synchrotron radiation, allows resonant excitation of different types of molecular states. In particular, core excitation of small molecules with repulsive intermediate states has attracted attention. In decay spectra, the dissociation is manifested by the simultaneous presence of molecular and atomic contributions. The core-excited molecule may fragment before de excitation (dissociation channel prior), leading to atomic (or molecular radical) decay lines, or the de-excitation is followed by dissociation (de-excitation channel prior), which leads to broad molecular features. The time for dissociation and the lifetime of the core hole have pronounced effects on line positions, line widths, transition rates, and vibrational fine structures. A fast dissociation results in sharp atomic lines governed by the different dissociation channels involved, while slower dissociation results in broad molecular features. If both molecular and atomic features are observed with similar intensities, the dissociation and the core-hole decay processes occur on the same time scale, i.e. typically in the 10^{-14} s range. The dissociative core-excitation processes have until now been studied in the non radiative deexcitation channel, while no results for the radiative channel has so far been presented. The radiative channel provides new insights owing to the dipole selectivity of the process, and the implementation of local selection rules [1, 2]. This provides a simple way to characterize the dissociated fragments. The lack of experimental data is due to the low fluorescence yields and instrument efficiencies associated with soft X-ray emission (SXE) in the sub-keV energy region which makes the measurements more demanding and intense synchrotron radiation (SR) sources are therefore a prerequisite.

In this work carbonyl sulfide (OCS) has been studied [3]. The OCS molecule has 30 electrons and a linear geometry in the ground state. The corresponding electronic configuration is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 6\sigma^2 7\sigma^2 8\sigma^2 2\pi^4 9\sigma^2 3\pi^4$. The 1σ , 2σ , 3σ , and 4σ orbitals correspond to the S 1s, O 1s, C 1s, and S 2s core levels, respectively, whereas the spin-orbit and molecular-field split S 2p levels are composed of the 5σ and 1π molecular orbitals. The remaining orbitals are associated with valence levels of mixed atomic character. The OCS molecule belongs to the $C_{\infty v}$ point group and it has three vibrational modes, ν_1 , ν_2 and ν_3 . These modes can be characterized as being due to C-S stretching, O-C-S bending, and C-O stretching, respectively. Bending of the molecule lowers the symmetry to the C_v group. We present high-resolution resonant and nonresonant SXE spectra of carbonyl sulfide near the sulfur $L_{2,3}$ absorption thresholds to demonstrate a first case of fragmentation in the X-ray scattering process [4]. Recently, it has been discussed whether the lifetime of the sulfur $L_{2,3} \rightarrow \pi^*$ core-excited states in OCS is long enough to allow a dissociation process to occur before the decay [5, 6].

Experiment

The experiments were performed at beamline 7.0 at the *Advanced Light Source*, Lawrence Berkeley National Laboratory. The beamline comprises a 98-pole, 5-cm period undulator and a spherical-grating monochromator [7] covering the spectral energy range between 60-1300 eV. The SXE spectra were recorded using a high-resolution grazing-incidence SXE spectrometer [8, 9]. The spectrometer was mounted parallel to the polarization vector of the incident photon beam with its entrance slit oriented parallel to the direction of the incident beam. The pressure in the gas cell was optimized to about 2 mbar for a maximum absorption of photons in the interaction region. The interaction region was viewed by the X-ray spectrometer through a 160 nm thick polyimide window, supported by a polyimide grid and coated with 30 nm of aluminum nitride. During the SXE measurements, the incident photon beam entered the gas cell through a small pinhole of 100 μ m diameter and the pressure in the experimental chamber was

about 1×10^{-7} Torr due to the outgassing from the pinhole. With 0.30 eV resolution of the monochromator of the beamline, a near-edge X-ray absorption (NEXAFS) spectrum of sulfur was measured using the photocurrent from an electrode situated inside the gas cell where the incident photon beam entered the gas cell through a 100 nm thick silicon nitride window. The spectra were normalized to the incident photon flux using a gold mesh in front of the gas cell. The bandwidth of the synchrotron light during the sulfur, carbon, and oxygen emission measurements was set to 0.2 eV, 0.7 eV, and 1.1 eV, respectively. The resolution of the X-ray emission spectrometer is estimated to be 0.2 eV, 0.7 eV and 0.8 eV, respectively.

Results and Discussion

S 2p X-ray absorption spectrum

Figure 1 shows a NEXAFS spectrum measured in the region of the S $L_{2,3}$ -edges used as a reference for the SXE measurements. The spectrum consists of three strong resonance peaks followed by a weaker Rydberg series, and a shape resonance structure in the continuum, just above the ionization thresholds, presumably with multielectron excitations superimposed.

The positions of the indicated $L_{2,3}$ -edges are based on experimental photoelectron data [10]. The first peak in the NEXAFS spectrum is solely excitation from the $2p_{3/2}$ (L_3) channel which is also the case for peak number 5, while the remaining peaks are mixtures of excitations from both channels [5]. Peak number 6 has contributions from many Rydberg levels converging to the ionization potential. The fine structure of the Rydberg energy region is complicated due to the role of intermediate coupling. The 2p spin-orbit splitting creates a double-peak structure in the sulfur SXE spectra of the OCS molecule when the excitation is tuned to the mixed states (such as peaks 2,3 and 4) or the shape resonance.

Fig. 1: A NEXAFS spectrum measured at the sulfur $L_{2,3}$ -edges used as a reference for the emission measurements.

S 2p X-ray emission spectra

Figure 2 shows a series of experimental sulfur $L_{2,3}$ SXE spectra on a photon energy scale. The spectra were resonantly excited at the absorption peaks, denoted by the numbers 1 through 7 in Fig. 1. The spectral shape changes substantially when going from the nonresonant and Rydberg excited topmost four spectra to the π^* and σ^* excited spectra. In the latter spectra the emission peaks are substantially more vibrationally broadened and the peaks also appear at somewhat lower energy due to the screening effect of the spectator electron. The larger screening resulting from a spectator electron in the first unoccupied MO's (π^* or σ^*) than from an electron in a Rydberg orbital is most apparent in the third spectrum from the bottom (excited at 166.9 eV). This excitation energy corresponds to two transitions, $2p_{3/2} \rightarrow 4s$ and $2p_{1/2} \rightarrow \sigma^*$. In the emission spectrum the $2p_{3/2} 4s \rightarrow 9\sigma^1 4s$ transition results in a narrow peak with a small spectator shift, whereas $2p_{1/2} \sigma^* \rightarrow 9\sigma^1 \sigma^*$ transition yields a broader feature with a larger spectator shift. The narrow intense atomic line at a photon energy of 150.2 eV in Fig. 2 shows up when the incident photons are tuned to the second absorption peak at 165.4 eV, whereas another atomic line at 0.4 eV higher emission energy (150.6 eV) is observed when exciting to the third absorption peak at 166.9 eV. The atomic lines completely disappears at the higher excitation energies where the incident photon energy is tuned to Rydberg states. The atomic lines have a width of 0.26 eV, which can be attributed to

the instrumental spectrometer resolution (of about 0.2 eV) and the natural lifetime broadening (20-40 meV) of the sulfur $L_{2,3}$ core-hole [11]. The $9\sigma \rightarrow L_{2,3}$ double-peak feature at about 155 eV photon energy reflects the spin-orbit splitting of the L -shell excitation. Peaks No. 2, 3, 4, 6, and 7 (165.4, 166.9, 168.1, 169.9 and 177.5 eV) are due to excitations from both the L_1 and L_2 core levels. In these cases the filling up of the core levels by an electron from a single valence orbital results in two peaks.

It has been shown from angle-resolved ion-yield experiments that the OCS molecule induces a bending vibrational mode for the π^* excitations and that the dominating dissociation mechanism involves the breakup of the OC-S bond and the production of CO and S fragments at an angle of about 130 degrees [5, 6]. Thus, when an electron is placed in the π^* orbital, the potential energy is lowered by the bending motion, which can be understood as a Renner-Teller vibronic coupling effect [12, 13]. The atomic lines in the resonant SXE spectra can be considered as the result of a competition between the dissociation and the decay channels.

Comparing the intensity ratio of the atomic line to the molecular background in the three lowest SXE spectra shown in Fig. 2, one can conclude the presence of dissociation for all three, but to different extents. The dissociation time, t_D , can be estimated with the simple formula; $t_D = -\tau \ln(1-n)$, where τ is the core-hole lifetime and n is the 'molecular fraction' [14]. Here, a larger molecular fraction corresponds to a longer dissociation time and we assume the SXE yield to be the same for the molecule and the fragment. The first spectrum (164.2 eV), $L_1 \rightarrow \pi^*$ excitation, shows an atomic peak that contributes to about 15 % of the total intensity. If we assume the core-hole lifetime to be 22 fs (30 meV core-level width), a dissociation time of about 40 fs is found. In the second spectrum (165.4 eV) where there is a mixture of excitations from both the $L_2 \rightarrow \pi^*$ and $L_1 \rightarrow \sigma^*$ channels, the molecular fraction is smaller than for the first spectrum. This indicates a steeper potential path for σ^* than for π^* dissociation. Thus, the dissociation time is also smaller, about 30 fs. In the third spectrum (166.9 eV), the atomic contribution is still significant, however, in this case dissociation only occur from the $L_{2,3}^{-1} \sigma^*$ intermediate state, and the $L_1^{-1} 4s$, which is also excited, only result in a molecular contribution. The estimated dissociation time is about the same as in the first spectrum (about 40 fs). At higher excitation energies, i.e., for ionization as well as core excitation to Rydberg states, the atomic contribution completely disappears.

Fig. 2: A series of X-ray emission spectra of the S $L_{2,3}$ excitations of OCS.

Summary

We show the first evidence of molecular dissociation prior to de-excitation in resonant soft X-ray emission. Resonant and nonresonant *L*-shell X-ray emission spectra for sulfur in the carbonyl sulfide molecule were measured by the use of monochromatic synchrotron radiation. In the case of S *L*-shell excitation to the π^* and σ^* orbitals a strong competition is observed between de-excitation and dissociation resulting in atomic-like lines in the SXE spectra. The line shapes of the molecular features in those spectra are also strongly affected by the dissociative character of the core-excited states.

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Determination of Boron Coordination in Nuclear Waste Form Glasses by Soft X-Ray Synchrotron Radiation and Nuclear Magnetic Resonance Techniques

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INTRODUCTION

A multitude of individual components comprising borosilicate nuclear waste glasses are currently being investigated using x-ray absorption fine structure (XAFS) and nuclear magnetic resonance (NMR) techniques along with a host of other characterization methods. The focus of boron studies in glasses is to determine the amount of three- versus four-coordinate boron, the latter of which is generally accepted as being obtained through association with alkali ions. Structural characterization of boron is of particular importance as the knowledge of the interactions between B, O, Na, and other species is essential for building a fundamental understanding of glass durability.¹ One accepted method to obtain local structural information about boron is via ¹¹B NMR. Boron coordinated to three oxygens in a trigonal planar configuration gives rise to an asymmetric electric field gradient and a characteristic NMR line shape which is significantly different from tetrahedral four-coordinate B. NEXAFS spectroscopy of the B K edge has been well-characterized and the distinctive π^* electronic feature characteristic of B sp^2 hybridization arising from a trigonal planar environment provides a signature of three-coordinate boron. NMR requires specially formulated glasses to avoid paramagnetic interferences whereas real glasses may be used in NEXAFS investigations.^{2,6} An initial comparison of the NEXAFS and NMR results obtained from representative alkali borosilicate glasses can be made.

EXPERIMENTAL

The alkali borosilicate glasses were prepared at PNNL and characterized by standard analytical methods. The glasses are referred to by weight percent of boron as B₂O₃ (B-3 is 3 wt%). Results from boron reference compounds were used to establish the photon energy calibration and to ensure proper instrumental response. The glasses were ground to -325 mesh for all investigations. The solid state magic angle spinning (MAS) NMR measurements were made of specially-prepared glasses B-3, B-16, and B-24 at PNNL.⁷ The NEXAFS measurements at the B K edge (191 eV) of the borosilicate glasses, plus the two additional glasses S1 and S2 with unknown boron coordination that are not amenable for NMR, were performed on Beamline 7.0.1 or Beamline 9.3.2 of the Advanced Light Source at LBNL. Experiments were done under high vacuum conditions ($\sim 5 \times 10^{-9}$ Torr) with the glass powders pressed into indium. NEXAFS spectra were collected in the total electron yield (TEY) mode and on Beamline 7.0.1 in the partial fluorescence yield (PFY) mode as well. The performance characteristics of the beamline and x-ray emission spectrometer have been previously described.^{8,9} NEXAFS spectra were measured with the monochromatic x-ray beam incident at $\sim 75^\circ$ to the substrate normal.

RESULTS

The B K edge PFY spectra obtained from the glasses and normalized to the incoming photon flux are shown in Figure 1. The data were collected in the PFY mode, thereby emphasizing the bulk contribution from boron.¹⁰ Simple inspection of the overall NEXAFS signal shows that the spectra correlate nicely, as expected, to the concentration of B in the glasses. Furthermore the differences in boron spectra between the two identical glass melt compositions, one processed at 1300°C and the other at 1500°C, are clear in Figure 1. The most prominent features of the B spectra in Figure 1 are the peaks appearing just below 192 and 194 eV, respectively. An

exception is the B-3 spectrum that has much less intensity from the feature at lower energy. Examination of the spectra shows that the relative intensities of the two prominent features change with the boron content of the glasses. The peak located at 191.8 eV is well-known from NEXAFS spectroscopy of the boron K edge and is readily assigned as a transition to a π^* state.²⁻⁶

Figure 2 shows the PFY NEXAFS spectrum of hexagonal BN (h-BN), the B-24 glass, and two spectra collected from B_2O_3 with different modes of detection for comparison. The π^* transition in the glasses is indicative of structurally three coordinate boron. The higher energy peaks from the glasses resemble and occur at the same energy as the transitions observed in the PFY spectrum from three coordinate boron in B_2O_3 , as shown in Figure 2. However, the peaks do not have the same linewidths and correlate to the four-coordinate boron from the reference glass materials. The TEY spectrum of B_2O_3 in Figure 2 also exhibits a π^* peak from three coordinate boron. This feature arises from near surface boron defects and are distinguished as a result the difference in surface sensitivity between the surface sensitive TEY and bulk sensitive PFY collection modes.¹⁰

Figure 1. The raw partial fluorescence yield boron K edge NEXAFS spectra collected from the borosilicate glasses normalized to the incident photon beam current.

The relative fractions of three- to four- coordinate boron from the glasses were obtained from peak intensities of the PFY boron NEXAFS spectra. The PFY spectra were utilized for this purpose rather than the TEY spectra since this yields a bulk value comparable to the MAS-NMR results from the specially prepared glasses. The boron NEXAFS was calibrated to the MAS-NMR results. The relationship between boron coordination obtained via standards from NEXAFS to NMR are related as 2.57 ± 0.07 . Thus, knowledge of the glass compositions and some initial MAS-NMR results coupled with the boron NEXAFS peak ratios, permits the experimental determination of the amount of three coordinate boron in glasses S1 and S2. The S1 and S2 glasses are found to have approximately 82% and 84% four coordinate boron expressed in terms of atomic fraction, with the high temperature S2 glass having slightly more four coordinate boron. This may be a result of higher temperature forming four coordinate boron environments more effectively. Furthermore, these initial results suggest that the higher temperature glass lost some boron content during melt processing.

Figure 2. Boron K edge NEXAFS spectra from relevant B reference materials and the B-24 glass. The B_2O_3 spectra have been collected in two detection modes which have differing surface sensitivities. The spectra have been normalized to equivalent heights relative to the largest respective spectral feature.

CONCLUSIONS

The total NEXAFS signal at the boron K edge reflects the boron concentration in borosilicate glasses. The results show that boron K edge NEXAFS investigations can determine the amount of three coordinate versus four coordinate boron in borosilicate glasses once a suitable calibration is established. Most importantly, the results validate an experimental approach capable of ascertaining boron coordination in glasses that are not amenable to NMR methodologies. Boron K NEXAFS spectra can be obtained quickly and the interpretation of the data is straightforward once transitions are identified. The PFY and TEY modes of NEXAFS afford the opportunity to emphasize bulk or near surface region contributions to the spectra from which the information is extracted. Furthermore, there is potential to examine B coordination in glasses containing real waste, including radioactive constituents, by NEXAFS on ALS soft x-ray beamlines.

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Electronic and Geometric Structure of Pu Compounds: A High-Resolution Photoelectron Spectromicroscopy Study

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INTRODUCTION

There is a great need to study the interactions of Pu species with solid surfaces. Knowledge of these fundamental interactions is critical to the understanding of a variety of processes in the areas of environmental and nuclear materials, including sorption reactions of Pu species from solution onto mineral grain surfaces in an environmental setting; interactions of Pu compounds in waste and process streams with contacting surfaces; and surface reactions of Pu at phase boundaries in actinide materials systems. Furthermore, studies of these reactions will allow us to extend the understanding of the chemistry in these strongly f-electron dominated systems. This is critical, as it is one of the unique challenges in chemistry and materials science at our national laboratories, as exemplified by the greater than \$25M annual budget of the nuclear waste programs at Los Alamos National Laboratory.

These experiments described below investigated the oxidation states of plutonium in molecular solids using photoelectron spectroscopy and the interactions of these molecular compounds with well characterized model environmental surfaces. Chemical shifts in photoemission spectra have long been used to identify the oxidation states of atoms in chemical compounds. Very simply, these chemical shifts depend upon the amount of charge transfer between the emitting atom and its ligands. Lower oxidation states have smaller chemical shifts than do higher oxidation states with respect to the neutral atom. Determination of the oxidation state of an actinide can be made by measuring the chemical shift of the photopeaks from an actinide compound and comparing the shifts to appropriate standards. Unfortunately, a detailed tabulation of chemical shifts is presently not available for the actinides. Our first measurements at the Spectromicroscopy Facility at Beam Line 7.0.1 involved the measurement Pu in oxidation states of III, IV, V, and VI. Core Level and Valence Band Photoemission spectra were measured to probe the occupied electronic structure of the f electrons in plutonium. Pu 5d NEXAFS spectra were also collected in order to study the unoccupied 5f electrons of Pu. Core Level photoemission spectra were taken from the constituents of the ligands.

The sorption of actinides on to silica and brucite was also studied using photoelectron spectroscopy. Oxidation states of the adsorbed actinide compounds will be determined by comparison of the observed chemical shifts with those from the standards described above. In the determination of oxidation state, photoelectron spectroscopy has a clear advantage over near edge X-ray absorption fine structures spectroscopy (NEXAFS) measurements performed with hard X-rays. The features assigned to different oxidation states of the same element often overlap in NEXAFS spectra making determination difficult, while the chemical shift information in photoemission spectra is usually easily resolved. This feature of the photoemission spectra will allow us to determine if Pu species adsorb in multiple oxidation states or in a single favored oxidation state.

RESULTS

Pu 4f core level spectra were collected from various Pu molecular compounds with Pu in oxidation states ranging from III to VI. There were some difficulties with differential charging as these

Figure 1: The Pu 4f core level spectrum from plutonium(VI) hydroxide is shown. This spectra was decomposed into 3 spin-orbit split components. The two components at binding energies of 417 and 419 eV indicated that two chemical states of plutonium were present. The third doublet at a binding energy of 428 eV is a satellite state known to occur whenever the plutonium(IV) state is measured.

samples were non-uniform pressed powders. We will only show here spectra (Figure 1) collected from Pu(VI)OH crystallized at a pH of 9. Three components were observed in the spectrum. A satellite structure characteristic of Pu(IV) was observed. The Pu 4f spectra did not change as a function of time and as such did not suffer from beam related damage. This indicates that during shipment some fraction of the samples was converted into Pu(IV).

These spectra were deconvolved using 2 Doniac-Sunjic lineshapes and with a Gaussian component representing the satellite. The average FWHM of the peaks was 1.33 eV. To our knowledge, these are the sharpest core level spectra observed for Pu compounds. These spectral lines were about half the width of peaks typically measured in an XPS system at Los Alamos National Laboratory. These spectra then allow us to estimate the natural linewidth of the Pu 4f core level.

Pu 4f core level spectra were collected from Pu sorbed onto silica, brucite, and MgO from solutions containing Pu(III to VI). This data is not shown here. The data suggests that Pu may sorb into a preferred oxidation state.

Figure 2: Resonant Photoemission data from Pu(VI) sorbed on SiO₂.

Resonant photoemission spectra were collected of the 5d-5f resonant transition from the above materials. This transition allowed us to directly measure the 5f density of states in the valence band. Resonant photoemission data from Pu (VI) sorbed on silica is shown in Figure 2.

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Electronic and Geometric Structure of Pu Metal: A High-Resolution Photoelectron Spectromicroscopy Study

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INTRODUCTION

The physical characteristics of any given material are largely derived from the behavior of its valence electrons. Valence electrons are the lowest energy electrons in a material and are responsible for the formation of chemical bonds. Typically, in a metal, electrons are either localized around a particular atom or are delocalized (i.e. shared by all the atoms in the crystal) throughout the entire metal. The actinide series is interesting because as the atomic number increases across the series, the electrons in the actinide metals transition from delocalized 5f electrons (Ac–Pu) to localized 5f electrons (Pu–No). Plutonium (element 94) is located right at this transition. This placement in the series leads to plutonium metal being one of the most complex materials known. Metallic plutonium displays six allotropic phases (α , β , γ , δ , δ' , and ϵ) at standard pressure. A 20% volume expansion occurs during the change from the α phase to the δ phase. These physical properties have been attributed to the 5f valence electrons changing from delocalized states to localized states as the crystal structure changes from the α to the δ phase.

Soft x-ray techniques (photon energy in the range of 10–1000 eV) such as photoelectron; x-ray emission; and near-edge, x-ray absorption spectroscopies have been used to determine the electronic structure of many (in fact most) materials. However, these techniques have not been fully utilized on the actinides. The safety issues involved in handling the actinides make it necessary to minimize the amount of radioactive materials used in the measurements. To our knowledge, the only synchrotron radiation source in the world where soft x-ray measurements have been performed on plutonium is the Spectromicroscopy Facility at Beam Line 7.0.1 at the Advanced Light Source (ALS).

The Spectromicroscopy Facility is designed so that measurements can be made on small quantities of hazardous material. This facility has a photon flux of 10^{13} photon/sec at a photon energy of 100 eV with 0.01 eV resolution. The high photon flux allows one to focus the beam down to a size of 50 microns and still have enough light intensity at the sample for measurements to be conducted in a reasonable time frame 1–10 minutes per spectrum. Therefore, the sample size can be on the order of 100 microns in diameter. This greatly minimizes the amount of plutonium on site during the experiment.

RESULTS

We performed core-level photoemission, valence band photoemission, and near-edge x-ray absorption spectroscopy on both polycrystalline α -plutonium and δ -plutonium microcrystals. Only the photoemission experiments will be described here. Photoelectron spectroscopy is predicated upon the photoelectric effect first described by Einstein in 1905. An incident photon is absorbed by an atom in the solid, and an electron is ejected. An electron energy analyzer is used to measure the direction and kinetic energy of the emitted electron. The kinetic energy of the photoelectron is directly related to its binding energy in the solid.

Figure 1 shows the Pu 4f core-level photoemission spectra from the α - and δ -plutonium samples.

Figure 1: Core-level photoemission spectra from a large crystallite δ -plutonium sample and a polycrystalline α -plutonium sample are shown. These spectra were collected with a photon energy of 850 eV and an analyzer pass energy of 6 eV. Note that two large components are visible in each spectrum, a sharp feature at low binding energy and a broad feature at higher binding energy.

The spectrum arising from core-level photoemission is sensitive to energy differences in the initial state (no core hole) and the final state (core hole and free photoelectron). The two core-level spectra in Figure 1 are similar in that they both show two features, a sharp feature at low binding energy and a broad feature at higher binding energy. The low-binding-energy feature can be ascribed to a metallic initial state with a delocalized final state. As the 5f electrons are more delocalized in the α - than in the δ -plutonium, the greater number of delocalized electrons in the α -plutonium leads to greater intensity in this peak than the δ -plutonium.

Presently, the higher-binding-energy feature is not completely understood. It is likely that this feature has two states contributing to it. We believe that, in simplistic forms, one possible component contributing to the feature is made up of emission to an electronic final state with localized 5f electrons. If this is the case, it suggests that both localized and delocalized 5f electrons are present in the α - and δ -plutonium phases. The second possible component of this feature is from an initial state that has been oxidized.

Valence band spectra show that a small amount of oxygen remains on the surface after the sample preparation. The binding energy of PuO_x is higher than that of the metal and would be expected to

Figure 2(a): The 5d–5f resonant photoemission spectrum with analyzer pass energy of 1 eV showing the 5f density of states in the valence band from a large crystallite δ -plutonium sample.

be seen around the position of the unknown high-binding-energy feature. A final determination of the exact nature of this high-binding-energy feature will shed light on the poorly understood valence electronic structure of plutonium, as well as on the presence of localized and delocalized 5f electrons in the different plutonium phases.

Our initial goal of the valence electronic structure measurements was to determine the density-of-states of the 5f valence electrons in α - and δ -plutonium. This experiment can be directly compared with electronic structure calculations performed by theoreticians. Figures 2(a and b) show the resonant photoemission spectra of the valence band from δ - and α -plutonium, respectively. In a resonant photoemission experiment, valence band photoemission spectra are collected as the photon energy is scanned through a core-level absorption edge. This can result in an enhancement of the emission from specific valence levels. In the case of plutonium, scanning the photon energy through the 5d absorption edge results in a resonant enhancement of the 5f valence emission. The 5d–5f resonant photoemission measurements in plutonium are a measurement of the 5f contribution to the valence density of states.

Two types of information are obtained in the resonant photoemission measurements that can greatly enhance the understanding of plutonium metal. Two-dimensional data slices can be taken in either the constant-photon-energy direction or the constant-binding-energy direction. Slices taken with a constant photon energy are the equivalent to standard photoemission spectra with the exception that specific valence states are emphasized. Different states turn on or become enhanced at different photon energies.

The data in Figures 2(a and b) show clear differences in the resonant photoemission spectra from the α - and δ -plutonium. This is most evident in the state at binding energy 0 eV. If this peak is followed as the photon energy is varied, one notices that in the δ -plutonium (Figure 2a) after 100 eV, the peak smoothly increased to a maximum and then smoothly decreased after the maximum was reached. In direct contrast, the α -plutonium (Figure 2b) showed oscillatory behavior after the ini-

Figure 2(b): The 5d-5f resonant photoemission spectrum with analyzer pass energy of 1 eV showing the 5f density of states in the valence band from a polycrystalline α -plutonium sample.

tial maximum was reached. Theoretical calculations of the resonant photoemission are currently ongoing to try to understand these differences.

A large theoretical effort has been undertaken to understand the plutonium data that we have collected. The next phase of the valence-band, electronic structure measurements will involve measuring the electron dispersion relation (band structure) of the valence electrons in δ -plutonium, and the data will be compared with theoretical calculations. The band structure can only be measured on a single crystal of a material, and it is imperative to have excellent crystals for the measurement. Future investigations will be based upon spin-resolving and photon-dichroic photoelectron spectroscopy. The photon-dichroic measurements include the variant magnetic x-ray linear dichroism.

The unique 5f valence electronic properties of plutonium metal cannot be explained by the typical one-electron calculations used to describe prototypical metals. Calculations on plutonium metal incorporate these properties into calculations in an ad hoc manner. We can measure these effects directly to further our understanding of one of the most complex materials known.

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Electronic Structure of Single Wall Carbon Nanotubes Studied by Resonant Inelastic X-Ray Scattering

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Carbon nanotubes have in recent years attracted increasing interest as a new modification of carbon, related to the fullerenes and graphite. Especially for single wall carbon nanotubes (SWNTs) interesting electronic properties have been predicted early on. [1] For these nanotubes, the electronic structure strongly depends on the chirality vector defining the type of nanotube: (n, n) tubes ("armchair" type) are predicted to be metallic, while (n, m) tubes with $n \neq m$ are wide-gap or narrow-gap semiconductors, depending on the particular m and n . If $2n+m$ or $n+2m$ is an integer multiple of 3, the SWNT is predicted to be a narrow-gap semiconductor with good room temperature conductivity.

This behaviour can be understood in a straightforward quantum confinement approach starting from the bandstructure for a single graphene sheet. Due to the boundary conditions for electron wavevectors, only a subset of states ('slice') in the graphene BZ will be allowed in a SWNT. [7]

Just as in graphite or a graphene sheet, where the metallicity stems from degenerate states at the K -point in the BZ (Fig. 1), the nanotube will only be metallic if the K -point is contained in the set of allowed states. For simple geometric reasons, this is always the case for (n, n) nanotubes, as shown in Fig. 2. Further BZ geometry reveals that for all other nanotubes, a slice can only cut through K if $2n+m$ or $n+2m$ is an integer multiple of 3. In nanotubes, however, the degenerate point is slightly shifted away from the K -point. As a result, the degenerate point can only be reached exactly in (n, n) SWNTs, for $(m, n-m)$ nanotubes the calculations show a gap of at least a few meV ("narrow-gap SWNTs"). [1]

For SWNTs to exhibit good conductivity at room temperature, filled and empty states close to E_F are necessary. As outlined above, these states are derived from states in the immediate vicinity of the K -point in the bandstructure for a vicinity of the K -point in graphite. Depending on the orientation and number of k -space slices, nanotube (even at T).

Fig. 1: Band structure of a single graphene sheet. Adapted from Ref. [13]. Please note that E_F is located at about -9 eV (-0.33 Hartrees) on the energy scale.

Fig. 2: Illustration of the slices through the 2-dimensional BZ of Graphene in order to find the SWNT states fulfilling the periodic boundary condition. Γ - and K -point are indicated by full circles, the degenerate point close to K is marked by an open circle. The rectangular Brillouin zones of the SWNTs and the slices (dashed lines) are shown. (a) SWNT of (n, n) "armchair" type. A slice will always cut through the degenerate point. (b) SWNT of $(n, 0)$ "zigzag" type. A slice can only cut through the K -point (and hence in the immediate vicinity of the degenerate point) if the BZ is cut into an integer multiple of 3 equal parts. Adapted from Ref. [1].

Only recently has it become possible to synthesize larger amounts of SWNTs with high purity and narrow distributions in the tube diameter [3], making more detailed experimental studies of the electronic structure as a function of tube size and/or chirality possible. Of particular interest is experimental evidence for the existence of SWNTs with electronic states close to E_f , as their presence in samples prepared in various ways has been a matter of debate. As we will demonstrate below, our results indicate that such SWNTs with high room temperature conductivity are present in our sample and that their electronic structure can be selectively probed.

We report on studies of SWNTs using soft x-ray emission (SXE) and resonant inelastic soft x-ray scattering (RIXS). In SXE, the fluorescent decay of a previously created core hole is monitored. In particular, transitions from occupied valence states to the unoccupied core state yield information on the density of states of the system under investigation. As a dipole transition to a localized core orbital is involved, only states with the appropriate symmetry character that are localized in the vicinity of the core orbital will contribute to the spectra. Hence, the spectra measure the local partial density of occupied states (occupied LPDOS). In RIXS, a closely related technique, additional information can be obtained on the wavevector of occupied electronic states, similar to angle resolved photoemission. [4, 5] Here, a core vacancy is created by selectively promoting the core electron into unoccupied states of a chosen energy. Under certain conditions, valence band electrons with the same wavevector as the excited electron will then contribute predominantly in the consecutive SXE process. [6] As a result, parts of the BZ can be probed selectively by variation of the excitation energy. Simply put, RIXS enhances those occupied states in the spectra that have the same crystal momentum as the excited electron.

Fig. 3: STM image from a free-standing sheet of buckypaper. The image size is 250 nm x 250 nm. The organization of individual SWNTs into microbundles and ropes can be seen. Individual SWNTs as typically 1.2 nm in diameter and show up as fine stripes. [8]

We have studied SWNTs in a disk of purified "buckypaper" [7], prepared as described by Rinzler *et al.* [3] The material is a paper-like felt, where SWNTs form microbundles which in turn form ropes. These ropes are randomly woven to form the felt. In Fig. 3 we present a scanning tunneling microscope image recorded on the intact buckypaper showing the organization of individual SWNTs into microbundles and ropes. [8] TEM analysis shows a narrow diameter distribution for the individual SWNTs strongly peaked at 1.2 nm. [3]

RIXS was performed at beamline 7.011 of the Advanced Light Source, Berkeley, using a grazing incidence Rowland spectrometer, employing a 5m grating with 400 lines/mm in first order and a 20 μ m entrance slit. In this configuration, the experimental resolution in the emission channel was determined to be about 0.7 eV. The resolution for RIXS excitation was 0.4 eV. SXE was excited by 3 keV electrons using a 10 μ m entrance slit but otherwise the same setup as for the RIXS spectra. Both techniques are bulk sensitive with an information depth of about 0.1 μ m.

The SXE spectra (not shown, see Ref. [7]) indicate that the valence band electronic structure of our sample is similar yet distinctly different from both graphite and C_{60} and cannot be interpreted as a superposition of the spectra from those materials.

For a more detailed analysis of the electronic states we now discuss the RIXS spectra. The excitation energies for the RIXS spectra are shown together with the absorption spectra of SWNTs, C_{60} and graphite in Fig. 4. For the raw RIXS data see Ref. [7]. Here, we present in Fig. 5 the RIXS spectra after subtraction of (1) the elastic peak due to diffuse reflection/recombination and (2) the k -unselective ("incoherent") contributions. [14, 15]

Fig. 4: Soft x-ray absorption of single wall carbon nanotubes (solid line), C_{60} (dashed line) and non-oriented graphite (dotted line). Vertical lines indicate excitation energies for RIXS spectra.

Fig. 5: (right) Resonant inelastic soft x-ray scattering spectra of single wall carbon nanotubes (solid line) and non-oriented graphite (dotted line). The excitation energies in eV are indicated at the respective spectra. The high energy excited spectra were obtained with 400 eV photon excitation (SWNTs) and 3 keV electron beam excitation (graphite). The incoherent contributions to the raw data have been subtracted, as well as a Voigt curve to account for the diffuse reflection/recombination (arrows). Features A and B arise due to states at the K -point in the BZ.

The different spectral features in the graphite RIXS have been assigned by Carlisle *et al.* [11] in a k -conservation framework in the single electron approximation. While the validity of the single electron approximation has been questioned by van Veenendaal and Carra [12], these excitonic effects do hardly affect the very lowest and very highest states at the K -point (labeled $P_{1,1}^+$ and $P_{1,1}^-$ in Fig. 1. As pointed out above, the states at the K -point are of particular interest for the electronic structure of SWNTs.

In the graphite RIXS spectrum excited at 285.0 eV, the broad emission feature at 270 eV emission energy labeled *B* is due to emission from the lowest two occupied bands at the K -point, corresponding to states around 13 eV below E_F in the bandstructure reproduced in Fig. 1. These states can be unambiguously assigned, as they are the only states in this binding energy range within the whole BZ. Preferential emission from the K -point is expected for this choice of excitation energy just at the absorption threshold (Fig. 4), as the core electron is promoted into the first available unoccupied states, which are at the K -point (see Fig. 1).

For the SWNT sample excited at 285.0 eV, we observe an emission feature of the same shape and at the same emission energy as in graphite. For the same reasons as in graphite, we assign this feature to emission from low energy states at the K -point. This is consistent with threshold excitation into the lowest unoccupied states, as those are always derived from states in the immediate vicinity of the K -point, as outlined above. We would like to point out that RIXS with threshold excitation probes selectively those SWNTs within the buckypaper which have their lowest unoccupied states as low in energy as possible, i.e. at E_F . Due to the finite width of the radiation used for excitation (0.4 eV) and the C 1s core level involved in the absorption transition (0.09 eV), we can not distinguish metallic and narrow-gap SWNTs, but wide gap SWNTs are easily discriminated against.

We now turn our attention to the highest energy RIXS feature labeled *A* in Fig. 5. This feature is located around 284.1 eV emission energy. For the spectra recorded using an excitation energy of 285.0 eV, this spectral feature is in the immediate vicinity of the intense peak due to diffuse reflection (subtracted at position of arrow, see Ref. [7]). For graphite, this feature has been assigned to emission from the highest occupied states, located at the K -point. For the SWNTs, we observe intensity in the RIXS spectrum at the same energy. For the same k -conservation reasons as in graphite, this feature can unambiguously be assigned to emission from states at the K -point. We can therefore directly observe those occupied states at E_F which are

degenerate (or quasi-degenerate) with the unoccupied states at K and which are responsible for the high room temperature conductivity of SWNTs with suitable (n, m) .

Emission from these states can be seen more clearly in the RIXS spectra when the excitation energy is increased to 285.5 eV, as the intense elastic peak is then further separated in energy. Comparing the spectra from the SWNTs and the graphite, we see that the emission feature is clearly visible in the SWNTs spectrum, but it is less intense than in graphite. This difference in intensity is due to the fact that at this energy, wide gap nanotubes can be excited as well. These nanotubes do not contribute to the high energy emission feature, as they have no occupied states close to E_F . When the excitation energy is further increased, more states within the BZ are probed according to the dispersion of the unoccupied bands. As a result, the spectra are not specific for the K -point anymore.

In conclusion, we have studied the electronic structure of SWNTs in "buckypaper". Using threshold excitation, we have selectively investigated SWNTs with *unoccupied* states in the immediate vicinity of E_F . Our RIXS studies show that these states correspond to states in the close neighborhood of the K -point in graphite. For these SWNTs, we find *occupied* states at or close to E_F at the K -point as well, in agreement with predictions from bandstructure calculations. These (quasi-)degenerate states are responsible for the good room temperature conductivity of metallic and narrow-gap SWNTs.

While we can directly access those states by RIXS spectroscopy, a quantitative determination of the amount of metallic tubes in the sample is not possible, as pure reference samples with just one (n, m) SWNT do not exist. However, a follow-up scanning tunnelling spectroscopy study [8] on the same buckypaper sample shows the fraction of metallic SWNTs in the sample to be $34 \pm 6\%$, which is in qualitative agreement with our RIXS data.

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Electronic Structure of Ti_xC_{60} Fullerides Studied by X-ray Emission Spectroscopy

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ABSTRACT

For metal-fullerene compounds, it has been found that metal atoms can be bonded to fullerenes, resulting in different structures.¹ Some of the alkali and alkaline-earth metal intercalated C_{60} compounds have shown the properties of superconductivity.² According to the estimation of the energetical calculations, based on the assumption of the ionic bonding, the stable metal- C_{60} compounds are only those with alkali and alkaline-earth metals, or mercury.³ However, several studies have shown some evidences that transition-metal fulleride can be formed.⁴⁻⁶ The results suggest that the bond in this compound is covalent-like with a partial charge transfer from Ti to C_{60} . No detailed information of the exact bond nature was obtained in those studies and the further studies with complementary techniques are required.

In this work we present the results from $\text{C K}\alpha$ x-ray emission of Ti_xC_{60} . Our results demonstrate that the combined measurements of absorption and emission spectra can be used to provide electronic structure information of molecules. The information is element specific and selective and so is useful for the study of hybridization and bonding. This method has been successfully employed for the electronic structure analysis of fullerenes.^{7,8}

The samples were made by co-evaporation of C_{60} and titanium from a Knudsen-type effusion cell and an e-beam evaporator, respectively. Films deposited in an ultrahigh vacuum growth chamber. After co-evaporation, a vanadium capping layer ($\sim 500\text{\AA}$) was deposited on the surface of the sample to protect it from oxidation during the delivery for XES measurement. The preparation and characterisation of the films have been described in detailed in Ref. 6.

XES experiments were performed at beamline 7.0. A grazing incident soft x-ray fluorescence spectrometer (Grace) was used to measure the x-ray emission spectra.⁹ Figure 1 displays non-resonant (a) and resonant (b) XES spectra of Ti_xC_{60} and C_{60} films with the excitation energy of 300 eV and 284.5 eV, respectively. The spectrum from the $\text{Ti}_{2.1}\text{C}_{60}$ sample exhibits a similar profile with respect to the energy position and intensity distribution of the pure C_{60} emission bands. The one for $\text{Ti}_{3.6}\text{C}_{60}$ presents the same linewidth as to pure C_{60} with respect to the total emission band, but the sub-band structures are smeared out. The emission band E_3 for $\text{Ti}_{3.6}\text{C}_{60}$ has a small shift towards to lower photon energy, showed in Fig. 1 (a).

With 284.5 eV photon excitation, resonant XES spectra of Ti_xC_{60} and pure C_{60} were obtained and shown in Fig. 1 (b). A sharper peak of the emission at 284.5 eV, marked as e , appears due to the processes of atomic recombination and diffuse scattering. Five distinguishable emission bands are resolved in the resonant XES spectrum of C_{60} . According to *ab initio* Hartree-Fock frozen orbital model calculations,¹⁰ the first emission band E_1 corresponds to the highest occupied molecular orbital of C_{60} with the $4h_u$ symmetry, while the second band E_2 represents a combination of the nearly degenerate $4g_g$ and $7h_g$ orbitals of C_{60} . Bands E_3 and E_4 contain more

complicated molecular orbital combinations, in which are included three h_g , three g_u , one h_u , one g_g , one a_g , and one t_{1u} states. Band E_5 contains the $2h_u$, $3t_{1u}$ and $2g_g$ orbitals of C_{60} . The resonant XES spectrum of $Ti_{2.1}C_{60}$ shows similar spectral profiles of these emission bands to the one of the pure C_{60} . Some intensity variations, compared with pure C_{60} , were observed for the bands E_1 , E_2 , and E_5 . The observed variations of the intensities for these emission bands upon the excitation energy in the case of pure C_{60} , has been assigned as a result of symmetry selectivity and parity conservation of the resonant inelastic x-ray scattering process.^{10,11} The spectrum from $Ti_{2.1}C_{60}$ sample shows a decrease in intensity of the emission bands E_1 and E_5 , which may indicate that the formation of a new compound phase reduces the symmetry. With the increase of titanium content, the structures for these bands are smeared out and the intensity of E_5 band was further decreased in the resonant spectrum of $Ti_{3.6}C_{60}$.

Figure 1 (a) $C K\alpha$ non-resonant XES spectra of Ti_xC_{60} and C_{60} films, excited by the photons with the energy of 300 eV. (b) $C K\alpha$ resonant XES spectra of Ti_xC_{60} and C_{60} films, excited by the photons with the energy of 284.5 eV.

Figure 2. $C K\alpha$ resonant inelastic x-ray scattering spectra of Ti_xC_{60} and C_{60} films with the excitation energy of 282.7 eV. The spectra are smoothed using a binomial method.

Figure 2 shows XES spectra structure of Ti_xC_{60} and C_{60} films with detuning the excitation energy to 282.7 eV (at 1.8 eV below the C/s absorption threshold). For the $Ti_{2.1}C_{60}$ sample, at 272.8 eV, the peak has decreased obviously and is smeared out in $Ti_{3.6}C_{60}$, indicating Ti atom has bonded with carbon atom of C_{60} . Whereas the emission intensity of the peak from pure C_{60} has been almost depleted for both samples. Only a weak peak can be observed for $Ti_{2.1}C_{60}$ and $Ti_{3.6}C_{60}$ at the same energy position as the peak of pure C_{60} (272.8 eV). Also the intensity of this C_{60} characteristic peak decreases as the titanium concentration increases. Thus, one can attribute the structures in the spectrum of $Ti_{2.1}C_{60}$ film to the formation of the chemical bonding between Ti and C_{60} cage. These features also existed the spectrum of $Ti_{3.6}C_{60}$ film but it is broadened at 278.5 eV, which reveals the tendency towards titanium carbide, *i.e.*, C_{60} cage may start to be broken at this concentration of titanium.

The C $K\alpha$ x-ray emission spectra of the Ti_xC_{60} films show the same total emission bandwidth as that from the pure C_{60} sample. Resonant and non-resonant XES spectra of the $Ti_{2.1}C_{60}$ film exhibit an x-ray spectral shape similar to pure C_{60} , while the spectra of $Ti_{3.6}C_{60}$ film show some amount of contribution from the titanium carbide phase. All the experimental results indicate that a titanium fulleride is formed in the co-evaporation process of C_{60} and titanium, although some evidences for titanium carbide formation was obviously observed for $Ti_{3.6}C_{60}$ film.

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Energy-scanned Photoelectron Diffraction Determination of the Structure of Oxygen on Cu{100} at Low Coverage

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INTRODUCTION

The presence of atomic adsorbates above a critical coverage leads to the reconstruction of many common transition metal surfaces. To gain an understanding of the driving force of such reconstructions it is informative to study the atomic adsorption site prior to the reconstruction. For example, using energy-scanned photoelectron diffraction (PhD) recorded at the ALS we have previously determined the local adsorption site of C on Ni{100} at low coverage (0.15 ML) and in the clock-reconstructed (2x2)p4g phase. The results show that the reconstruction is not driven by expansion strain as previously suggested, but rather the structural data imply that the reconstruction is caused by the relief of C-induced Ni-Ni repulsions [1].

In this report we detail the preliminary results of a quantitative structural study of O on Cu{100} at a coverage of 0.1 ML. At higher O coverages the surface undergoes a missing row reconstruction to give, at a coverage of 0.5 ML, a ($\sqrt{2} \times \sqrt{2}$)R45° structure. In the reconstructed phase the O atoms are located at the former hollow sites next to the missing rows. There have been two STM studies of the phase prior to the reconstruction. In a study by Leibsle it was proposed that Cu-O-Cu rows were formed [2], while a later study by Fujita et al refuted this suggestion and claimed instead that the O atoms lay in 4-fold hollow sites in small c(2x2) domains consisting of about four O atoms [3].

To get quantitative structural information on atomic adsorption sites at very low coverage, when there is no long-range order, we use the technique of photoelectron diffraction in the scanned-energy mode (PhD). In PhD the intensity of an adsorbate core level photoemission peak, in this case O 1s, is measured as a function of kinetic energy in several different emission directions. Modulations in the intensity arise from interference between the directly emitted component of the photoelectron wavefield and components which are elastically scattered from neighbouring atoms. The modulations thus depend on the local environment of the adsorbate. By comparing the experimental modulations with the results of multiple-scattering simulations for model adsorbate geometries, quantitative structural information can be derived.

EXPERIMENT

The PhD measurements for 0.1 ML O on Cu{100} were performed at the UltraESCA endstation of beamline 7.0.1. The high flux and high spectral resolution provided by the ALS are essential to get an adequate signal-to-noise ratio when studying adsorbates at low coverage. Moreover, it is possible to measure emission at very grazing angles, up to 70° away from the surface normal, allowing backscattering from near-coplanar substrate atoms to be detected.

The Cu{100} crystal was cleaned by Ar ion bombardment and anneal cycles. The surface order and cleanliness were checked with LEED and soft X-ray (synchrotron radiation) photoelectron

spectroscopy respectively. The coverage of O was calibrated using the O 1s intensity assuming a coverage of 0.5 ML when a sharp, intense ($\sqrt{2} \times \sqrt{2}$)R45° LEED pattern was seen. PhD spectra were recorded at room temperature for a wide range of polar angles in the two principal azimuths of the surface. Each PhD spectrum consisted of 146 electron distribution curves (EDCs) centred about the O 1s photoemission peak. For successive EDCs the wavevector of the incident light was incremented by 0.05 from a starting value of 3.6 to an end value of 10.9. The O 1s photoemission peak thus covered the kinetic energy range 50 to 450 eV.

The intensity modulation functions were obtained from the raw data by integrating the EDCs and then normalising the resulting intensity versus kinetic energy curves using a spline function to model the non-diffractive intensity.

PRELIMINARY RESULTS

The first stage of data analysis involves applying the so-called projection method [4] to determine the approximate adsorption site. The projection method works by effectively picking out the dominating backscattering modulations and comparing these with single-scattering calculations for a substrate atom at different test sites on a 3-D grid below the emitter. The maxima in the projection method map shown in Fig. 1 correspond to the most likely positions of the backscattering substrate atoms. There are two possible interpretations of the projection method map. The four maxima could represent four surrounding Cu atoms for the O atom in a 4-fold hollow site. Alternatively the maxima could represent the Cu atoms of Cu-O-Cu added rows which have a random distribution along the [001] and [010] directions.

Figure 1. Projection method map showing the likely positions of the nearest neighbour backscattering atoms for a horizontal cut 0.49 Å below the O atom which is at (0,0,0).

The second stage of data analysis involves comparing the experimental modulation functions to the results of multiple-scattering simulations for trial adsorbate structures. The PhD data (the full lines in Fig. 2) show strong modulations at 60° and 70° off-normal which implies backscattering from near-coplanar surrounding Cu atoms. If the O atoms are at a well-defined height low in 4-fold hollow sites then, at normal emission, there should be significant backscattering from the second layer Cu atom directly below the O atom. The normal emission spectrum, however, shows only weak modulations. One possibility is that there is static or dynamic disorder perpendicular to the surface which dampens the normal emission modulations. Assuming there is only one adsorption geometry for the O atom in the 4-fold hollow site, a good fit between experiment and theory (giving an R-factor of 0.21) can only be obtained if the O atom is given a large perpendicular vibration. A slightly better fit (with an R-factor of 0.19) is obtained without the need for an unusually large perpendicular vibration by assuming that there are two possible adsorption geometries for the O atoms in the 4-fold hollow sites. In one of the adsorption sites the O atom is located 0.65 Å above the surrounding four first layer Cu atoms which are moved down by 0.13 Å relative to the other first layer atoms. The second layer Cu atom directly below the O atom is moved up by 0.3 Å. In the second geometry the O atom is only 0.49 Å above the four surrounding first layer Cu atoms. In this case the surrounding first

layer Cu atoms are moved down by 0.13 Å while the second layer atom below is moved up by 0.23 Å. A comparison between the experimental modulation functions and the simulations for the two-site model is shown in Fig. 2.

The multiple-scattering analysis of the data is still continuing. In particular the possibility of added Cu-O-Cu rows is being investigated. Also, a new more detailed analysis of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure is being undertaken to enable a suitable comparison to be made of the structural parameters before and after the reconstruction.

Figure 2. Comparison between the experimental O 1s modulation functions for 0.1 ML O on Cu{100} (full lines) and the simulation for the O atoms distributed in two geometries in the 4-fold hollow sites (dashed lines).

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Energy-scanned Photoelectron Diffraction Study of Pd{110}-(2x1)p2mg-CO

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Saturation coverage (1.0 ML) of CO on many common fcc (110) surfaces leads to a (2x1)-glide plane LEED pattern. In all cases the CO molecules are believed to be located along the top of the ridges with adjacent molecules tilted in alternate directions away from the close-packed direction to minimise steric repulsion; it is this tilting which gives rise to the glide plane symmetry. The adsorption site of the CO on the ridges is dependent on the nature of the substrate. For example, on Pt{110} the CO molecules occupy atop sites while on Ni{110} the CO occupies 2-fold bridge sites. The adsorption site of CO in the (2x1)p2mg overlayer on Pd{110} has been the subject of some controversy. A quantitative LEED study found that the CO occupied the atop site [1]. This result was in disagreement with the accepted interpretation of vibrational data - the 2003 cm⁻¹ frequency of the C-O stretch had been taken to indicate a 2-fold bridge site [2]. Later work, including XPD [3] and theoretical calculations [4,5], strongly favoured the 2-fold short bridge site. An independent, fully quantitative investigation of the CO adsorption site has therefore been undertaken using the technique of energy-scanned photoelectron diffraction (PhD).

In PhD the intensity of an adsorbate core level photoemission peak is measured as a function of kinetic energy in the range 50-500 eV in a number of different emission directions. The kinetic energy dependence of the photoemission intensity results from coherent interference between the directly emitted component of the photoelectron wavefield and other components which have been elastically scattered at neighbouring atoms. Comparison of the experimental intensity-kinetic energy modulations with the results of multiple-scattering simulations allows the local structural environment of the emitter atom to be determined quantitatively.

In order to use PhD to study adsorbates on substrates such as Pd which have strong Auger features in the kinetic energy region scanned, it is essential to use high resolution, high flux synchrotron radiation sources such as the ALS. The high resolution is needed to effectively separate the adsorbate photoemission peak from the broader (fixed kinetic-energy) Auger peaks which pass through the background. All the PhD data in the current study were taken at the UltraESCA endstation of beamline 7.0.1. The Pd{110} crystal was cleaned by Ar sputtering and annealing to 720°C followed by exposure to 1x10⁻⁷ mbar of O₂ at 550°C for 5 minutes to remove residual carbon. The surface order and cleanliness were checked with LEED and soft X-ray (synchrotron radiation) photoelectron spectroscopy respectively. The crystal was cooled to -140°C and 4 L of CO was dosed to give saturation coverage and the required (2x1)p2mg LEED pattern. Even at the high resolution of this beamline the O 1s peak could not be resolved from the Pd 3p_{3/2} peak, so only C 1s PhD spectra were recorded. A total of thirteen C 1s PhD spectra were obtained covering a wide range of polar angles in the four principal azimuths of the surface. Each PhD spectrum consisted of 150 electron distribution curves (EDCs) centred about the C 1s photoemission peak. For each successive EDC the wavevector of the incident light was incremented by 0.044 from a starting value of 4.74 to an end value of 10.9. This gave a kinetic energy range of 85 to 450 eV for each PhD spectrum.

The individual EDCs of each PhD spectrum were integrated using a simple step-Gaussian function to fit the data. The high resolution provided by the ALS enabled the C 1s photoemission peak to be resolved and integrated as it passed over the broad Pd MNN Auger features at 240, 270 and 330 eV. The resulting peak intensity versus kinetic energy curve was normalised using a spline function to model the non-diffractive intensity and this gave the final modulation function. A representative selection of the modulation functions is shown in Fig. 1.

The data are currently being analysed by comparing the experimental modulation functions with the results of spherical-wave multiple-scattering calculations for different model adsorption geometries. It is planned to test all possible positions of the CO along the close-packed rows, not just the high symmetry atop and 2-fold bridge sites, to ensure that the true structure is found.

Figure 1. Modulation functions for C 1s photoemission from the (2x1)p2mg overlayer of CO on Pd{110}.

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***k*-Space Characterization of Electronic States in AlPdMn Icosahedral Quasicrystals**

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INTRODUCTION

Quasicrystals display near-perfect x-ray diffraction patterns, despite having an aperiodic crystalline order. Indeed, they display point-group rotational symmetries (5-fold, 8-fold, etc.) which are incompatible with long-range periodicity. In view of their intriguing symmetries and their (for a metallic alloy) unusual physical properties, these materials have received an enormous amount of theoretical and experimental attention since their discovery in 1984 by Schechtman et al.¹ Such has been the impact of these exotic materials that the very definition of crystallinity has recently been rewritten to include this family of alloys. An interesting aspect of quasicrystals is that their x-ray diffraction patterns, which sample the structure in reciprocal (momentum) space, retain the property of forbidden rotational symmetry combined with aperiodic translational order. Thus one might speculate that similar scattering of valence electrons occurs as well, leading to the formation of electronic bands. However, the response of the valence electrons to the unusual symmetry of the lattice is difficult to predict. Whether these states are localized, extended, or in a critical state between the two has yet to be resolved;² the best formalism for calculating their electronic states is still to be determined. In this study we use the well established method of angle-resolved photoemission to investigate the electronic states in quasicrystals with a view to determining whether they are localized or extended, i.e. free-electron-like. We clearly demonstrate the itinerant nature of the valence states in AlPdMn quasicrystals. Our results show that the electron states exhibit the symmetry and aperiodicity of the quasicrystals.

EXPERIMENT

Surface preparation of single-grain AlPdMn wafers, characterized with low energy electron diffraction (LEED) and core-level photoemission, followed the sputter/anneal procedure of Thiel et al. We believe our surfaces are quite close to the bulk in structure, a fact which was confirmed by comparing the stoichiometry and valence density of states between the as-prepared surfaces and surfaces prepared by cleaving. The LEED results were similar to those of Thiel et al.,³ and the core-level photoelectron diffraction patterns were identical to those presented by Aebi et al.⁴ Surface preparation and angle-resolved photoemission measurements were performed *in situ* at BL7.0 at the ALS, with combined instrumental energy resolution ~50 meV and with angular acceptance better than ~1.4 degrees. All measurements were obtained at room temperature. In our setup the sample's polar angle θ and azimuthal angle ϕ are varied, while the angle between the incident photon beam, the electron analyzer, and the sample's polar axis remain fixed.

We present three major conclusions from the energy- and angle-resolved photoemission results:

(1) Demonstration of quasicrystal bandstructure. Fig. 1(a) shows a series of angle-resolved photoemission spectra obtained at photon energy $h\nu=100.0$ eV. The lower spectrum, (thick solid line) obtained by averaging the angle-resolved spectra, simulates the total spectral density of states. The angle-resolved spectra in Fig. 1(a), deviate significantly from the integrated spectrum. Clear angular-dependent features occur in addition to the fixed integrated spectrum. To bring out these weaker features, we present in Fig. 1(b) the per cent deviation between the angle-resolved spectra and the fixed spectrum. Several groups of peaks are apparent. From the systematic shifts of these peaks with angle, we deduce that their binding energies exhibit dispersion with angle and thus with parallel electron momentum $k_{\parallel}$. To highlight this energy dispersion of the peaks in our data, we have plotted the data as an intensity map in Fig. 1(c). The states were plotted in the conventional bandmapping fashion as binding energy vs. electron momentum $k_{\parallel}=0.5124\sqrt{h\nu}\sin\theta$ parallel to the surface. It is quite clear that they display large bandwidths of up to 2 eV, which is on the order of bandwidths found commonly in metals. Thus we confirm the existence of electronic bands in i-AlPdMn.

Figure 1. (a) Valence band spectra as a function of angle q . The angle-averaged spectrum is shown below (darker line). (b) Relative deviation between the angle-resolved and -integrated spectra. (c) Intensity plot of the same data, plotted as Energy vs $k_{\parallel}$.

(2) Rotational Symmetry of the bands. A characterization of valence states in i-AlPdMn as a function of both azimuthal and polar angle demonstrates that they have 5-fold rotational symmetry. Figure 2 shows a polar intensity map, in which the radius is proportional to the polar angle θ , and where the angle in the images represents the azimuth angle ϕ . Fig. 2(a) shows raw data, which was acquired by fixing the electron energy to the Fermi edge, and rotating the sample through the ranges $-115^\circ < \phi < 115^\circ$ degrees and $\theta < 45^\circ$. (The intensity variation along the dashed line in Fig. 2(a) is the same as that at the Fermi edge in Fig. 1(a).) As the superimposed pentagon indicates, the data show a fivefold rotational symmetry, which is in agreement with the diffraction data for this quasicrystal orientation. The fivefold symmetry is already quite evident in the raw data, but fivefold symmetrization followed by smooth background subtraction (Fig. 2(b)) reduces experimental noise, and demonstrates the existence of sharply defined features in $k_{\parallel}$ -space. A stack of such plots for three different binding energies, the top one right at E_F (Figure 2(c)) reflects the observation, that the photoemission features have five-fold symmetry at all electron binding energies.

Figure 2. Constant-binding-energy surface (near the Fermi level) emission profile. (a) raw data; the pentagon indicates the 5-fold symmetry. Data along the dashed line in (a) is the same as the data along the Fermi level in Fig. 1. (b) symmetrized and background-subtracted data. (c) A sampling of data for three different binding energies; a total of 96 energy channels was acquired.

(3) Measurement of the Aperiodic Fermi Surface. The region around E_F encompasses the so-called pseudogap, which is thought to directly relate to the unusual physical properties of the quasicrystals. Detailed measurements of this energy surface in 3-dimensional k -space should provide great insight into the quasicrystal electronic properties, as well as provide a stringent test for theoretical models. By way of comparison, we first present such Fermi surface for a normal, periodic metal (Ag(100) surface) in Fig. 3(a). The lines represent the Brillouin zone boundaries as derived from the lattice constant of Ag and the known orientation of the crystal. That the Ag sp states near E_F obey the symmetry of the fcc reciprocal lattice is obvious, and the bright features with the shape of a truncated square correspond to the Fermi level crossings of the sp band. A similar set of data for i-AlPdMn is shown in Fig. 3(b) for a similar range of k values. The data are markedly different from crystalline Ag, in that no repetition of features along $k_{\perp}$ or $k_{\parallel}$ occurs. While there is an apparent symmetry of features around $k_{\perp}$, there is no repetition of features for larger values of $k_{\parallel}$.

In summary, we have observed a fivefold symmetric pattern of valence states in i-AlPdMn, which in itself demonstrates that these states feel the point symmetry of the quasicrystal. Clearly dispersing features in the valence level spectrum show that these states are bandlike in nature.

Figure 3. (a) The fermi surface of Ag(100), a normal, periodic crystal. Fermi-edge intensity is shown as a function of $k_{\perp}$ vs $k_{\parallel}$ (horizontal axis). (b) Fermi-edge data for i-AlPdMn quasicrystal, for a similar k -range as in (a).

and that these bands extend up to and beyond the quasigap. States near the Fermi edge exhibit a markedly different pattern in three-dimensional k -space from that observed in regular crystals, suggesting that the symmetry of valence level states is not only affected by the immediate atomic environment, but that they are also affected by the long range quasicrystalline atomic arrangement.

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Liquid Crystal Fluctuations Probed with Dynamic Soft X-ray Scattering

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INTRODUCTION

Robert Brown discovered the thermally driven motion of small particles in solution in 1828, and Albert Einstein provided a theoretical understanding of Brownian motion in 1905. The transverse coherence of lasers now allows us to measure reliably the Brownian motion of small particles in considerable detail, using dynamic laser light scattering. However, there are also interesting thermally driven motions of individual molecules and molecular fragments that are crucial to chemical reaction rates, catalysis, and biological function. How can we measure the molecular-scale motions of collective fluctuating systems? We cannot use laser-light scattering directly because the spatial resolution is set by the wavelength of the light, and the wavelength of visible light is much greater than the size of the molecules. However, to probe atomic- or molecular-length scales, we can in principle do the exact analogue of dynamic laser light scattering using hard or soft x-rays, assuming that sufficient coherent power is available. We report here on our initial efforts along these lines at the ALS.¹

Hard x-rays (at wavelengths near 1 Å) have recently been used to probe relatively slow (tenths of a second to hours) atomic motion.²⁻⁵ The measurement of fast (microsecond) molecular motion, however, requires more coherent photons than can be obtained at third-generation hard x-ray synchrotron sources. The available coherent flux of a hard or soft x-ray undulator is proportional to λ^2 . Given that the brightness of hard and soft x-ray undulators is comparable, one can in principle get 2000 times more coherent photons using 44 Å soft x-rays than from using 1 Å hard x-rays. The longer soft x-ray wavelengths can provide adequate spatial resolution to probe the molecular as opposed to the atomic length scale.

We have developed dynamic soft x-ray scattering and applied it to a relatively simple problem: measuring the layer fluctuations of freely suspended liquid-crystal films. We were able to achieve the same time resolution as with conventional laser-light scattering (about 1 microsecond) and 100 times better spatial resolution (44 vs. 6360 Å).

APPARATUS AND EXPERIMENTAL TECHNIQUE

A schematic of the scattering apparatus is shown in Fig. 1. Light from the 5 cm period undulator passes through the BL7 spherical grating monochromator, providing a beam with a resolving power of $E/\Delta E \sim 10^4$ and a coherent fraction $\sim 10^{-4}$. Light exiting the monochromator is spatially filtered using a two-pinhole spatial filter that selects one transverse mode. At a wavelength of ~ 4 nm, we achieve a coherent flux as high as 2×10^9 /sec, though this was reduced in later experiments due to the introduction of a multilayer mirror upstream of the spatial filter. This light is then Bragg-scattered off a free-standing liquid crystal film that had been prepared *in situ*. Light scattered off the sample and through a pinhole (I_1) is detected with a scintillator/phototube combination. The transmitted beam was also collected with a similar detector, and this provided a reference signal, I_0 .

Figure 1: Schematic of the scattering apparatus, including the 8 cm undulator, the BL12 VLS monochromator, the spatial filter, the sample and CCD detector.

EXPERIMENTAL RESULTS

The liquid-crystal films used in this experiment were heated into the smectic-A phase. In the smectic-A phase, the molecules organize into layers, and these layers of the crystal can "slide" back and forth easily relative to each other. Within a layer, the molecules are free to move in liquid-like fashion. If the incident beam is spatially coherent, the intensity of photons reflected will also fluctuate because of the thermally driven motions within the sample. Such fluctuations are normally measured in terms of a normalized intensity-intensity autocorrelation function. In our experiment, forming the ratio of the autocorrelation functions of the scattered to the transmitted photons allows us partially to normalize the correlated noise in the synchrotron beam. An example of such a ratio is shown in Fig. 2.

Figure 2: Normalized intensity autocorrelation function of 44 Å x-rays Bragg scattered from a free-standing smectic liquid crystal film, 40.8. The layer fluctuations are reflected by the hump for delay times less than 50 μ s.

By fitting such normalized functions to decaying exponential curves as shown in the figure, we determined the characteristic decay time of the layer fluctuations for a given film thickness. A

Figure 3: Characteristic decay time of the intensity autocorrelation function of light Bragg-scattered from five different free-standing smectic-A liquid crystal films as a function of film thickness.

plot of decay time vs. film thickness for the five crystal types studied shown in Fig. 3 exhibits an obvious linear relationship between delay time and film thickness. This linearity is in excellent agreement with the predictions of theoretical models and simple simulations.⁶ The product of the film thickness and the layer sliding viscosity divided by twice the surface tension gives the slope of each line. The fluctuations are thus related to 'drumhead modes' wherein the entire film fluctuates without compression of the layers. To probe the layer fluctuations will require off-Bragg scattering where presently we cannot operate due to insufficient signal. With future access to the raw undulator beam on Beamline 9.0.1 (unfiltered by a monochromator and not subject to losses from optical components), the available coherent flux will increase by 1000. In this case, we should have enough signal to measure the layer fluctuations themselves.

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Mechanisms of Electron Transfer to and Fe(II) Dissolution From Montmorillonite Clay Minerals

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Clay minerals are an environmentally important class of minerals known to play a central role in a variety of geochemical reactions. The most important particles from the standpoint of soil chemistry are approximately 1 μm in size. Substitutional iron atoms can alter the activity of these small clay particles. Although clays contain substitutional iron in the interior octahedral layers of the particle, they are known to be redox labile and can be readily and reversibly converted from Fe(III) to Fe(II) (eg. Stucki, et al., 1995). Once it has been reduced to Fe(II), structural iron in the octahedral layer of montmorillonite is easily removed from the mineral. Fe(II) is preferentially removed with respect to Fe(III) from montmorillonite under mildly acidic conditions (Grundl and Reese, 1997) or in the presence of organic ligands (Kostka, et al., submitted). A rise in pH causes a "green rust" like coating to precipitate. Green rust is another highly active compound that is known to play a role in the reduction of certain organic pollutants (Erbs et al., 1999, Haderlein and Pecher, 1998).

Our research conducted to date has concentrated on demonstrating the usefulness of Scanning Transmission X-Ray Microscopy (STXM) and X-ray Absorption Near Edge Spectroscopy (XANES) to better understand the process of Fe(II) dissolution out of montmorillonite and the subsequent precipitation as a mixed valent green-rust like coating. Soft x-ray absorption spectroscopy has been chosen because the rich L-edge fine structure of 3d transition metals provides information about the oxidation state, site symmetry, spin state, and crystal field splitting of the metal ions (Cressey et al., 1993). In addition, STXM opens up the possibility to study small particles in their wet fully hydrated states, which becomes especially important for layered compounds like clays or green rusts.

The samples investigated originated from a series of electro-osmotic experiments in which a low voltage electric field was applied to a montmorillonite sample. The resulting direct current flow of electricity is carried by cations in the interstitial water of the clay that, in turn, forces water to flow from anode to cathode. The voltages used are sufficient to electrolyze water, generating H^+ at the anode (the upstream electrode) and OH^- at the cathode (the downstream electrode). A low pH front caused by anodically generated H^+ ions migrates through the clay. Bulk chemical analyses indicate that Fe(II) originally in the clay is selectively leached by the low pH front, travels downstream and is precipitated near the cathode where the pH abruptly rises. In the precipitation zone, the clay turns a deep green color, suggestive of mixed valent iron precipitate. All samples were prepared and kept under strict anoxic conditions in a glovebox and transferred to the beamline without any contact to air oxygen.

Chemical analyses indicate that the original clay (41-B) contains approximately 32,000 ppm Fe (tot), of which 3900 ppm is Fe(II). The clay in the anodic zone (41-A) is slightly depleted in both Fe(tot) (approximately 26,000 ppm) and Fe(II) (1000 to 3100 ppm). The green precipitation zone (41-G), which is quite small with respect to the anodic zone, is enriched in Fe(tot) (40,500 ppm) and highly enriched in Fe(II) (14,200 ppm). This thin green, Fe(II)-rich zone that occurs exactly at an abrupt rise in the pH is presumed to be a zone where chemical conditions would strongly favor the formation of green rust-like coatings around clay particles. XANES, STXM

and X-ray Photoelectron Spectroscopy (XPS) experiments were performed on all three of these samples in order to corroborate the presence of a mixed valence iron coating and to study the distribution of oxidation states of iron within the precipitates and the clays. XANES spectra were obtained using total electron yield sample to ground measurements (TEY-XANES).

TEY-XANES of the original clay (41-B) and clay from the anodic zone (41-A) are essentially the same (Fig. 1) except 41-B shows a much higher signal to noise ratio compared to 41-A, probably because of less charging. The slight depletion in Fe(tot) of 41-A relative to 41-B may account for that. The equivalence of spectral features of both samples gives preliminary evidence that there is no pronounced preferential mobilization of a single charge state of iron from the probed overall sample depth of approximately 100 Å of the clay surrounding the anode. Thus, the mobilized Fe(II) which accumulates on 41-G may originate either from a very thin surface layer (<10 Å) or inner bulk structures of the clay particles, the latter of which would not have been probed by TEY-XANES and the former might have been diluted by the overall probing depth (~100 Å). Because of the poor signal to noise ratio we also cannot rule out that some of the mobilized iron(II) may come from the top 100 Å layer involving a bigger mobilization area within the electro-osmotic cell than was sampled. Figure 2 shows a second set of TEY-XANES spectra and the associated difference spectra of 41-B and clay from the precipitation zone (41-G). It is clear that 41-G has a stronger iron signal (white line intensity) and a strong contribution from a Fe(II)/Fe(III) component. The signal is indicative of surface accumulation of a mixed valent iron species, the signature of which could not unequivocally be assigned to a green rust compound. Both of these results are in agreement with the chemical data and could be reproduced by independent measurements on different days.

STXM differs from XANES in that it is a transmission technique and bulk composition of single grains or even profiles across single grains can be investigated within the spatial resolution limit of the instrument (~100 nm). Sample preparation follows the description given in Rothe et al. (1999). The reference clay sample obviously contains particles which almost exclusively contain iron in the 2+ charge

Figure 1. TEY-XANES of the original clay 41-B (reference sample) and clay 41-A (anodic zone).

Figure 2. TEY-XANES of the original clay 41-B (reference sample) and clay 41-G (cathodic zone) (a) and difference spectrum of both samples (b).

Figure 3. STXM image at the Fe L_{III} -edge of sample 41-B and XANES taken at different positions (1-6)

state (labeled 1 and 2 in Fig. 3) and others that are completely oxidized (labeled 3, 5, and 6 in Fig. 3). Both charge states of iron seem to be inhomogeneously distributed among all clay particles. The capability of detecting grain-to-grain variability is not possible using more standard techniques such as X-ray diffraction or bulk chemical testing and also gives complementary information to spatially averaged TEY-XANES. In general, 41-G (Fig. 5) shows more Fe(II) character than 41-A (Fig. 4), as expected from bulk chemical results. The bulk structure of 41-A seems to be depleted of Fe(II) which gives strong evidence that some of the iron accumulating on 41-G is from the bulk structure ($> 100 \text{ \AA}$ depth) of the original clay surrounding the anode. The spectral signature of Fe(II) containing grains of 41-G is completely different than the spectral features of Fe(II) containing particles of sample 41-B and is pointing more to a superposition of both valence states of iron. Again, STXM does show a certain amount of grain-to-grain variability in these samples. We also found clay particles in 41-G with Fe(III) as the dominant iron species (labeled 15, 16 in Fig. 5). In order to verify homogeneity of single particles with respect to iron charge state distribution, spectra were taken at the resolution limit along transects across single clay particles (indicated with a white line in Fig. 5). This technique did not work in these samples because the iron content within a given area at the resolution limit is too low and the spectra became noise limited. Future STXM experiments are planned on bacterially reduced clays that contain approximately 17% (170,000 ppm) iron and we hope to overcome this problem.

The most surface sensitive technique, XPS, has been applied as well. Experimental problems having to do with particle charging effects have been solved by changing sample preparation techniques. We are expecting useful information about surface iron composition soon.

Figure 4. XANES taken from different clay particles of a STXM stack of sample 41-A.

Figure 5. STXM image of sample 41-G and XANES taken at different positions (labeled with numbers)

From the research outlined above, we can draw the following conclusions and define directions for further research.

- Grain to grain differences are something that can be uniquely detected by this method. Grain to grain differences have also been found for Mn-nodules, green rusts, and magnetite.
- TEY-XANES spectra agree with chemistry and support the hypothesis that a green rust precipitate is coating the clay. An unequivocal identification of this coating using XANES is unlikely. Most Fe-oxide minerals (eg. goethite, hematite, lepidocrocite) yield largely the same spectra. If new XPS experimental techniques are successful, further information may be obtained about the surface coating.
- Upcoming work with reduced clays will allow the comparison of surface iron vs structural iron in these clays. These reduced clays contain much more Fe(II) than the current samples and will not be a subject to noise limitations. In addition, the Fe(II) is contained within the structural lattice of the clay and as such should yield distinctly different information from the current samples with surface iron.
- Comparison of these results to earlier test runs of the same samples has proven that our protocols for the strict anaerobic handling of these samples is essential to the study of iron valence states in clays.

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On the magnetic instability of ultrathin fcc $\text{Fe}_x\text{Ni}_{1-x}$ films

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The 'invar effect' in $\text{Fe}_x\text{Ni}_{1-x}$ alloys occurs when the Fe content approaches 65%. At this point, the magnetization falls to zero, and a martensitic structural transformation from a fcc to a bcc lattice occurs. This paper addresses the question: "What happens if this structural transformation is suppressed in an ultrathin alloy film?"

In the bulk, $\text{Fe}_x\text{Ni}_{1-x}$ alloys show anomalous behavior at a Fe content of ~65%, which is usually referred to as the 'invar effect'[1]. It has been observed that the structure changes from the fcc into the bcc phase as the Fe content increases. Simultaneously the Curie temperature T_c and the magnetic moment collapse[1]. The question arises to what extent the magnetic properties are modified if the fcc phase stability is extended beyond 65% Fe. From a theoretical point of view it is predicted that a moment collapse still takes place at a Fe content of 75%, which is accompanied by a reduction of the atomic volume of ~9% [2]. Experimentally an extended regime of fcc stability can be achieved via epitaxy on a Cu(100) substrate [3]. We report here on the correlation of the magnetic dichroism of the Fe 3p core level in photoemission with linearly polarized light (LMDAD) to the atomic volume[4]. In particular we focus on the thickness dependence for Fe concentrations around 75%.

Details of sample preparation can be found elsewhere[3]. The dichroism experiments were performed at the SpectroMicroscopy Facility on Beamline 7 at the Advanced Light Source, Berkeley [5]. For photoemission of the 3p core levels we utilized 190 eV photons (p-polarized) and collected electrons in normal emission more details have been published elsewhere[6]. We have demonstrated that LMDAD measures a quantity closely related to the element-specific magnetization[6]. In order to investigate the thickness dependence of the dichroism we did grow wedged shaped films with a typical slope of 2 ML/mm. We took then advantage of the small spot size (~50 nm) of the light. Growth, structural studies and SMOKE experiments have been performed with a different apparatus[7, 8].

In fig.1 we show the photoemission and difference spectra of the Fe 3p level for a 2 ML and 9 ML $\text{Fe}_{75}\text{Ni}_{25}$ alloy film. We can clearly see a different magnetic contrast between the 9 ML and 2 ML thick film. The thicker film has a dichroism of about 2% whereas for the thinner film one obtains a value of 10%. As discussed previously we can rule out changes in the growth mode or a reduction of T_c as the cause[3, 6]. In fact RHEED studies have shown that the in-plane lattice constant contracts between 2 and 4 ML for $\text{Fe}_{80}\text{Ni}_{20}$ alloy films[3]. This suggests a structural driven effect. We therefore

Fig.1: Photoemission (a)+b)) and difference spectra (c)+d)) for $\text{Fe}_{75}\text{Ni}_{25}$ films. Spectra a) and b) have been scaled to give the same peak height. The difference spectrum c) has been multiplied by a factor of 5.

performed LEED I-V studies to determine the perpendicular lattice constant. In fig.2 we compare the LEED I-V curves of the beam averaged (1,1) spot for 2 ML and 6 ML thick $\text{Fe}_{87}\text{Ni}_{13}$ alloy films. We can clearly observe that the peaks for the 6 ML film are shifted towards higher energies. This means that the perpendicular lattice constant is reduced. Together with the results of the RHEED experiments we conclude that the atomic volume is reduced by $\sim 3\%$.

Fig.2: Comparison between LEED I-V curves of the (1,1) spot for a 2 ML and 6 ML thick $\text{Fe}_{87}\text{Ni}_{13}$ alloy film.

At this point it is important to stress that our films are not truly fcc, but tetragonal distorted. However up to this point we do not know how important the broken symmetry is. For example it is known for $\text{Fe}/\text{Cu}(100)$ that the ferromagnetic phase is tetragonal distorted [9], which is different from the $\text{Fe}/\text{Cu}(111)$ case in which ferromagnetism occurs in the isotropic fcc lattice [10].

In order to demonstrate that this is not a surface effect similar to 'magnetic live surface layers'[11] we show the thickness dependence of the SMOKE intensity for a $\text{Fe}_{87}\text{Ni}_{13}$ in fig.3. We can see that for 4-10 ML a linear increase of the SMOKE intensity is observed. Furthermore a linear curve through the data intercepts close to the origin. This means that the whole of the film is magnetic.

Fig.3: Thickness dependence of the SMOKE intensity for a $\text{Fe}_{87}\text{Ni}_{13}$ alloy film.

Abrikosov et al. have calculated that in bulk fcc $\text{Fe}_x\text{Ni}_{1-x}$ alloys a moment collapse still occurs accompanied by a reduction of the atomic volume[2]. However they predict variations of the order $\sim 9\%$, which is significantly smaller than our value of $\sim 3\%$. Our value is also smaller than the change observed for $\text{Fe}/\text{Cu}(100)$ [9]. Also in contrast with their calculation we do observe a ferromagnetic response in the form of hysteresis loops and magnetic dichroism.

It is now established that fcc $\text{Fe}/\text{Cu}(100)$ exists in two phases with different atomic volumes ; the larger volume refers to a ferromagnetic high spin (HS) state and the smaller to an antiferromagnetic low spin (LS) state[12, 13] in agreement with theory [14].

The results of Keavney et al. suggest that a coexistence of phases is a possibility. They observed that by increasing the lattice constant of the substrate the average moment increases from 0.3-2.0 m_B [13]. However they found that the hyperfine field is not systematically dependent on the lattice constant. They described this as a change in the population of two coexisting phases. We would like to point out that we are not able to detect any antiferromagnetic order. Therefore we can not rule out the coexistence of antiferromagnetism and ferromagnetism. Our results clearly show that additional magnetic phases other than a non-magnetic (NM) and high-spin ferromagnetic HS phases must exist for fcc $\text{Fe}_x\text{Ni}_{1-x}$ alloys. This follows from the observation of smaller changes in

the atomic volume as predicted by Abrikosov et al. In general the formation of a moment requires an increased atomic volume.

We have observed a close connection between the Fe 3p asymmetry and the atomic volume. The observed reduction of the atomic volume at ~60-80% Fe content is significantly smaller than predicted by Abrikosov et al[2].

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One dimensional metallic phase and Peierls instability of In linear chains on a Si(111) Surface

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Abstract

One dimensional (1D) metallic systems are important for their exotic physical properties and readily tractable theoretical models. Up to now, very few materials have been shown to have quasi-one dimensional properties. Recently, we found that the 4×1 In overlayer on the Si(111) surface, which forms a linear-chain structure, has 1D metallic bands and undergoes a metal-insulator phase transition at ~ 130 K [1]. The resulting ground state was shown to be a " 4×2 " phase with periodic doubling along the linear chains as shown in low-temperature STM and LEED/RHEED data [1]. This finding is thought to provide a completely new type of 1D Peierls systems composed of well-ordered metallic chains on a solid surface.

In order to verify that this phase transition is due to a Peierls instability, we have measured the Fermi contours and surface bandstructures in detail for the room temperature 4×1 phase. The experiments were conducted on the photoemission end station of the ALS undulator beam line 7.0.1. The Fermi contours obtained from the 4×1 phase (see figure) show three electron pockets centered on the X point of the surface Brillouin zone. One of these three bands crosses the Fermi level at the zone center (middle of the Γ -X line) and has a virtually ideal one-dimensional Fermi contour, which gives a perfect nesting condition for the $4 \times 1 \rightarrow 4 \times 2$ Peierls transition. Detailed discussion of the data including those from the preliminary low temperature measurements will be presented.

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Figure. Fermi level intensity map of the 4×1 reconstruction acquired at room temperature for part of the surface Brillouin zone (SBZ) (solid lines). Surface state crossings appear as light features. For comparison, the low-temperature 4×2 SBZ is also indicated (dashed lines).

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Oxidation of Mn(II) catalyzed by spore coats of a marine *Bacillus*, strain SG-1

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BACKGROUND

Manganese oxidation catalyzed by bacteria may lead to a different sequence of oxidation states, minerals, and rates when compared to non-biological manganese oxidation under the same conditions of temperature, Mn(II) concentration, and time. Manganese oxide and hydroxide minerals are very reactive and play an important role in the mobility and bioavailability of heavy metals and organic contaminants. Therefore, an understanding of the products and rates of manganese oxidation, by both biological and non-biological processes, is essential to interpret biogeochemical cycles, as well as to recognize biosignatures in rocks.

Manganese oxidation may proceed directly to Mn(IV) in a one-step, 2-electron transfer, or from Mn(II) to Mn(IV) in a 1-electron transfer, with Mn(III) intermediates. Laboratory experiments of abiotic manganese oxidation provide evidence for the first step of a 2-step oxidation, leading to the formation of Mn₃O₄ or MnOOH:^{1,2}

The Mn₃O₄ should theoretically disproportionate to MnO₂ over time:

but the disproportionation reaction mechanism has not yet been entirely demonstrated in the laboratory.

Laboratory experiments of bacterially catalyzed manganese oxidation by the marine *Bacillus* spore SG1, isolated from a manganese coating on a sandgrain from marine sediments³, have shown evidence for both 2-step and 1-step manganese oxidation. Hastings and Emerson observed the formation of Hausmannite (Mn₃O₄) which aged to MnO₂ during a time scale of weeks.⁴ Mandernack et al. found evidence for a 1-step, 2 electron oxidation.⁵ Their evidence was based on oxygen isotopic analysis, x-ray diffraction and oxidation state analysis.

There is also strong evidence that mineral oxide surfaces not only promote the sporulation of SG-1 spores⁶ but can also catalyze the oxidation of dissolved Mn(II) in a pure chemical reaction.^{7,8} It is therefore to be expected that a rather complicated interplay of biologically mediated and pure chemical reactions may lead to a very complex sequence of pathways and products being formed. For most of the biological and chemical experiments so far, analytical differentiation between involved chemical species has been carried out by indirect methods like titrations or operational

reduction of the oxides formed. Thus, all of these methods can give only an average oxidation state of the minerals and species present.

Our objective is to achieve a more complete understanding of reaction steps involved during oxidation of Mn(II) by oxygen, catalyzed by proteins in the spore coats. Because of its rich spectral signature, XANES (X-ray absorption near edge structure) at the Mn L-edge is particularly well suited to address this question. We were using TEY-XANES (total electron yield) and STXM (Scanning Transmission X-ray Microscope) on beam line 7.0.1 and XM-1 (X-ray microscope 1) on beam line 6.1.2 to analyze the spatial distribution of Mn charge states on spores of *Bacillus* SG-1 directly.

We chose to repeat one of the experiments of Mandernack et al in which one of the early oxidation products was the mineral birnessite, $[(\text{Na,Ca})\text{Mn}_7\text{O}_{14} \times 2\text{H}_2\text{O}]$. We synthesized a non-biological sample of birnessite to compare with the biological experiments.

METHODS

The birnessite mineral was synthesized by the method of McKenzie.⁹ The bacterial spores were grown and cleaned according to Rosson and Nealson.¹⁰ A solution of MnCl_2 (10mM) with 75% seawater and a HEPES buffer at pH 7.5 were inoculated with a thick suspension of spores ($\sim 10^{10}$ spores/mL). In the first experiment, the spores were allowed to react for 3 days and 6 days, and the suspensions were sampled directly at the STXM beamline. In the second experiment, samples were reacted for 1 day, 2 days and 5 days, washed, and frozen. These frozen samples were then thawed and sampled at the STXM beamline. Suspensions from all of the reactions showed a change in spore color from light to dark. Controls with no spores showed no evidence of manganese oxidation. Two μl of these suspensions were sandwiched between two Si_3N_4 wafers which were then fixed to aluminum sample holders. Details about sample preparation and the microscopic techniques used are given in Rothe et al.¹¹

RESULTS

Figure 1 shows a soft x-ray image of a wet spore sample, taken at the XM-1 (BL 6.1.2). The spore structure shows a dark interior, surrounded by a lighter region. Some dark irregular protrusions can be seen along the exterior of the light region. These protrusions were assumed to be Mn-precipitates. However, taking images at photon energies selective for Mn, we were unable to identify these structures as Mn-precipitates using XM-1.

Complementary to XM-1, stacks of images at different photon energies were taken with STXM to get better spectral information of expected Mn-coatings around spore cells. Figure 2 shows the results obtained from a 5 days old spore preparation. Surprisingly, Mn-precipitates found on different spore cells from one sample were not uniform but seemed to vary from spore to spore. A similar picture was found for a 2 days old preparation indicating that reaction kinetics are complex. Comparing the STXM XANES spectra to TEY-XANES spectra of

Figure 1. XM-1 image of SG-1 spores. Bar is 1 μm .

reference compounds (Fig. 3), we have found spectra which almost perfectly coincide with Mn(II) (spectrum #1 in Fig. 2) and Mn(IV) (spectrum #4 in Fig. 2). Although spectrum 1 (Fig. 2) seems to coincide pretty well with the TEY-XANES spectrum of MnF_3 (Fig. 3) we are not yet sure whether we are seeing a pure Mn(III) valence state. Theoretical calculations using a modified version of deGroot's atomic multiplet theory¹² have shown that the spectrum of Mn_2O_3 (Fig. 3) probably represents Mn(III) best. MnF_3 is a very reactive compound and may have been oxidized already to some degree at the surface of single grains. We are currently verifying a true Mn(III) reference sample by collecting spectra of high purity Mn_2O_3 and freshly synthesized manganite ($\gamma\text{-MnOOH}$).

Figure 2 STXM image of spore sample and XANES-spectra averaged over single spore cells as indicated

CONCLUSIONS

We have shown that STXM can be used to determine the average oxidation state of Mn precipitates on individual spore cells of size $\sim 1\ \mu\text{m}$. Spore structure was verified using XM-1. Oxidation was rapid, with Mn(IV) present on some spores within 2 days. This supports the argument for biological oxidation. Reasons for observed variations in oxidation states of attached Mn between single spore cells are manifold. Accessibility of outer spore cell membranes within the suspensions for Mn(II) and oxygen as well as spore dependent differences in membrane structure itself may account for the found heterogeneity. Because of uncertainty in our standards, we cannot decide yet that we were seeing a pure Mn(III) valence state. Spores or specific sites on spore coats (proteins) are probably initializing a sequence of adsorption and/or heterogeneous nucleation of Mn(II). The possibility of a stable Mn(III) intermediate implies that either chemical oxidation occurs simultaneously with the biological oxidation, that the biological oxidation occurs in 2 steps instead of one, or that some other process is reducing the Mn(IV) to Mn(III). Future experiments, with better controls, standards, and measurement of chemical changes with time, should help clarify these issues.

Figure 3. Mn $L_{2,3}$ TEY-XANES of reference compounds

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Oxygen K Emission spectra of Sr_2CuO_3

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INTRODUCTION

The fundamental physical properties of low-dimensional and correlated systems have attracted a lot of interest in recent years [1-3]. Ladder-type copper-oxide materials form an interesting class of compounds that combine one-dimensionality (1D) with electronic correlations. Experimentally, Sr_2CuO_3 is found to be the best realization of the quasi-1D spin-1/2 antiferromagnetic Heisenberg model.

Figure 1 shows the structure of the Cu-O chains in Sr_2CuO_3 . These chains are comprised of one copper and two inequivalent oxygen atoms denoted as O(1) and O(2). Chains of oxygen corner sharing CuO_4 plaquettes run along the b direction and the parallel Cu-O chains shift along the a direction.

Soft x-ray emission (SXE) spectroscopy with tunable excitation allows one to study occupied electronic structure of a specific atomic site in a compound [4]. In this work, we have recorded oxygen $K\alpha$ emission spectra of Sr_2CuO_3 in two arrangements (see Fig. 1) with various incident angles.

Figure 1. Structure of Cu-O chains in Sr_2CuO_3 . (A) $E // ac$ arrangement. (Perpendicular). (B) $E // bc$ arrangements. (Parallel). (C) Configuration of the O $2p$, p , and Cu $3d_{x^2-y^2}$ orbitals.

EXPERIMENTAL

The oxygen $K\alpha$ spectra of Sr_2CuO_3 single crystal were recorded using a high-resolution grazing incidence x-ray fluorescence spectrometer [5] at beamline 7.0. During the O $K\alpha$ SXE measurements, the resolution of the beamline was 0.5 eV and the resolution of the fluorescence spectrometer was set to 0.4 eV.

Two geometry of Sr_2CuO_3 were measured with various incident angle. In the arrangements, one is in the $E//ac$ arrangement in which the incident photon polarization E is in the ac plane and perpendicular to the chain (Fig. 1, (A)) and another is in the $E//bc$ arrangement in which E is in the ab plane and has a component parallel to the chain (Fig. 1, (B)). The incidence angle of the photon beam was about 20, 45, and 70 degrees to the sample surface, here incoming angle + outgoing angle = 90 deg.

Figure 2. The off resonance O $K\alpha$ soft-x-ray-emission spectra of Sr_2CuO_3 with various incident x-ray angles.

The experiments were performed at room temperature with a base pressure of 4×10^{-8} Torr in the experimental chamber. The clean surface was prepared by cleaving just before introduction into the vacuum chamber.

RESULTS

Figure 2 show the O $K\alpha$ SXE spectra of Sr_2CuO_3 in two arrangements with various incident x-ray angles. The energy of excitation was 9 eV above the O 1s threshold, with this excitation energy only O $2p \rightarrow \text{O } 1s$ transitions are possible and the spectra are regarded as excited off resonance. The intensities of the spectra are normalized to the peak maximum. Dashed and solid curves show the spectra in $E//ac$ and $E//bc$ arrangements, respectively.

The significant differences are observed in the O $K\alpha$ spectra recorded with incident angle of 20 deg. (outgoing angle of 70 deg.), at the high-energy side (526-529 eV) the $E//ac$ spectra have higher intensity than that of the $E//bc$ spectra. At off resonance condition with low incident angle (20 degrees), O $2p_z$ and $2p_x$ orbitals contribute mainly for the $E//ac$ and the $E//bc$ arrangements, respectively. Therefore, the O $K\alpha$ intensity around 526-528 eV is attributed to O $2p_z$ orbital which hybridized with Cu $3d_{yz}$ and d_{zx} orbitals.

At higher incident angle (70 degrees), no intensity difference around 526-528 eV between two arrangements is detected which is consistent with that the O $2p_y$ orbital can contribute for the both $E//ac$ and the $E//bc$ arrangements. The difference around 529 eV may be attributed to the Zhang-Rice singlet state which is the hybridized orbital O $2p_y$ with Cu $3d_{x^2-y^2}$.

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Particle Size Effect on the Electronic Structure of Metal Oxide thin films studied by X-ray Absorption Spectroscopy

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INTRODUCTION

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view considering the tremendous amount of high-tech applications of nanostructured metal oxide materials devices such as for instance dye sensitized solar cells, displays and smart windows, chemical and biosensors, lithium batteries, supercapacitors likewise magnetic materials, catalysts, optoelectronics and nanoscale semiconductor technology. Indeed, further improvement and optimization of such devices will be reached providing that better fundamental understanding of their unusual, fascinating and unique physical properties and electronic structure e.g. quantum confinement, surface states, electron tunneling will be available as well as a better matching between the materials design and the required device applications. From a fundamental approach, UHV techniques and core level spectroscopies such as XPS and XAS performed at synchrotron facilities make excellent tools to study the effect of particle size, morphology and film texture on the electronic structure of nanostructured materials.

BACKGROUND

One of the major parameter to assess is the interfacial free energy of the system in order to control the growth of the materials. A model, based on Gibbs adsorption equation attempt to quantify the variation of the water oxide interfacial tension with the chemical composition of the interface and the dispersion conditions [1]. Proton (or hydroxyl) ions surface adsorption do increase the surface charge density yielding to the lowering of the water-oxide interfacial tension of the system. At maximum surface charge density, i.e. when the surface is electrostatically saturated, the interfacial tension is decreasing sufficiently allowing the system to attain thermodynamic stability. Assuming a zero interfacial tension at equilibrium, a quantitative expression of the variation of the water oxide interface is obtained, yielding to the stability conditions of the system. In the stable area, limited by the PZIT (Point of Zero Interfacial Tension), the particles are stabilized and consequently secondary growth phenomenon such as Ostwald ripening is unlikely to occur. Therefore, the size of the particle is directly related to the precipitation conditions such as pH and ionic strength. The results on aqueous precipitation of magnetite (Fe_3O_4) has showed [2] that thermodynamic stability of nanoparticles may be achieved and that the average particle size may be monitored over an order of magnitude showing narrow size distribution. The excellent agreement between theoretical modeling and experiments yields strong evidence for general efficient growth control of metal oxide nanoparticles under low interfacial tension conditions and draws great expectations for future development of nanomaterials and optimization of their tremendous physical properties.

Recent model refinement and novel development for thin film processing [3] allow to design nanostructured thin films with controlled morphology, orientation and size of crystallites

[4] as well as the overall film texture of n-type semiconductor likewise metallic transition metal oxides such as TiO_2 , ZnO , Fe_2O_3 and RuO_2 thin films respectively on various substrate including polypropylene or Teflon FEP.

EXPERIMENTAL

XAS studies of size dependence on the electronic structure of metal oxide are reported here on TiO_2 material.

Sample 1 of nanostructured TiO_2 (nano 1) was prepared according to reference [5]. Typically, hydrolysis-condensation of Titanium tetraisopropoxide is carried out in acidic medium at room temperature, followed by hydrothermal treatment at 200°C yielding to monodisperse spheroidal colloid suspension of about 20 nm in diameter. Thin films were prepared from the concentrated colloidal dispersion spread out the F-SnO₂ conducting glass (Libbey Owens Ford 8 Ω /) using scotch tape as spacer yielding to thin films of about 5 μm in thickness.

The second sample (nano 2) was prepared by spin coating thermodynamically stable suspension of non-stoichiometric TiO_{2-x} clusters of about 1 nm in diameter.

Thin films were subsequently heat treated at 450°C in air for 30 minutes leading to well crystallize TiO_2 thin film with anatase as only detectable crystallographic phase by powder x-ray diffraction.

The soft x-ray absorption experiments were performed at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator covering the spectral energy range between 60-1300 eV [6]. XAS spectra were obtained in two detection mode: measuring the total electron yield (TEY) from the sample current and measuring the x-ray fluorescence yield (FY). The resolution of the monochromator was set to 0.50 eV for the O 1s absorption edges. The XAS spectra were normalized by means of the photocurrent from a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam.

RESULTS AND DISCUSSION

Figure 1 shows O 1s XAS spectra of nanostructured TiO_2 of various size likewise the typical polycrystalline TiO_2 XAS spectra (bottom spectrum). As one may notice, the spectra can be divided into two regions below and above the ionization threshold (~ 536 eV), respectively. In polycrystalline TiO_2 the first region is attributed to oxygen 2p, weight-hybridized in states of predominantly Ti 3d character [7-9]. The second, above the threshold, is attributed to oxygen p character hybridized with Ti 4s and 4p states [11]. It is concluded that the large-energy spread (some 15 eV) of oxygen 2p states is an indication of strong covalency in the TiO_2 compound.

In a purely ionic model, oxygen would have the configuration $1s^2 2s^2 2p^6$ and the $1s \rightarrow 2p$ channel would be closed in the x-ray absorption process. Covalency reduces the number of filled states with O 2p character, so that the strength of the O 1s signal at the threshold is related to the degree of covalency [10]. The decrease in intensity of the first-region bands, relative to the second-region bands is consistent with the observation in a O 1s XAS study going across the

transition-metal series [7]. The dominant reason for this was the decrease in number of unoccupied 3d states available for mixing with O 2p states.

Concerning the nanostructured samples, the main effect of decreasing the particle size is to increase the surface to volume ratio, which means increasing the amount of atoms at the surface. This contributes to an overall decrease of the octahedral symmetry due to the surface non stoichiometry likewise the appearance of unoccupied surface states/intra band gap states of 4s and 3d orbital character associated with Ti^{3+} states [12]. Due to the contracted (core-like) nature of the 3d orbitals (narrow bandwidth), the hybridization with 4s are expected to be of greater importance and a more pronounced broadening of the second region of the O 1s spectra is foreseen as particle size is decreasing. An excellent agreement is obtained with the XAS experiments and very promising results are expected for mapping the electronic structure of transition metal oxide and to assess the orbital character of localized band gap states for instance.

Figure 1. O1s absorption spectra of various TiO_2 materials (see text for details).

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Photoemission Fermi Surface Topology Studies of Magnetic Alloys

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ABSTRACT

Cuts through the Fermi Surfaces of CoNi and FeNi alloy films epitaxially grown on fcc Cu(100) reveal topological features in angle-resolved photoemission. Changing the stoichiometry of these pseudomorphic films permits us to observe changes in the Fermi surfaces. Increasing Co or Fe content, increases the ferromagnetism from that of pure Ni. The average moment increases linearly in the case of CoNi alloys but is arrested and sharply declines in FeNi. This work attempts to identify the electronic features underpinning this difference.

INTRODUCTION

Measurements with the surface magneto-optic Kerr effect (SMOKE) and magnetic dichroism of the Fe, Co, and Ni 3p core levels in photoemission with linearly polarized light (XMLD) have shown that the elemental moments remain constant and finite, while the magnetization increases with increasing Co and Fe content [1]. In the FeNi alloys, this linear increase of the average magnetic moment, shows a sharp decrease for richer Fe concentrations [2]. Mössbauer spectroscopy and SQUID magnetometry have shown that in the Fe-rich FeNi alloys an antiferromagnetic phase emerges, which coexists with the ferromagnetic phase [3]. It is this 'mixed' phase, rather than any collapse in the magnitude of the magnetic moments that is, believed to be responsible for the observed decrease in the ferromagnetic order.

RESULTS AND DISCUSSION

States at the Fermi energy are recorded in the high symmetrical k-plane for films 8 ML thick to avoid any contribution from the Cu substrate. Patterns 1(a), (b), (c) and (d) show data for a (110) cut through Brillouin zone in extended k-space. The alloy concentrations are from left to right: pure Co (a), Co₆₀Ni₄₀ (b), Co₄₀Ni₆₀ (c), pure Ni (d). In this (110) plane, one feature remains characteristic of the whole concentration range and sharply defined. It connects the L points in the fcc Brillouin zone more or less continuously throughout momentum space. This feature is due to the sp band and forms a 'dogbone' hole pocket, similar to that in copper.

As the number of holes in the alloy increases going from pure Ni towards pure Co, emission from new states occurs at the center of the zone as well as across the neck of this 'dogbone' structure. In simple terms, with increasing Co concentration the Fermi level shifts to lower energies and cuts through the d-band in the center of the zone near the Γ point, as suggested by the pseudomorphic bandstructures of Cu, Ni, Co, and Fe [4]. Also with increasing Co concentration, the exchange splitting of the minority and majority d-bands increases in a way that would indicate that this intensity surrounding the zone center is due mainly to minority spin polarized d-states. The 'dogbone' structure, a characteristic feature due to the sp-band collects some d-character but does not change dramatically. This 'dogbone' is a characteristic feature of these fcc 3d materials. Across the neck of this dogbone an increase of intensity is observed with increasing number of holes suggesting increasing hybridization with the sp-band close to the Fermi level in this particular region of k-space. This enhances electron scattering between d and sp-states.

Figure 1. Fermi contour maps in the [110] plane obtained in the photon energy range between 80 eV and 195 eV of a pure fcc Co film (a) fcc alloy films $\text{Co}_{60}\text{Ni}_{40}$ (b), fcc $\text{Co}_{40}\text{Ni}_{60}$ (c), and a pure fcc Ni film (d), all grown epitaxially on Cu(100).

The FeNi alloys show a similar evolution of states at the Fermi energy with increasing Fe content. Again, we observe a strong contribution due to the sp-band and a clearly defined 'dogbone' feature. Enhanced intensity in the center of the Brillouin zone and across the neck of this dogbone again appears with increased emptying of the d-bands. We observe well defined states in this momentum space, which is a strong indication that the muffin-tin potential on the different atomic sites, Fe, Ni, respectively Co is very similar. Any increased diffuseness in the patterns appears mainly in the d-states, which is expected since the lifetimes of these states is less due to increased scattering out of these states.

Figure 2. Fermi contour maps taken with a photon energy of $h\nu=160$ eV of a (a) Cu(100), (b) pure fcc Ni film on Cu(100), and (c) pure fcc Co film on Cu(100). (d) calculated bandstructure at E_F in the (100) plane.

Figure 2 compares Fermi surface photoemission plots from single crystalline Cu (a), and pure fcc films of Ni (b), and Co (c) on Cu(100). All the films have a thickness of 8 ML and the photon energy was fixed at $h\nu = 190$ eV while the angle was varied between 0 and 30° off normal and $\pm 120^\circ$ in the surface plane. At this specific photon energy, a sector of the energy sphere just encloses the (100) plane at the zone boundary, for emission angles smaller than $\pm 20^\circ$. Also shown in Figure 2d is the calculated bandstructure in the (100) plane for Ni [5]. For Cu, contributions from the sp bands on the spherical parts of the Fermi surface are observed, whereas in Ni and Co the d-hole pockets at the X points make an appearance. The sp band feature in Cu begins to shrink

towards the Γ -point, while the d-hole pockets grow around the X-point, in good agreement with the calculated bandstructure.

CONCLUSION

We have measured contour maps of states in momentum space at the Fermi energies of a series of binary alloys of the magnetic transition metals. These alloys possess the same fcc crystallographic structure as that of the Cu(100) substrate when grown as ultrathin epitaxial layers. This implies that the position of the Fermi level is a function of the hole concentration in the d-band, which we vary by alloying the various elements. This is why we expect the Fermi surface contours in k-space to evolve gradually with alloy stoichiometry, greatly aiding identification. We observe sharply defined sp-states throughout k-space characterized by the same ‘dogbone’ structure as that observed in copper. Emptying the d-band leads to states appearing localized in the dogbone region and as a diffuse region at the zone center. Mixing of d- and sp-states, mainly of minority spin polarization, occurs in specific regions of k-space from which derive the “spanning wavevectors” responsible for Fermi surface oscillations and coupling between magnetic layers in spin-valve heterostructures [6]. Future studies will concentrate on these Fermi surface spin-polarized “hotspots”.

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Photoemission Studies of Quantum Well States in Magnetic Heterostructures

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INTRODUCTION

Magnetic artificial nanostructures such as ultrathin films and multilayers exhibit fascinating behavior such as the giant magnetoresistance (GMR)¹ and the oscillatory magnetic coupling^{2,3} that are important for applications in magnetic information storage. Since these new properties originate from the behavior of the electrons in the system, angle-resolved photoemission spectroscopy (ARPES) is an ideal tool to untangle the puzzle of how changes in the electronic structure lead to new magnetic properties. In layered systems, the reflection of electrons at the interfaces can lead to standing electron waves known as quantum well (QW) states⁴ that are confined inside a particular layer (Fig. 1), similar to an optical Fabry-Perot interferometer. Unlike bulk states, these QW states occur only at particular energies. This is analogous to a guitar string, which can vibrate only at certain discrete frequencies. The great interest in these QW states arise from their *spin-polarized* character, which is believed to play an important role for the oscillatory magnetic coupling, GMR, magneto-optics, and other magnetic phenomena.

Figure 1. Quantum well states are standing electron waves that form due to reflections at the interfaces.

The results obtained in 1998 were (1) understanding of how the QW states lead to the oscillatory magnetic coupling,⁵ and (2) directly probing the spatial variation of the QW wavefunction.⁶

SPECIAL CAPABILITIES OF THE ALS

These experiments were performed at beamline 7.0.1.2 to take advantage of the high photon intensity and small spot size (~50-100 microns). This enables the use of wedged samples for detailed thickness dependent studies of the QW states. By scanning the photon beam across a wedge or double-wedge, many independent measurements can be performed on a single sample. A typical scan over a double-wedge sample consists of ~2500 independent measurements corresponding to ~2500 different combinations of film thicknesses. Such capabilities are unparalleled and the experimental results obtained in 1998 demonstrate the new type of questions which can be investigated using third generation synchrotron sources.

PROJECT I: QW STATES AND THE OSCILLATORY MAGNETIC COUPLING

A ferromagnet/non-magnet/ferromagnet trilayer exhibits a magnetic coupling such that the magnetization of the two ferromagnetic (FM) layers will be either parallel or antiparallel, depending on the thickness of the non-magnetic layer. While this phenomena is present in many trilayer systems, the Co/Cu/Co(100) system has emerged as a model system because of the good epitaxial growth and simple Fermi surface of Cu. In 1992-1993, ARPES experiments on a Cu

thin film on fcc Co(100) identified spin-polarized QW states forming inside the Cu layer.^{47b} Since the thickness dependence of the QW states seemed to match that of the oscillatory magnetic coupling, it was suggested that the QW states are responsible for generating the oscillatory magnetic coupling. In this work, ARPES was used to measure both the QW states and the magnetic coupling on the same sample (Fig. 2). This enabled a direct comparison of the electronic behavior (QW states) and the magnetic behavior (oscillatory coupling) for the first time.

The sample involved a Cu wedge grown on top of fcc Co(100).⁹ Subsequently, a Co capping layer was deposited on half of the sample, as shown in Figure 2a. The magnetic coupling was measured on the side with the Co cap, and the QW states were measured on the side without the Co cap. In this manner, the Cu thickness on the two sides are exactly matched and a direct comparison is possible.

For the QW measurement, the density of states was measured (DOS) at the belly and neck of the Cu Fermi surface.¹⁰ These points in momentum space correspond to the two extremal spanning vectors of the Cu Fermi surface for directions parallel to [100], and thus are believed to contribute most to the magnetic coupling in Co/Cu/Co(100). The DOS at the belly of the Fermi surface was measured with 83 eV photons and a normal emission geometry (Fig. 2b), and exhibits oscillations with a 5.6 ML periodicity of the Cu thickness. The DOS at the neck of the Fermi surface was measured with 77 eV photons and 11 degrees off-normal emission (Fig. 2c), and exhibits oscillations with a 2.7 ML periodicity of the Cu thickness.

For the magnetic coupling measurement, the magnetization direction of the top Co layer was measured by magnetic x-ray linear dichroism (MXLD)¹¹ in the Co 3p photoemission peak (Fig. 2d). The coupling exhibits two periods of oscillation (5.6 ML and 2.7 ML) which match those of the QW states.

The QW data was then used to calculate the magnetic coupling. The periods and phases of the magnetic coupling were determined from the QW states, and the relative strength of the long- and short-period couplings was used as a fitting parameter. Comparing this calculation (Fig. 2e) with the experimental data (Fig. 2d) shows that the periods and phases of the magnetic coupling are determined by the momentum-resolved QW states.

Figure 2. (a) Schematic drawing of sample used to compare the QW states with the oscillatory magnetic coupling. The QW states are measured on the side without the Co cap, and the coupling is measured on the side with the Co cap. (b) Long-period QW states: DOS at the belly of the Fermi surface oscillates with 5.6 ML periodicity of the Cu thickness. (c) Short-period QW states: DOS at the neck of the Fermi surface oscillates with 2.7 ML periodicity of the Cu thickness. (d) Magnetic coupling: Magnetic x-ray linear dichroism of the Co 3p photoemission peak was measured to determine the magnetization direction of the top Co layer. Light (dark) regions correspond to antiferromagnetic (ferromagnetic) coupling. (e) Calculated coupling based on the period and phase information from the QW states at the neck and belly of the Fermi surface. Light (dark) regions correspond to antiferromagnetic (ferromagnetic) coupling.

PROJECT II: SPATIAL VARIATION OF THE QW WAVEFUNCTION

The quantum confined electrons form standing waves with nodes and antinodes of the envelope function, pictured by the red curves in Fig. 1. New methods need to be developed to measure the position of the nodes and antinodes. In this work, we develop one such method that is analogous to measuring the nodes and antinodes of a vibrating guitar string. In the latter case, lightly touching the string near a node will not change the sound. However, lightly touching the string near the antinode will cause the sound to be damped. Thus, by touching different positions along the string, one can map out the spatial variation of the vibrations.

Similar to lightly touching a vibrating string with a finger, the QW electron standing wave in a Cu thin film was "touched" with an atomic layer of Ni. By touching different positions of the standing wave, one can map the wavefunction because the result depends on whether the Ni is at a node or an antinode of the QW envelope function. Figure 3a shows the double-wedge structure used to probe many different positions inside the QW on a single sample. First a Cu wedge is deposited onto a Co(100) substrate, followed by a monolayer of Ni. Then a second Cu wedge with the same slope as the first is deposited along the perpendicular direction. Going from point B to D, the overall Cu film thickness is constant, and the Ni position within the film continuously changes from one side to the other. Going from point A to C, the Ni remains in the center of the Cu film and the overall Cu thickness increases. In this manner, it is possible to independently vary the Ni position and the overall Cu thickness.

Figure 3. (a) Schematic drawing of the double-wedge sample used to probe the QW wavefunction. This enables independent variation of the overall Cu film thickness and the position of the Ni monolayer. (b) Density of states at the Fermi level using normal photoemission on this double wedge. The oscillations with the Cu thickness are from the QW states, as in Fig. 2b. The new result is the oscillations with the Ni position (horizontal direction), which arise from the Ni monolayer being located at a node or antinode of the QW envelope function.

Figure 3b shows the DOS at the Fermi level for the normal photoemission. The oscillations in the Fermi level DOS as a function of Cu thickness (vertical axis) are due to the formation of QW states at the Fermi level, as in Fig. 2b. Each peak labeled by v corresponds to a different QW state at the belly of the Fermi surface. Choosing a particular QW state (i.e. fixed Cu thickness), one may then sweep the Ni "touch" layer from one side of the film to the other. The new result is that the DOS oscillates as a function of Ni position (horizontal axis). These oscillations occur because the Ni monolayer will have a different effect depending on whether it is at a node or antinode of the QW envelope function. Qualitatively, the intensity maxima (minima) should correspond to the antinode (node) of the QW envelope function. In this manner, the spatial variation of the QW states has been mapped out for a series of QW states labeled by $v = 1, 2, 3, \dots$

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Polymer microstructure studies using soft X-ray spectromicroscopy

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INTRODUCTION

There are many interesting problems in polymer physics and chemistry that require detailed and quantitative chemical analysis (speciation) at the sub-micron spatial scale. These include issues such as: the chemical basis of phase segregation; determination of the morphology and interface chemistry of blends and co-polymer systems; mechanisms of formation and structure of 'self-assembled' nano-patterned structures. This document describes recent studies of some fundamental aspects of polymer microstructure using the ALS BL 7.0.1 scanning transmission X-ray microscope (STXM), both to report on the science and to provide an indication of the quality of the images and spectroscopy that can now be achieved.

SELF-ORGANIZATION OF CONFINED, FREE STANDING POLYMER FILMS

Patterning of thin polymer films is attracting increasing interest, both from a fundamental point of view, and on account of potential technological applications. However the thermal stability of these films can be a limitation on account of hole formation driven by dispersion forces which amplify structural instabilities at the film surface. Mechanical confinement of polymer films offers the possibility of control over this instability which in turn raises possibilities for unique self-assemblies of polymers on surfaces patterned on submicron length scales. We have used STXM to study very thin (~50 nm prior to annealing) polystyrene films confined between thin continuous layers of silicon oxide. The SiO_x layers prevent hole formation. However aggressive annealing at temperatures well above T_g generates a novel in-plane structure driven by the attractive dispersion force between the SiO_x-air surface [1]. These structures offer an attractive test-bed for understanding and developing control mechanisms for one of the fundamental forces governing self-assembly of polymer structures.

In order to fully model the mechanisms for this spontaneously generated lateral morphology, it is important to measure the thickness of the trapped polymer film throughout the structure. The optical density (OD) obtained from STXM readily provides

Figure 1. Images and spectra of a trilayer structure consisting of a 60 nm film of polystyrene (pS) coated on each side with 30 nm of SiO_x. Annealing causes the indicated morphology. Profiles and spectra show there is still significant pS in the dark regions.

this information. Prior to these measurements it had been assumed that there was almost complete exclusion of the polystyrene from the dark, non-continuous regions. However, STXM indicated ~30% residual PS in those areas (see Fig. 1). Further investigation of trapped thin film polymers of materials with different strengths of interaction with SiO₂ are planned.

MICROSTRUCTURE OF LATEX PARTICLES

Latex particles with internal structure are attractive for a number of applications, including coatings, adhesives, chemical delivery and separation science [2]. In order to optimize these structures for particular applications (e.g. pheromone delivery for environmentally benign, controlled release pest management; highly selective affinity separation resins and catalysts) it is important to be able to visualize their internal structure, determine its origin, and chemically analyze (speciate) the composition of various structural components. While transmission electron microscopy (TEM) of cross-sections of latex spheres readily reveals the presence or absence of internal structure of few micron sized latex particles, the limited chemical sensitivity of TEM means that one cannot be sure if the observed structure arises from a genuine chemical difference in the various regions (e.g. core versus shell) or whether it is a consequence of a density and/or thickness variation (perhaps driven by some underlying chemical difference). STXM images at a range of photon energies provide a means to quantify the relative contributions of chemical versus density/thickness contrast. Fig 2 shows examples of a current study of crosslinked acrylic-polystyrene latex particles which have been synthesized in a two-step process to intentionally segregate all of the poly-acrylate (pA) component to the shell region. There are three levels of contrast reversal. The spectral basis for this can be ascertained from comparison of the spectra of the polystyrene (pS) core, the pS-pA shell, and the epoxy support material (Fig. 3).

Figure 2. Selected energy STXM images of a styrene-based core-shell latex sample containing 70% poly-acrylate in the shell region. The energies of each image, and thus the origin of the dramatic changes in chemical contrast, are indicated in the next figure. The lower right image is a bright field electron micrograph for comparison.

Figure 3. C 1s NEXAFS spectra of the three chemical components in the styrene-based core-shell latex sample with 70% poly-acrylate in the shell. The vertical lines indicate the energies of the STXM images presented in the preceding figure.

Figure 4. Normalized C 1s spectra of the shell region of styrene-acrylate latex particles of different composition. The insert plots the compositional dependence of the heights of the styrene and acrylate π^* peak signals.

Figure 5 Amount (mol-%) of acrylate in the shell region, determined from the acrylate NEXAFS signal, plotted versus the synthesis composition. The insert shows the acrylate signal, isolated by subtracting the spectrum of pure polystyrene from each shell spectrum.

In order to test our ability to quantify internal chemical composition in latex systems, a number of preparations with systematic variation of the composition of the $\sim 0.8 \mu\text{m}$ shell region were examined. **Fig. 4** compares C 1s spectra of the shell region of samples with 50%, 70% and 100% acrylate in the shell, extracted from line-scans across several particles. The shell composition was determined from both the styrene $\pi^*(\text{C}=\text{C})$ signal at 285 eV (method-A) and the acrylate $\pi^*(\text{C}=\text{O})$ signal at 288 eV (method-B). **Fig. 5** plots the mol-% poly-acrylate determined from the method-B approach (both peak height and peak area), in comparison with the compositions predicted from the synthetic methodology. The agreement is reasonable, but there are still significant deviations. Study of a larger number of samples and development of a more precise means of extracting the shell signal, to the exclusion of the core and matrix signals, is expected to lead to significant improvements over the level of quantitation accuracy shown in Fig. 5. That study is in progress.

A more challenging goal for polymer STXM is the study of spontaneous internal organization of latex particles, either in the synthesis, or from subsequent modification (e.g. loading with other species, time evolution of a loaded particle, etc.). **Fig 6** compares TEM and STXM images of an interesting latex particle sample which shows a ‘tree-ring’ morphology. While electron microscopy reveals this internal morphology, it is unclear from the TEM work whether the ring pattern arises from simple density / thickness variations, or whether it is the result of chemical

inhomogeneity. The observation of the 'tree-ring' morphology only at specific photon energies in the STXM study clearly points to a strong chemical compositional origin of this morphology. From this observation we believe that the tree-ring structure is most likely generated by heterogeneous chemical oscillations in the one-step synthesis used to prepare this sample.

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Figure 6. Selected energy STXM images of a latex particle prepared by a single step synthesis. A 'tree-ring' structure is detected in the STXM image recorded at 285 eV, and by TEM (upper right). The diminution of the 'tree ring' structure in images at other energies (lower right) indicates it is associated with variable composition. It is likely this arises from chemical oscillations in the polymerization of the mixed, styrene, chloro-styrene system. The intensity profile across the particle (lower left) indicates that the chemical variation responsible for the ring structure involves only a few % compositional change.

Probing the local electronic structure in the H induced metal-insulator transition of Y

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INTRODUCTION

The interest in the optical properties of the lanthanide hydrides increased significantly with the discovery of the hydrogen induced optical switching, causing metallic Y film to become transparent upon H loading [1]. Although this metal-insulator (M-I) transition is conceptually simple, the details of the changes in the electronic structure is not fully understood. The previous understanding of the transition was based on band structure calculations [2], where a band gap of ~1.5 eV was obtained. Recent state of the art band structure calculations failed, however, to reproduce these results [3,4]. Furthermore, theoretical calculations focusing on the relation between the crystallographic and the electronic structure [5] are found to be inconsistent with the interpretation of recent experimental results [6,7]. Optical transition probabilities depend on matrix elements for electric dipole transitions between occupied and unoccupied states, which in turn depend on the local symmetry [5]. Accurate knowledge of the crystallographic structure is thus essential for theoretically establishing the correct mechanism for the changes in the optical properties upon hydrogen loading.

Here we explore the density of states close to the Fermi level by soft X-ray emission and absorption spectroscopy, as well as by first principles calculations, and discuss the intrinsic changes of the electronic structure upon hydride formation. Thereby, we attempt to address the contribution of the metallic states to the optical and electric properties of the yttrium hydrides. The existence of a direct band gap for the trihydride state will be demonstrated, as well as the formation of a hydrogen induced sub-band below the Fermi level. All the experiments were performed on well characterised single crystal films.

Soft X-ray emission spectroscopy (SXES) allows direct probing of the site specific angular momentum components for the electronic energy distribution, furthermore due to the relatively large penetration depth of the X-rays, it yields information on bulk properties. Thus, the use of soft X-ray absorption spectroscopy (SXAS) in combination with SXES allows the determination of the DOS of the occupied and the unoccupied part of the valence band. Hence the appearance of a band gap for e.g. insulators can be obtained and the details of the electronic structure in the vicinity of the Fermi level can be investigated.

EXPERIMENT

The samples were grown using MBE techniques described in detail elsewhere [8]. Niobium is used as a buffer to prevent reaction between the rare earth metals and the oxide substrate. The epitaxial relationships at the sapphire/niobium interface are (1120)S//[110]Nb, [0001]S//[111]Nb and at the niobium/yttrium interface (110)Nb//[0001]Y, [001]Nb//[1120]Y.

The samples were charged with hydrogen in an UHV-based hydrogen reactor. The samples were heated to elevated temperatures during the hydrogen exposure, to further reduce the strain induced defect formation. After the loading, the samples were analysed by X-ray diffraction (θ - 2θ). A single Bragg peak corresponding to YH_2 was observed in the dihydride sample with an fcc lattice parameter $a=0.5224$ nm. The bulk value at room temperature is 0.52095 nm [9]. The lattice parameter is known to decrease as the H/Y atomic ratio exceeds 2. The trihydride sample exhibits a dominating YH_3 Bragg peak (hcp lattice parameter $c=0.6614$ nm, cf. bulk $c=0.6659$ nm [10]) and a small YH_2 peak (fcc $a=0.5210$ nm). The ratio of the dihydride and the trihydride phases was estimated to be below 1/300.

The experiments were performed at 7.0.1 undulator beamline at the ALS, LBNL [11]. In the present work the $\text{Y M}_{4,5}$ soft X-ray emission was recorded by a grazing incidence grating spectrometer with a resolution of 0.35 eV [12]. The monochromatised synchrotron radiation beam impinged at 60° from the sample surface normal and the emission was recorded at right angle with respect to the incoming beam, and parallel to the polarisation of the beam. The excitation energy bandpass was <0.1 eV and the X-ray emission energy scale was calibrated and related to the excitation energy scale using the elastic (recombination) peaks.

RESULTS AND DISCUSSION

Figure 1 depicts the $\text{Y } 3d_{5/2} - 4p_{3/2}$ emission spectra of the yttrium metal, yttrium dihydride, and yttrium trihydride, respectively. The width of the transitions are broader in the hydrides than that of the Y metal and shifted towards lower photon energies. The shift originates from the decreased energy separation of the involved levels. If the binding energy of the $3d$ level increases, the shift of the $4p$ level has to be of the same sign and larger. On the other hand, if the binding energy in the $3d$ level decreases, the shift of the $4p$ level can be of the same sign, but smaller. X-ray emission measurements on a series of Y compounds [13] revealed large shift of inner $1s-2p$ and $1s-3p$ transition on Y^{3+} ions with respect to those of the Y metal. In the present case, the $\text{Y } 3d_{5/2} - 4p_{3/2}$ line shifts to lower energies, which is consistent with an increased electron charge at the Y sites. When electron charge is added to a site of an atom, decreased binding energy of core electrons is expected (based on Coulomb interaction in the one-electron picture, see for example Ref. [13]). Thus, if the formation of the hydride increases the electron charge at the yttrium sites, one would expect the $3d-4p$ X-ray transition to be shifted towards lower photon energies, which is indeed observed.

Figure 2 shows the valence-core SXES spectra of the three samples along with the corresponding soft X-ray absorption spectra (SXAS) recorded in fluorescence yield mode. The emission spectra were all normalised with respect to the integrated intensity of the $3d_{5/2} - 4p_{3/2}$ transitions (Figure 1). The $M_{4,5}$ emission reflects the p character partial DOS, as the core state is of d symmetry. Since yttrium metal should have weak $5p$ character, the intensity is expected to be low, in accordance with the observations (the free Y atom does not possess $5p$ electrons, whereas in the solid, $5p$ states are induced by hybridisation). A sharp edge is observed at the top of the valence band in Y, a feature which is identified as the Fermi level (at 156.0 eV). The SXAS shows an onset at this energy, which implies an overlap between the valence band and the lowest part of the conduction band. Thus, the absorption-emission compound spectrum shows the unbroken density of states crossing the Fermi level, reflecting the metallic character of Y.

Figure 2. Emission and absorption spectra which map occupied and unoccupied states close to the Fermi level, respectively.

A substantial change is observed in the X-ray emission with increasing hydrogen content, as seen in Figure 2. The total intensity (normalised to the $3d-4p$ inner-core transition) increases considerably, and a strong feature appears at around 6-7 eV below the Fermi level. This observation is in agreement with a general behaviour of transition metal hydrides, in which the hydrogen and the host lattice form a sub-band below the Fermi level [14]. The trihydride spectrum displays a clear reduction of the DOS in the region corresponding to the Fermi surface of the metal, resulting in a band gap with the estimated width of 2.5 eV.

Symmetry and anisotropy induced intensity enhancement are expected to cancel by the normalisation to the $3d-4p$ transition. Thus, the $M_{4,5}$ X-ray emission results supports the view of hydrogen as electron donor, which is in line with the interpretation of the core-to-core spectra discussed above. These findings are in agreement with studies of the electronic structure of Y hydrides by positron annihilation [15,16] which also is a bulk sensitive technique.

In summary, the results show a hydrogen induced band-gap in the trihydride phase of Y. The obtained DOS are in qualitative and semiquantitative agreement with calculations of the transition probabilities. A formation of a sub-band some eV below the Fermi level are observed, and the results strongly support the protonic-like type of bonding of H.

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Resonant Angle-Resolved Photoemission of URu₂Si₂

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INTRODUCTION

Heavy fermion compounds are characterized by a large linear specific heat coefficient (γ) which signals large ('heavy') effective masses of electrons forming the Fermi surface [1]. Resonant photoemission spectroscopy of polycrystalline samples has contributed to the understanding of rare earth and actinide heavy fermions by identification of the *f*-electron weight contribution to the states at E_f . For many rare earth systems this weight can be analyzed and related to γ within a single impurity picture [2, 3]. Nonetheless from general theoretical ideas [4] and early experimental de Haas-van Alphen studies [5] it has been appreciated for very many years that this weight should be part of the dispersions which define the Fermi surface. One finds that issues concerning the band width and dispersion of this *f*-weight and the appropriate starting point (single-impurity models versus band-theory) for the theoretical description of various heavy fermion materials are commonly raised in the literature [6]. High-resolution angle-resolved photoemission spectroscopy (ARPES) of single crystal surfaces holds largely unfulfilled promise for addressing these issues.

The goal of this work is to carefully quantify the variation of *f*-weight of the heavy fermion URu₂Si₂ as a function of crystal momentum by combining ARPES with resonant photoemission at energies near the U *5d*→*5f* absorption threshold. URu₂Si₂ has a moderately large linear specific heat coefficient of $\gamma \sim 65$ mJ/mol-K² [7] compared to ~ 1 for a simple metal and >1500 for CeAl₃. URu₂Si₂ is a paramagnet that undergoes antiferromagnetic ordering at 17.5 K and then becomes superconducting at 1.2 K [8]. Additional interest in this material is due to evidence for the coexistence of antiferromagnetism and superconductivity, properties generally thought to be mutually exclusive. Also, the Ce analog to this compound, CeRu₂Si₂, is well-known in the literature for excellent agreement between de Haas-van Alphen measurements and renormalized band theory, i.e. the number, size and effective masses of Fermi surface orbits well account for its T-linear specific heat value of ~ 350 [9].

EXPERIMENT

URu₂Si₂ has the ThCr₂Si₂ crystal structure and a body-centered tetragonal Brillouin zone. Samples were cleaved in ultra-high vacuum (1.2×10^{-10} torr) at room temperature exposing the [001] surface and then cooled to ~ 150 K for ARPES measurements. Crystals with a ~ 3 mm diameter typically produced at least one ~ 1 mm² flat uniform terrace suitable for analysis. ARPES experiments were performed on the ALS Beamline 7.0.1.2 with an experimental endstation originally designed for highly-automated angular and energy-dependent photoelectron diffraction. The inherent motion of the beam on the sample surface with sample rotation presented an experimental challenge to keep the 100 μ m beam spot on the millimeter-sized uniform cleave terraces. A total instrumental resolution of ≈ 80 meV and full angular acceptance of $\approx 1.4^\circ$ (10% of a Brillouin zone width) was employed. These ARPES measurements in the photon energy range of 80-220 eV complement previous lower photon energy measurements (14-34 eV) performed at the SRC synchrotron in Wisconsin.

Figure 1. Fermi-edge intensity angular maps of URu₃Si₂ (001) at two photon energies. (a) 85 eV and (b) 112 eV, below and above the U 5*f* resonance. (c) Representative sizes of Fermi-surface orbits measured by magnetoresistance.

RESULTS

Figure 1 shows Fermi-edge angular intensity maps for two photon energies below and above the U 5*d*→5*f* resonance. The maps are acquired by monitoring the intensity within a 0.2 eV wide energy window centered on E_F while the sample is rotated over a 45° or 90° azimuth range out to a maximum polar angle of 25°. The full azimuth images, obtained by symmetrization, represent curved surfaces in k -space and are plotted versus k -parallel with a partial Brillouin zone overlaid for reference. Below resonance (85 eV) the most distinct Fermi surface feature is a ring structure centered on XP. In addition, intensity maxima are observed at Γ Z at normal emission and in the second Brillouin zones. Above resonance (112 eV), strong intensity modulation of the U 5*f* weight is observed with maxima along Γ Z and approximately half-way between Γ and Z. Additionally, the XP ring structure is observed to fill in with *f*-weight.

The origin of the E_F intensity modulations is investigated with angle-resolved spectra at the Γ , Z, X and M k -points as displayed in Figure 2. The Γ -point spectra along normal emission at 97 eV (Fig. 2a) shows a sharp peak near E_F that is measured to have a finite binding energy at lower photon energy (18 eV). In addition, the build-up of weight at 0.6 eV is a key signature of the

Figure 2. Major Fermi surface regions in k -space: (a) small hole pocket at Γ (97 eV), (b) tiny hole pocket at Z (125 eV), (c) medium-sized hole surface at X (85 eV), and (d) a large electron-like dispersion centered on Γ (156 eV).

Γ -point that repeats as a function of photon energy (18, 50, 97, 156 and 220 eV) and allows the determination of a crystal inner potential ($V_0=12$ eV) that sets the k_z -scale for all measurements. In contrast, this 0.6 eV binding energy weight is absent at the Z-point at normal emission at 125 eV. The sharp dispersive weight at E_f at Z is shown at low photon energy to be a tiny hole surface. The XP-point ring structure, Fig. 2c, is observed to be a small hole-surface. As a function of photon energy the intensity of this ring is observed to form a tube of intensity. This tube structure is believed to originate from an ellipsoidal Fermi surface centered on the X or P points and then k_z -broadened as a result of the finite inelastic mean-free path of the outgoing electron. Finally a larger electron-like surface becomes very distinct in the spectra at 156 eV, Fig. 2d, and probably accounts for the E_f intensity maxima halfway between Γ and Z in Fig. 1b.

ANALYSIS

Meaningful comparison of band dispersions along short polar arcs near normal emission can be made to calculated band structures for URu₂Si₂ [10-12]. An intensity representation of such a polar series at 156 eV is shown in Fig. 3a in which image normalization and enhancement has been employed to bring out the weaker band features at higher binding energy. The experimental band dispersions are digitized and overplotted (dots) in Fig. 3b with a calculated band structure along Γ MZ [12]. Good agreement is observed in the higher binding energy (d -band) dispersions. In particular the symmetric dispersion to a maximum binding energy of 1.5 eV between Γ and Z and the close approach of the hole-like dispersion at Z are well reproduced. In addition, the band edge energies at Γ are in good agreement with calculations.

However, in the near E_f region there is significant disagreement with theory. A small theoretical electron surface at Γ is predicted instead the observed hole-like dispersion and the large electron-like dispersion centered on Γ has no correspondence in the band theory. In addition, the various band calculations predict none or a small electron surface at X (not shown) in contrast to the observed medium-sized hole surface along XP. The discrepancy between the calculated and experimental Fermi surface topology is also exhibited in quantum oscillation measurements [13, 14]. Four orbits are observed in magnetoresistance [14] whose cross sectional areas are illustrated in Fig. 1c, plotted with the same k -parallel scale as the E_f intensity maps. The largest orbit with a frequency of 1.1 kT is qualitatively observed to match well with the XP ring structure. Also the small hole surface at Z is a candidate to match one or two of the smaller orbits. Effective

Figure 3. (a) Normalized intensity plot of polar series of spectra along [100] at 156 eV. (b) Comparison of experimental (dots) bands to calculated band structure along Γ MZ (lines).

masses of 6-12 m_e are measured for these orbits and are not sufficiently large to fully account for the 65 mJ/mol-K² linear specific heat coefficient. The topology of the large electron surface, Fig. 2d, has not been quantified, but if spherical, it would correspond to a 13 kT oscillation frequency.

The discrepancy between relativistic band calculations and measurements of ARPES and magnetoresistance can be attributed to many body effects. The relativistic calculations treat three U 5*f*-electrons as part of the valence band without any correlation between *f*-electrons. Renormalized band theory, not performed to date for URu₂Si₂, empirically modifies the *f*-electron scattering phase shifts in order to account for correlations resulting in much flatter *f*-bands and hence larger Fermi-surface effective masses. In the case of CeRu₂Si₂ and UPt₃, the Fermi surface is only slightly modified after renormalization. An alternate theoretical approach is to start with the single-impurity Anderson description of *f*-electron correlations and add lattice effects [15]. Signatures of this periodic Anderson model include renormalization of the bare *f*-binding energy to just above E_F , and *f*-*d* mixing in the vicinity of a *d*-band crossing E_F . The observed dispersion and rapid loss of intensity of the sharp *f*-weight away from E_F (Fig. 2) is currently being analyzed in terms of this many-body model *f*-*d* band mixing.

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Resonant inelastic scattering study of insulating cuprates at the Cu L-edges

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We have performed some initial measurements of resonant inelastic scattering spectra for three parent cuprates (La_2CuO_4 , $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$) at the Cu L2 & L3 edges. They all show similar features - a very strong excitation band of dd type around 2 eV and a charge-transfer excitation feature around 5 eV. L-edge spectra have larger intensity at the dd channel compared to the Cu K-edge results we have from Brookhaven [1,2]. Such resonant profile measurements are important to characterize the dd excitations channels (optically forbidden) in these compounds as they are relevant for antiferromagnetic and superconducting properties which arise when these insulators are doped with different concentrations. More detailed study is underway.

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Resonant inelastic soft-x-ray scattering study of heavy-fermion systems

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INTRODUCTION

As previously demonstrated [1], resonant inelastic x-ray scattering spectroscopy at some core thresholds is an efficient tool for probing both intra-atomic neutral and inter-atomic charge-transfer excitations in rare-earth compounds. As a result of creation-annihilation of a core hole there are radiative transition back to the ground and low-lying excited states so that the final states of the spectroscopic process can be described as eigenvalues of the ground state Hamiltonian. For correlated systems with significant configurational mixing in the ground state, resonant x-ray scattering spectra can be interpreted within the framework of a localized, many-body approach based on a single-impurity Anderson model (SIAM). The ground state values of the charge-transfer energy and hybridization strength which are used as model parameters to characterize charge-transfer excitations can be estimated with higher accuracy from analysis of these data.

The SIAM is very often used for the description of various transport and spectroscopic properties of Ce- and Yb-based systems with the pronounced heavy fermion behavior [2]. The model predicts a significant temperature dependence of the f occupancy which value is crucial for the interpretation of various physical properties. However, the validity of the SIAM for heavy fermions has been questioned [3] based on the inconsistency of experimental data obtained by electron spectroscopies. In particular, the existence or lack of the Kondo resonance in valence-band photoemission spectra of heavy fermion materials is heavily debated. A large surface contribution to the spectra often complicates the analysis of the bulk component. In this case, the bulk sensitivity and element-specific nature of resonant soft-x-ray scattering spectroscopy is particularly useful.

This abstract presents soft-x-ray scattering data recorded at different excitation energies across the Ce 4d absorption edges of CeB₆, CeAl, γ -Ce, and α -Ce.

EXPERIMENTAL DETAILS

A single crystal of CeB₆ was grown by the floating-zone method [4]. The CeAl sample was a polycrystal prepared by induction melting from stoichiometric amounts and checked by x-ray diffraction and microprobe analysis. The Ce-metal sample was a 1.0-mm thick film of the 99.9 % purity which was supplied by Alpha Aesar Co. Fresh surfaces of the samples were obtained by scraping with a diamond file. To study the γ - and α -phases of Ce the measurements were carried out at 300 K and 40 K, respectively, using a closed-cycle cryogenic system.

The experiments were performed at beamline 7.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory with a spherical grating monochromator [5]. The scattering spectra of Ce-based materials were recorded using a grazing-incidence grating spectrometer [6] with a two-dimensional detector. The spectrometer resolution was set to about 140 meV. The incidence angle of the photon beam was about 20° from the sample surface and the spectrometer was placed in the

Figure 1. Resonant inelastic soft-x-ray scattering spectra of CeB_6 . The elastic peak is set at 0 eV. The excitation energies used to obtain these spectra are indicated by arrows on the total fluorescence spectrum at the Ce 4d edge shown in the top panel.

structures move to the high energy loss side with increasing excitation energies. The movement of the structures in different spectra is indicated with lines in Fig. 1.

The lowest inelastic scattering structure which is clearly resolved has an energy loss of about 3.7 eV. It gains intensity as the excitation energy is tuned towards the main Ce 4d absorption edge. In Fig. 2 the 4-eV-energy-loss structure is also observed in the resonant soft-x-ray scattering spectra of $\alpha\text{-Ce}$. Tuning the excitation energy across the Ce 4d edge gives rise to a distinct resonance of this structure. Its intensity reaches a maximum at an excitation energy of about 124.5 eV but decreases at 133.3 eV. A similar structure was previously observed in low-energy electron-energy-loss spectra of Ce [7,8] and was assigned to inter-band f-d transitions. Here, the selection rules

horizontal plane at an angle of 90° with respect to the incidence beam. To determine the excitation energies, total fluorescence yield spectra of the Ce 4d edge were recorded in the same experimental geometry using the spectrometer detector. During the absorption and scattering measurements, the resolution of the monochromator was set to about 120 meV.

RESULTS AND DISCUSSION

Fig. 1 shows resonant soft-x-ray scattering spectra of CeB_6 which reveal pronounced inelastic scattering structures within 30 eV below the elastic peak when the excitation energy is close to the main Ce 4d absorption edge. Due to dipole selection rules, the structures with low energy losses represent transitions to the final states of 4f symmetry via creation-annihilation of a 4d core hole (the scattering cross-section for the 6p states is much lower). Lines at energy losses of about 19.5 and 22 eV correspond to transitions to the final states of 5p symmetry. The CeB_6 spectra also show non-resonant x-ray fluorescence structures which mainly reflect the 4f-4d radiative decay. These

Figure 2. Resonant inelastic soft-x-ray scattering spectra of α -Ce. The excitation energies used to obtain these spectra are indicated by arrows on the total fluorescence spectrum at the Ce 4d edge shown in the top panel.

dictate that the 4-eV structure must have 4f character. A comparison of inelastic scattering spectra of different systems (Fig. 3) recorded at the same excitation energy shows that the energy loss of this structure somewhat increases on going from systems with weakly hybridized 4f states to those with strongly hybridized 4f states.

The 4f nature of the 4-eV-energy-loss inelastic scattering structure, its resonant behavior and dependence on the hybridization strength strongly suggest that the structure corresponds to charge-transfer excitations resulting from configurational mixing in the ground and intermediate states of a coherent second-order optical process. For the ground state described as a linear combination of f^1 , f^0 , and f^2 configurations, the 4-eV structure is expected to have mainly f^0 character as the lowest observable excitation peak (excited states of the f^1 configuration separated by the Kondo energy $k_B T_K$ from the singlet ground state can not be resolved with the experimental resolution used).

In the present case, the derived energy of 4 eV required for charge-transfer excitations to the f^0 state is higher than the binding energy of the f^0 peak (2.5 eV) in valence-band photoemission spectra [2]. The difference between the two techniques can be a result of probing systems with a different number of electrons. The x-ray scattering process is charge neutral while photoemission spectroscopy probes the $N-1$ particle system. The difference is not surprising when considering strong configurational dependence of the SIAM parameters [9]. The reduction in the value of the hybridization matrix element V_{km} between f and conduction states with respect to that derived from first principle calculations or from the analysis of low-energy thermodynamic properties is required to describe photoemission data. As follows from the present interpretation of the scattering spectra, both the bare energy ϵ_f of f states and V_{km} which contribute to the energy separation between f^1 and f^0 configurations can be larger than those obtained from fitting photoemission data.

Figure 3. A set of inelastic soft-x-ray scattering spectra of several Ce-based systems recorded at the excitation energy of 124.5 eV. The spectra were normalized to the same intensity of both non-resonant fluorescence structures and background.

Finally, the elastic peak which corresponds to transitions back to the ground state shows an intriguing dependence on the Kondo temperature of the studied systems. Its intensity scales as α -Ce (1.0); γ -Ce (0.4); CeAl (0.19); CeB₆ (0.06) which is consistent with a Kondo-scale behavior (note, measurements on CeAl and CeB₆ were done at different temperatures). However, unknown contributions from diffuse scattering due to surface roughness of the samples and self-absorption effects introduce a very large uncertainty. Further measurements using smooth surfaces and experimental conditions reducing the diffuse scattering contribution are necessary to firmly establish this

behavior.

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Resonant Photoemission and Linear Dichroism in Gd*

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Abstract

Magnetic Linear Dichroism in Angular Distributions (MLDAD) from Photoelectron Emission was used to probe the nature of Resonant Photoemission. Gd 5p and Gd 4f emission were investigated. Using novel theoretical simulations, we were able to show that temporal matching is a requirement for “True” Resonant Photoemission, where the Resonant Photoemission retains the characteristics of Photoelectron Emission.

Discussion

Resonant Photoemission is the phenomenon where the emission of 4f and 5p electrons from rare-earth metals and their compounds is strongly enhanced because a second emission channel opens up, e.g the photon has just enough energy to excite a 4d electron to an unoccupied 4f level. In a generic picture, the indirect channel of the resonant photoemission is interpreted as due to a process where a 4d electron in the initial state is first excited to the unoccupied 4f level, forming a tightly coupled, bound intermediate state, 4d core hole plus 4f electrons. Then a decay via autoionization occurs into the final state, thus producing a final state identical to that obtained by a direct photoemission process for the ejected electron. [1] The transition rate is greatly enhanced if the excited state decay is by a Coster-Kronig or a super-Coster-Kronig [(s)CK] process. [2,3] The key question is whether these processes are coherent or incoherent: Is it truly “resonant photoemission” or merely the incoherent addition of a second emission channel? Should the overall intensity be treated as a squaring of the sum of the amplitudes (coherent) or summing of the squares of the amplitudes (incoherent)? A true “resonant photoemission” process should be coherent, involving interference terms between the direct photoemission and indirect photoemission channels. Possibly, incoherence would give rise to the loss of photoemission characteristics in the process, with a domination of Auger-like properties.

To this problem we have applied the new photoelectron spectroscopy technique of magnetic linear dichroism in angular distributions (MLDAD). [4-7] This technique is related to but distinct from the techniques of magnetic x ray circular dichroism (MXCD) in photoelectron spectroscopy and x ray absorption. [8-14] The key is that while large dichroic effects in ferromagnets can be observed with MXCD-photoemission and MXCD-absorption, the large MLDAD effects in ferromagnets is solely a photoemission, not an absorption-driven, process. This is because the chirality which gives rise to magnetic sensitivity is due to the vectorial configuration in MLDAD as opposed to the intrinsic chirality of circularly polarized x rays in the MXCD techniques. In absorption, where there is an essential averaging over all emission angles, the vectorial chirality is lost. Thus, MLDAD is the ideal measurement to distinguish between photoemission and absorption processes. Angle-resolved photoemission in a magnetic

system should show an MLDAD effect: x ray absorption and thus auger-like emission will show no MLDAD effect. Experimental details can be found elsewhere. [15-19] Theoretical spectra were calculated in intermediate coupling using Cowan's relativistic Hartree-Fock code.[20] Radiative transitions were taken into account to first order and (s)CK transitions to infinite order. [21-23] Line broadening of the photoelectron state and experimental resolution were included by a convolution with a Lorentzian and a Gaussian, respectively. For the 4f emission the interference effects between the different photoemission final states and between direct and resonant channel were fully included. The interference term was excluded in the 5p calculation.

The study included an extensive theoretical and experimental data set, collected "on" and "off" resonance. Some of the spectra can be seen in Figure 1. These spectra, coupled to results not shown here [17-19], lead to the following conclusions. The Gd 4f resonant photoemission is confirmed to be photoemission-like, because it shows an MLDAD effect on resonance. The Gd 5p resonant emission is shown to be dominated by Auger-like contributions, owing to the absence of an MXLD effect at resonance. The experiment results are confirmed by the theoretical simulations. It appears that temporal channel matching is a requirement for channel interference and the persistence of photoemission effects. The Coster-Kronig decay that occurs in the 5p emission occurs on a time scale of about 10^{-15} sec. [2] The super-Coster-Kronig delay of the 4f should be significantly faster. [2,3] This would speed up the indirect channel, bringing it nearer to the time duration of x ray absorption (10^{-17} sec or less) that dominates the

Figure 1. A series of experimental and theoretical 4f and 5p photoemission spectra (for the two opposite magnetization directions) and normalized difference curves. The photon energy was 150 eV for the 4f and 151 eV for the 5p; (a) Gd 4f, photoelectron spectra, experimental; (b) Gd 4f, photoelectron spectra difference, experimental; (c) Gd 4f, photoelectron spectra, theory; (d) Gd 4f, photoelectron spectra difference, theory; (e) Gd 5p, photoelectron spectra, experimental; (f) Gd 5p, photoelectron spectra difference, experimental; (g) Gd 5p, photoelectron spectra, theory; (h) Gd 5p, photoelectron spectra difference, theory. EDC is energy distribution curve. The spectra in (a), (c), (e), & (g) are EDC's, where the photon energy is held constant and the kinetic energy is scanned. PND stands for peak normalized difference, where the dichroism difference at each binding energy is divided by the sum of the two intensity maxima, one from each pair. The photon energies of 150 eV and 151 eV are "on" resonance.

direct photoemission channel. Thus, not only must the energies of the two channels match but also the time duration, in order to observe "true resonant photoemission".

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Resonant Soft X-ray Emission Spectra and Outer Valence Molecular Orbitals of Uranium

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INTRODUCTION

The universality of formation of inner valence molecular orbitals (IVMO) for actinide compounds has been previously examined using x-ray photoelectron spectroscopy (XPS) and fixed energy electron excited x-ray emission spectroscopies.¹⁻⁶ The degree of participation of the IVMO electrons in bonding was rationalized in terms of the physical and chemical properties of the actinide compounds. The correlation of spectral parameters with uranium oxidation state, symmetry of the local uranium environment, and the distance from uranium to nearest neighbors also was established.¹⁻³ However because of resolution constraints, studies of the outer valence molecular orbitals (OVMO) in uranium compounds was not possible.

Third generation VUV/soft x-ray sources make possible obtaining high-resolution resonant x-ray emission spectra (RXES) which have proven to be an efficient tool to study the electronic structure of correlated systems like lanthanides and actinides.⁷⁻¹² The structure of the RXES spectra shows a strong resonant behavior and dependence on the localization degree of the U 5f electrons. For actinide compounds the localization effects for 5f electrons are pronounced.¹⁻³ As an example, in UO₂ the 5f electrons are strongly localized unlike in UO₃, where the 5f electrons participate in the chemical bonding.^{1,2} Resonant valence-to-core x-ray emission spectroscopy makes it possible to directly investigate the U 5f - O 2p electron interaction. Comparative RXES studies of uranium compounds allows assessment of the nature and degree of participation of the U 5f in the chemical bonding. The results of the U 5d near edge x-ray absorption fine structure (NEXAFS) and the U 5f → U 5d RXES permits the exploration of the uranium outer valence molecular orbital formation.

EXPERIMENTAL PROCEDURE

NEXAFS and RXES spectra were collected at undulator Beamline 7.0.1 of the Advanced Light Source (ALS) at the Ernest O. Lawrence Berkeley National Laboratory (LBNL).^{10,11} Experiments were done in the XES branchline chamber at approximately 5×10⁻⁹ Torr. The RXES spectra were measured with the beam incident at ~75° to the substrate normal. A grazing-incidence fluorescence grating spectrometer was used to measure the RXES spectra and energies were calibrated to the elastic scattering features.^{12,13} NEXAFS spectra were collected in the total yield mode with the beam incident normal to the substrate.

All uranium materials used in this study were depleted. The samples of carbon-coated uranium metal and U₆Nb alloy were prepared at the Lawrence Livermore National Laboratory as discs of ~5 mm diameter and transported under vacuum to limit surface oxidation. The UO₂, UF₄, UF₅, U₃O₈, and UO₃ samples were prepared at LBNL by pressing powders into indium.

RESULTS AND DISCUSSION

The U 5d total electron yield NEXAFS spectra of carbon-coated uranium metal, UO₂, U₃O₈, and UO₃ are shown in Figure 1A and agree with previously obtained results.^{13,14} The bars schematically identify the U 5d_{5/2,3/2} binding energies (O₄ and O₅ thresholds) for α-U and the

uranium oxide materials on the basis of the XPS data.¹¹¹⁵ The NEXAFS spectra of the uranium metal and the uranium oxides differ greatly. For example, in the spectrum of UO_3 as well as uranium metal, there is a shoulder at ~ 108 eV, which is absent in the spectra of UO_2 and U_3O_8 . This indicates the presence of uranyl compounds (hydroxides and carbonates) on the metal surface. Thus, the feature at ~ 108 eV is a transition to an orbital formed in the uranyl group (UO_2^{2+}). The shoulder at ~ 101.5 eV in the spectrum of uranium metal is similar to that from UO_2 and is explained by the presence of oxide layer on the metal surface. The features of the NEXAFS spectra were used to determine the excitation energies for the RXES measurements.

RXES spectra were collected from the uranium materials at the excitation energies indicated by arrows in the NEXAFS spectra of Figure 1A. The spectral information obtained from these studies at the various photon energies is summarized in Table 1. Features with a spin-orbit splitting of ~ 10 eV are the transitions $\text{U } 5f \rightarrow \text{U } 5d_{5/2,3/2}$. Figure 1B is representative of the quality of XES spectra (except that most spectra span ~ 25 eV) and shows the spectra collected at the excitation energy A from U, UO_2 , UF_4 , UF_5 , U_3O_8 , and UO_3 . The features in these spectra are attributed to the ff -excitation process and agree with earlier results. As expected, the ff -excitation peaks are stronger in materials with ionic bonding like UO_2 , UF_5 , and especially UF_4 . The features in the spectrum of uranium metal are similar to those in UO_2 again indicating the presence of UO_2 on the surface. Figure 1B highlights the spectral differences in the uranium materials, that is evidence for differences in the formation of the electronic structures. For more reliable and accurate interpretation of the ff -excitation process in uranium compounds, detailed theoretical calculations of the valence band structure taking into account many body and charge transfer effects must be carried out.

Figure 1. (A-left panel) Total electron yield NEXAFS spectra of carbon coated uranium metal, UF_4 , UF_5 , UO_2 , U_3O_8 , and UO_3 . Intensities normalized to the peak at 100 eV. Arrows indicate the excitation energies for RXES spectra. (B-right panel) RXES spectra showing ff -excitation process in U, UO_2 , UF_4 , UF_5 , U_3O_8 , and UO_3 collected with excitation energy A. Energies are aligned relative to the elastic scattering peaks. Intensities are normalized to the elastic scattering peaks.

Table I. Resonant soft x-ray emission transitions and energies in eV for metallic uranium, UO_2 , UF_4 , UF_5 , U_3O_8 , and UO_3 .

Peak	Transition	U_{metal}	UO_2	UF_4	UF_5	U_3O_8	UO_3
1	$5d_{5/2} \leftarrow 5f$	89.9	91.0	90.4	90.9	91.6	91.6
2	$5d_{3/2} \leftarrow 5f$	100.8	100.3	100.0	100.3	100.8	100.8
3	$5d_{3/2} \leftarrow \text{OVMO}$	105.5	105.5	104.7	106.3	105.9	105.9
4	$5d_{3/2} \leftarrow \text{OVMO}$	107.4	107.9	---	---	108.2	108.2
5	$5d_{3/2} \leftarrow \text{OVMO}$	110.4	111.8	109.5	111.7	---	---
IS	$\text{OVMO} \rightarrow \text{OVMO}$	---	---	---	---	4.2	4.0

*Distance from the elastic scattering peak.

The RXES spectra collected at excitation energy B (not shown) show significant differences between U, UF_4 , and the uranium oxides. The $\text{U } 5f \rightarrow \text{U } 5d_{3/2}$ transition does not occur at this energy. This indicates that electrons from U $5d_{3/2}$ core level are not promoted to U $5f$ level directly, but to another valence orbital formed from the interaction of U $5f$, $6s$, $6d$ – O $2p$ electrons. This is then followed by the $\text{U } 5f \rightarrow \text{U } 5d_{3/2}$ transition. Apparently such orbitals do not form in U and UF_4 or the excitation energy is insufficient to promote the U $5d_{3/2}$ electrons to a more energetic orbital. This demonstrates the difference in formation of the MO system for uranium with oxygen and non-oxygen ligands.

Inelastic scattering features are also observed in the RXES spectra and are especially evident in the UO_3 spectra. This process occurs when part of excitation photons lose energy to promote electrons from one valence molecular orbitals to a higher one. This transition is associated with the participation of the OVMO formed in the uranyl group UO_2^{2+} . A similar process is evident in the XPS spectrum of UO_3 .⁵ Thus, the XPS spectrum of the U $4f_{7/2}$ electrons has a satellite located at 3.9 eV from the basic line.⁵ This satellite forms due to the dynamic effect, when photoelectrons escaping the sample lose a part of their energy to excite electrons from a valence orbital to a higher one. This demonstrates the complementary nature of the XPS and RXES results. The same inelastic scattering takes place in U_3O_8 , but not in uranium metal, UF_4 , UF_5 , or UO_2 . This demonstrates the difference in the electronic structure of the OVMO in uranium and its compounds.

CONCLUSION

RXES has proven to be an effective tool to study of the electronic structure of uranium compounds. The structure of the RXES spectra shows a strong resonant behavior and dependence on the localization of the U $5f$ electrons. The spectral structures of the uranium compounds investigated are differ significantly and can be interpreted by the formation of the outer valence molecular orbitals from the interaction of the U $5f$, $6s$, $6d$, and O $2p$ electrons. The RXES spectra were interpreted in the one-electron MO LCAO (molecular orbitals as linear combinations of atomic orbitals) approximation. These considerations are valid provided the formed molecular orbitals retain their partial atomic nature. For a more reliable and accurate interpretation of the RXES spectra of uranium compounds, precise and detailed theoretical calculations of the valence band electron structure taking into account many body and charge transfer effects, have to be carried out.

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Resonant x-ray Raman scattering spectra of Cu *dd* excitations in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

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The energies of the lowest excitations in the Cu-based superconductors are basic quantities of interest in the ongoing struggle to determine the underlying electronic structure and elementary excitations. The energies of the local on-site *dd* excitations have been a topic debate recently.

FIG. 1. Polarization-dependent x-ray resonant Raman spectra at the Cu M_3 resonance (74 eV). The angle between the emission direction and the sample normal is 30°, 40°, and 60°, from top to bottom. The last spectrum is also shown reduced by a factor of 200.

Resonant x-ray Raman spectroscopy (RXRS) has the makings of a powerful technique to study the elementary excitations in solids. Using excitation energies at specific core-level thresholds one can identify the excitations, determine their atomic origin, and, as shown by choosing core level with strong spin orbit coupling, one can also observe the local spin flip excitations whose energies are determined by exchange and superexchange interactions with neighboring spins [1]. Only recently has the resolution of RXRS become sufficiently high to study valence-valence excitations. Molecules and wide-band solids have attracted considerable interest [2], but the method has also been used to study charge-transfer excitations in correlated systems [3] and *dd*-excitations in MnO [4].

We present resonant x-ray Raman scattering results on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, a model compound for high- T_c superconductors [5]. The experiment was performed at beamline 7 of the Advanced Light Source (ALS) at Berkeley. The *dd* excitations can be observed and show that the polarization dependence can be used to identify the *dd* excitations. We find the transition from the $d_{x^2-y^2}$ ground state to the d_{xy} excited state at 1.35 eV and to the degenerated d_{xz} and d_{yz} excited states at 1.7 eV. From analysis of the polarization dependence we conclude that the $d_{x^2-y^2}$ orbital energy is at 1.5 eV and not in the mid infrared (0.5 eV) as recently suggested. We use recent theoretical arguments to show that the $d_{x^2-y^2}$ excitation is accompanied by a local spin flip resulting in a shift upwards of 0.2 eV due to the exchange interaction with neighboring spins.

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Scanning Photoelectron Microscopy of GaN Thin Films Grown on Silicon

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INTRODUCTION

GaN and related nitride semiconductors have attracted a great deal of attention in view of their use for optoelectronic devices in the blue-green spectral regions (e.g. light emitting diodes and laser diodes). Sapphire is usually used as a substrate material. To combine GaN with conventional silicon technology, growth of GaN directly on Si would be desirable. However, nucleation of GaN on Si presents a major challenge, due to its large lattice-mismatch (17 %), different thermal expansion coefficient, and the ease of formation of silicon nitride. We therefore investigated a GaN thin film grown at high temperature on a Si (111) surface without buffer layer using MOCVD.

The main questions we were interested in was imaging the chemical composition of the sample. The Scanning Photoelectron Microscope (SPEM) at beamline 7.0.1.1 is well suited for this kind of experiment [1]. It measures spatially resolved chemical composition by scanning a focussed x-ray spot over the sample surface, recording the intensity of photoelectrons emitted out of characteristic core levels. Electron spectra are then measured at selected regions on the sample for detailed analysis. The lateral resolution of this instrument is presently about 300 nm.

Results

Figure 1 shows an image ($40\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$) taken on the center of the sample. For this image the emission of the Ga 3d core levels was recorded using a photon energy of 550 eV. As the analyzer collects electrons at grazing emission, topographical information can be obtained from the images. In Fig. 1 hills are visible. Those in the upper right part of the image appear more dark. XPS Survey spectra, taken at different locations on the sample surface (A-E, as indicated in Fig. 1) are shown in Fig. 2. By comparing the peak areas for the Ga 3d and the N 1s peak, it is evident that the Ga/N-ratio differs for different positions on the sample. Moreover, Si is visible in the spectra as indicated by the appearance of the Si 2s core level at a binding energy of 150 eV. An image, recorded by using the emission from the Si 2p core level is shown in Fig. 3. This image has been corrected for topographical artefacts, showing the true distribution of Si on the sample surface. By comparison to Fig. 1, it is evident that the Si signal is not due to emission from the substrate material through holes in a GaN film that is not completely closed. Instead the maximum Si signal is recorded on the hills. This indicates a segregation of Si to the sample surface. Furthermore, the smallest Ga/N-ratio is measured at the regions showing the highest Si content which indicates that Si is present on the surface in the form of SiN.

Figure 1. Ga 3d image of a GaN thin film grown on a silicon (111) surface ($h\nu=550$ eV) The letters indicate locations on the sample surface where electron spectra were recorded (see Fig. 2).

Figure 2. Survey spectra taken at different locations on the sample surface as indicated in Fig. 1.

Figure 3. Si 2p image of the GaN thin film. The image has been corrected for topographical artefacts.

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Scanning Photoemission Microscopy Characterization of the Pyrite FeS_2 (001) Natural Surface

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INTRODUCTION

The study of pyrite has been mainly driven by its prominence in aqueous environmental systems and by its possible usefulness as a photovoltaic material. Pyrite is the most abundant sulfide mineral, and often coexists in ores of other desired minerals. The behavior of pyrite in mineral deposits in various aqueous environments is of great concern. The release of H_3O^+ and concomitant drop in pH resulting from pyrite surface oxidation can lead to the release of more toxic metals such as Cd, Pb, Zn and Cu, commonly referred to as acid mine drainage. Pyrite has been identified as a medium for the uptake and possible reduction of toxic uranyl U(VI) compounds.¹ In that study, it was proposed that partial reduction to uranium U(IV) may be correlated with the oxidation state of the pyrite surface, based on an apparent correlation of U sorption sites with pyrite oxidation zones. However, the separation of pyrite surface oxide from uranyl compound oxygen signals is not straightforward with conventional techniques, and the issue is further complicated by a gradual photo-reduction of U(VI) to U(IV) caused by incident x-rays.

We are focused on two issues: pyrite oxidation processes in general, and the sorption of uranyl compounds and their subsequent reduction. In the case of oxidation, it is difficult to distinguish pyrite oxide signals from those arising from oxide impurities. In a parallel experiment, we are characterizing the clean pyrite surface through XPS and X-ray photoelectron diffraction (XPD) measurements of the S_{2p} core level.² It is important rule out possible contributions from oxide-related features to establish the intrinsic pyrite structure.

In sorption studies, where the kinetics can vary greatly depending on the substrate composition, it is important to establish whether the deposits are associated with the nominal mineral surface or occur only in the vicinity of impurities. In both cases, Scanning Photoemission Microscopy (SPEM) is a valuable technique for separating signals from trace impurities from the overall XPS signal. The SPEM chamber employs a zone-plate scheme which focuses the synchrotron beam to ~ 150 nm. The sample is stationary during imaging and the zone plate is rastered in the illumination field to carry the focused spot across the sample surface. An order sorting aperture (OSA) is positioned within 0.5 mm of the sample surface, and the zone plate assembly is cut back on one side to allow a line of sight for the PHI spectrometer. The zone plate/OSA used for this study was optimized for $h\nu \sim 705$ eV, the energy used in our experiment. A light sputter/anneal method was chosen to prepare pyrite samples for its capability to produce a clean, flat, and stoichiometric surface.

Figure 1. Conventional XPS of pyrite FeS_2 (001) surface. The surface was prepared by light sputter/annealing. Small amounts of oxygen are always detected. A carbon over-layer develops over time in ambient UHV.

Figure 2. Scanning Photoemission Microscopy (SPEM) images of the FeS_2 (001) surface. Contrast represents the relative concentration of oxygen. a) A typical $80 \times 80 \mu\text{m}$ region, showing one major feature. b) Detailed image of an oxygen impurity elsewhere on the sample. Photon energy was 705 eV.

RESULTS

A conventional XPS survey of a natural pyrite surface cleaned by sputter/annealing is shown in Figure 1. Carbon can always be removed by this cleaning method, but gradually accumulates on the surface over a period of days in ambient UHV; this spectrum was acquired one week after cleaning. In addition to the characteristic FeS_2 signature, a relatively small amount of oxygen is present, and could not be removed by repeated sputter/anneal cycles. To establish whether the S and Fe levels in XPS and XPD measurements accurately represent clean (unoxidized) pyrite, we measured the distribution of the oxygen using the SPEM chamber on BL7.0.1. The SPEM image shown in Figure 2 represents the contrast between the signal at the O 1s core level (527 eV BE) and the adjacent background (520 eV BE). A single prominent feature is visible in Fig. 2a, representing a high concentration of oxygen. The detailed image in Fig. 2b shows another feature elsewhere on the sample. We have found that the vast majority of the surface contains negligible amounts of oxygen except in sparse concentrated regions.

To identify the character of the nominal clean pyrite surface as well as features such as in Fig. 2, we obtained spectra, shown in Figure 3, with the beam focused on and away from these features. A typical spectrum representing a featureless region is shown in Fig. 3a. Oxygen is absent from this area of the sample, and the only impurity seen in the spectrum is carbon. Much of the carbon can be attributed to signal from the zone plate, and the rest is a result of the gradual carbon deposition from one week exposure to ambient UHV (the two carbon contributions can be separated by biasing the sample by -5V to separate the peaks, as seen in the spectra). This result gives credence to our

Figure 3. Spectra of FeS_2 (001) surface using a zone-plate system with an incident spot size of $0.15 \mu\text{m}$. Spectra represent a) a pure region, b) an impurity, c) impurity with FeS_2 component subtracted, d) & e) other impurity difference spectra. Photon energy was 705 eV.

assumption that oxidized pyrite is not represented in the S_{2p} core level structure in the XPS and XPD measurements of clean pyrite.² In Fig. 3b, with the beam focused on the feature seen in Fig. 2b, the spectrum shows significant Si, Al, and O signals, and a reduced signal from Fe and S, suggesting an aluminosilicate mineral inclusion. An accurate signature of the inclusion, shown in Fig. 3c, was obtained by subtracting the FeS_2 component of Fig. 3a from Fig. 3b. Difference spectra from other impurities are shown in Figs. 3d and 3e. We found several inclusions with similar composition to Fig. 3d, containing U, As, and Ca. In other spectra (not shown) we have identified also Pb, and $CaCO_3$ inclusions. The trace presence of U, Pb and other heavy metals as well as As in natural pyrite is well known, but we were surprised by their relative abundance. The consistent coexistence of U and As on the sub-micron scale suggests a mineralogical association. For instance, the deposition of U may be promoted by the presence of As through a reductive process. It is clear from these measurements that a sub-micron characterization of the surface is necessary before conducting uranyl sorption studies to identify already existing U and possible reactive sites.

It is also important to consider the presence of inclusions in measurements of sorbed species such as oxygen. The reactivity of defect sites could be enormously different than for the pure FeS_2 surface, and it would be difficult to isolate their contribution to "oxidation". Indeed, several studies have reported very little chemical change in Fe and S core levels, while observing the adsorption of H_2O , OH, and related species.³ Such inclusions are likely a general feature of natural pyrite surfaces, however they may easily go undetected with less surface-sensitive x-ray lamp XPS.

CONCLUSION

We have used SPEM to better characterize a typical natural FeS_2 (001) surface. The small oxygen signal seen in conventional XPS is seen to be concentrated in trace mineral inclusions. The S_{2p} core level structure we have observed in parallel XPS and XPD experiments is thus intrinsic to unoxidized pyrite. We have identified several trace impurities in the inclusions: U, As, Ca, C, Si, Al, Pb, and of course O. U is always accompanied by As in our measurements, suggesting that they are associated. It will be essential to characterize a given sample region in this way before and after sorption studies to establish the nature of the sorption process.

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Si(100) dimers on clean and acetylene covered surfaces

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The properties of acetylene adsorption on Si(100) are an example of the behavior of small hydrocarbons on silicon surfaces. There is considerable interest in bonding units that can be used for attaching functional groups to silicon surfaces, which would have a wide spectrum of applications¹. The surface science understanding of Si surfaces has made key contributions for “wet” chemistry adsorption applications. Since near-flat (100) surfaces have two domains we use the property that a miscut of 3.5° or large gives a single-domain 2×1 surface, which reduces the complexities of surface-structure analysis. The 2×1 net is the result of Si surface atoms forming dimer pairs.

The Si(100) surfaces were cleaned by widely used methods which primarily consists of desorbing an oxide layer by heating in the ultrahigh vacuum condition. The well known surface components for the Si 2p level and the valence bands (VB) are obtained. A high energy-resolution energy distribution curve (EDC) is shown in Fig. 1, where the Si 2p peak is fitted with component lines. During the fitting, a Lorentzian width of 0.085 eV, a spin-orbit splitting of 0.602 eV and a branching ratio of 0.5 is used for all components. There are five of them, which could give concern for over interpretation of the data, but careful analysis and examination of the residual between the data and the fit demonstrates the appropriateness of the results. The line fitting is very close to that reported by others and we agree with their component assignments^{2,3,4}.

The surface is saturated with acetylene which is 0.5 monolayer (ML) film. The spectrum and its component lines are shown in Fig. 2, where only three components are found. Note, that the “minimum” between the spin-orbit pairs in the EDC is gone in the latter case because of the change in the environment of the Si atoms. Figure 3 shows the associated C 1s EDC. The valence band spectra that accompany the above spectra are shown in Fig. 4. It is again found that the surface state is extinguished by 0.5 ML of C₂H₂. The adsorption shifts the spectral features by about 200 meV due to the change in surface-Fermi-level position.

After C₂H₂ adsorption there remains only two of the component lines found in the clean surface EDC; B is for bulk Si atoms, S' is for Si atoms in a site in the surface region, and is attributed to atoms in the second layer.. The small line C could be Si atoms in the third layer or at defect locations. The components S and SS are attributed to the up and down

Si atoms in the asymmetric surface dimers and are the lines are extinguished by the adsorption process.

What is the origin of the new component line A in the covered spectrum? It is attributed to first-layer Si dimer atoms which are no longer in an asymmetric configuration. The line has about the combined areas of the lines S and SS. The “singleness” of the line indicates that all the first-surface-layer Si atoms are in chemically-equivalent sites but not geometrically-equivalent sites. The symmetry and lack of the obvious components in C 1s spectra (Fig. 3) supports this assignment. As we have reported elsewhere the acetylene molecule is bonded to four surface Si atoms which supports the chemical-equivalency assignment for all the Si surface atoms.

The conclusion is that surface Si atoms still have dimers-like bonds and they are symmetric.

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Fig. 1. Curve-fitting of Si 2p EDC for clean Si(100)-2 $\times$ 1 surface. The solid line is the fit line and the solid circles are experimental data. Component are assigned to Si atoms: B for bulk atoms; S for up atoms in dimers; SS for down atoms in dimers; S' for second-layer atoms; C for atoms at defects or in the third layer.

Fig. 2. Curve-fitting of Si 2p EDC for a saturated C₂H₂/Si(100)-2 $\times$ 1 surface. The solid line is the fit line and the solid circles are experimental data. Component A is due to Si atoms in dimers which bond to acetylene. Components B and S' are found in the clean EDC and are due to bulk and second layer atoms, respectively.

Fig. 3. High-energy-resolution C 1s core-level spectrum for 0.5 ML of acetylene at room temperature (RT).

Fig. 4. The valence band spectra of (a) the clean surface; (b) the surface exposed 0.5 ML acetylene at RT. The surface state (S) is totally extinguished.

Soft X-ray spectromicroscopy studies of industrial polymers

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INTRODUCTION

Soft X-ray spectromicroscopy, using the ALS BL 7.0.1 scanning transmission X-ray microscope (STXM) offers many unique opportunities for chemical micro-analysis of materials of industrial relevance. Over the past year we have made significant progress in several areas, including quantitative speciation of mixed phases and analyses of artificial thin film structures. These capabilities are illustrated with results from studies of polyurethanes (Dow) and photoconducting films (Xerox). Unless indicated otherwise, all data was recorded at the ALS.

POLYURETHANES – QUANTITATIVE CHEMICAL ANALYSIS (SPECIATION)

Polyurethane polymers, in the form of free-rise or molded foams, are widely used in the automotive and furnishings industries. World-wide polyurethanes is a \$2 billion business, of which Dow Chemical is a market leader. Quantitative, spatially resolved analysis of functional group composition (particularly the urea and urethane content) is needed to help understand the chemical basis for the microstructure of polyurethane polymers [1] and to correlate with physical and mechanical properties. We have demonstrated the quantitative analysis capabilities of NEXAFS spectromicroscopy [2] through a study of three test polyurethane polymers in which a controlled variation of the urea and urethane content was achieved by careful adjustment of the water content in the formulation. The C 1s, N 1s and O 1s edges were all investigated for their analytical potential; the C 1s spectrum was found to be most suited for quantitative analysis. **Fig. 1** illustrates the fit of the C 1s spectrum of one of these three standard species to the optimized sum of reference spectra [3].

Fig. 1 Quantitative analysis of a urethane (carbamate)-rich polyurethane [2]. E=ether, U=urea, C=carbamate. Bottom: comparison of spectrum (dots) with optimized sum (lines). Top: compositional variation of residuals with ratio of other two components fixed. The fit is sensitive to few % changes in composition.

MATRIX : Σ 4 spectra

PRECIPITATES : Σ 4 spectra

Fig. 2 Quantitative composition of matrix and precipitates based on fitting spectra [3]. This analysis was the first direct confirmation that precipitates in water-blown polyurethane foams are driven by urea insolubility in the reaction. (this data was recorded in point spectral mode at the Stony Brook STXM at NSLS)

Comparison with predictions from formulation chemistry indicates that C 1s NEXAFS can determine the content of chemical components at the 4-20 mol% level, with 10-20% accuracy. This is a remarkably good level of quantitation given the relatively small spectral differences which are the basis for this quantitative chemical analysis (mainly a shift of ~ 0.4 eV between the urea and urethane $\pi^*_{C=O}$ signals around 290 eV), and the extensive overlap of these key features with broad underlying σ^* resonances. The good energy resolution provided by the ALS BL 7.0 STXM (~ 0.1 eV) is very beneficial in being able to track the subtle changes in the line shapes in the 288-291 eV range which provide the sensitivity to quantitative composition.

Fig. 2 illustrates application of this analysis to a 'real world', macro-phase segregated polyurethane [4] (for the test samples every effort was made to avoid heterogeneity). As illustrated, it is possible to obtain quantitative analysis near the limits of the spatial resolution. The image and spectra in Fig 2 were recorded with the Stony Brook STXM at NSLS, which has lower beam intensity but faster point spectral acquisition than the ALS. In order to obtain similar data at the ALS a 'stack' or 'linescan' approach is required. These methods are now being used routinely to obtain reliable, high spatial resolution analysis of radiation sensitive samples.

POLYURETHANES – CO-POLYOL POLYMER (CPP) PARTICLES

In order to make foams with higher hardness several different strategies are presently employed [5]. Copolymer polyols (CPP) – polymer dispersions in polyether polyol, inorganic fillers, and low molecular weight cross-linker polyols are preferred for stiffening slabstock foams. In order to understand how these co-polymer polyols affect mechanical properties such as elastic modulus, tear strength and resiliency, and in order to develop improved CPP substances, it is important to have analytical techniques which can probe the chemistry at the required spatial scale. While traditional chemical spectroscopies such as infrared or NMR are excellent at chemical speciation, they do not have adequate spatial resolution to address questions relating to the submicron composition of blends containing CPPs. Analytical transmission or scanning electron microscopy has superb spatial resolution but in many cases the high energy electron beam causes extensive radiation damage in fully focussed mode. In addition the chemical sensitivity of NEXAFS is better than electron energy loss spectroscopy on account of higher energy resolution.

STXM images at selected photon energies allow unambiguous identification of styrene-acrylonitrile (SAN)-based and poly-isocyanate poly-addition product (PIPA)-based particles down to particle sizes at the limits of STXM spatial resolution (50 nm) (**Fig. 3**) [6]. Surprisingly, the particle size distribution derived from the STXM images extends to smaller particle sizes than that from a TEM image [6]. This suggests that, in selected cases, X-ray microscopy may have advantages over electron microscopy even in primarily imaging applications, owing to superior chemical contrast mechanisms. A further aspect of the CPP study is the determination of the composition of individual SAN-CPP particles by fitting to sums of the component polymer spectra (pS, pAN). A number of particles were analyzed to study compositional distributions [6].

Figure 3. STXM images of a polyurethane made with both SAN and PIPA copolymer polyol (CPP) fillers. Both types of CPP are at high contrast in the left image (285 eV) whereas only the SAN is high contrast in the right image (287 eV).

ANALYSIS OF PHOTOCONDUCTING IMAGING FILMS

Polycarbonate (PC) capping layers are used to protect the photosensitive layer used to convert the image to charge in the xerographic process. The PC cap layers are doped with compounds which allow transfer of charge from the photosensitive layer to the outer surface, where the toner particles are deposited, patterned via electrostatic attraction, and ultimately transferred and fixed to paper. The ALS STXM has been used to investigate the spatial distribution of the charge transfer compound in an experimental xerography film. **Fig. 4** shows a STXM image of the film made in the N 1s energy region. Intensity profiles extracted from this image or linescans (**Fig. 5**) indicate a high degree of spatial uniformity of the charge transfer compound. N 1s spectra extracted from linescans across the film, showed that N 1s NEXAFS could readily distinguish the chemical form of the imaging agent and the charge transfer compound, and thus investigate the uniformity of contact between these two species, a critical aspect to the performance of the xerographic film.

Subsequent to the ALS STXM measurements, a complementary analysis was made of the same sample (same grid) using the McMaster high performance JEOL-2010F TEM/STEM equipped with a windowless X-ray fluorescence (EDS) detector, and pEELS. While the spatial resolution of the TEM images was significantly higher than STXM, the analytical information was inadequate to address the problem. In particular, pEELS did not see the nitrogen edge, and the N elemental map from EDS with ~70 minutes integration was insufficient to conclude anything about spatial uniformity, and gave no chemical speciation information (see **Fig. 6**).

Fig. 4 Image at 410 eV of a cross-section of a photoconducting film embedded in epoxy. The optically active layer is at the PC-PET boundary. The analysis focussed on the degree of uniformity of a N-containing charge transfer agent in the polycarbonate (PC) cap layer. The line indicates the position of the linescan displayed in the next figure.

Fig. 5 Optical density profiles at different photon energies in the N 1s region extracted from a linescan across the PC layer of the photoconducting film. Aside from the irregular particles of the optically active component, the N-content in the PC layer is uniform to ~5%.

Fig. 6 Bright field and X-ray fluorescence (EDS) images (windowless detector) of the photoconducting film recorded using a JEOL 2010 scanning transmission electron microscope. Only a small amount of N in the region of the optically active layer was detected. In the N image each dot represents 1-5 counts. The image size was (256x256) with a total record time of 70 minutes (McMaster, May 1998).

SUMMARY

These examples clearly demonstrate the power of NEXAFS spectromicroscopy for studies of the chemical basis of sub-micron structure. The technique is particularly useful for quantitative analysis of radiation sensitive materials or systems which require subtle chemical differentiation, such as the urea-urethane distinction in polyurethanes. An additional attractive aspect is the ready ability to adapt STXM to a wide variety of environments, including studies of polymer and other particles in an aqueous environment (see presentation of hydrated super-absorbent polymers elsewhere in this compendium).

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Soft X-ray Spectroscopic Study of $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$

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INTRODUCTION

C_{60} reacts with alkali and alkaline earth metals to form ionic intercalation compounds or fullerides. Very few reports have been published on the formation of fullerides based on transition metals and C_{60} . This can be due to the fact that such compounds may be thermodynamically unstable and separate into bulk metal and pure C_{60} . In a recent study, however, it was suggested that a Ti_xC_{60} compound could be synthesized by co-evaporation of Ti and C_{60} [1]. This was also confirmed by soft x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) [2].

In the present study we have used XES and XAS to study the oxidized low Ti-content C_{60} film. This may be a useful method to learn about the origin of these titanium fulleride compounds, as XES has a few particularly interesting properties. Firstly, it allows direct probing of the site and element specific angular momentum components of the density of states (DOS), and, secondly, it provides bulk information owing to the relatively large probing depth.

EXPERIMENTAL

The Ti_xC_{60} film was made by co-evaporation of C_{60} and Ti from a Knudsen-type effusion cell and an e-beam evaporator, respectively. The reference film C_{60} was made at the same conditions without Ti evaporation. The films were deposited on Si(100) substrates in a UHV deposition chamber with a base pressure of 5×10^{-10} Torr [1]. After oxidation the composition of the sample was determined to $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ by XPS.

The experiments were performed at beamline 7.0 at ALS, LBNL. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [3]. XAS spectra were obtained by measuring the total electron yield from the sample current. The resolution of the monochromator was set to 0.20, 0.40 and 0.80 eV, respectively, for the C *1s*, Ti *2p* and O *1s* absorption edges. The XAS spectra were normalized by means of the photocurrent from a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam. The XES spectra were recorded using a high-resolution grazing-incidence grating spectrometer [4]. During the x-ray emission measurements, the resolution of the beamline was the same as in the XAS measurements, and the resolution of the grating spectrometer was set at 0.5 eV, 0.7 and 1.0 eV, respectively, for C *K*, Ti *L* and O *K* emission spectra.

RESULTS AND DISCUSSION

Figure 1 displays the C *1s* absorption spectra of $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$, pure C_{60} and $\text{TiC}_{0.61}$. The C_{60} XAS spectrum presents four π^* resonances with the lowest unoccupied molecular orbital (LUMO) located at 284.5 eV and many discrete absorption features (multi-electron excitations) superimposed on a shape resonance in the near-continuum part. The relevant π^* unoccupied molecular orbitals governing the XAS spectrum were found to be of t_{1u} (A_1), t_{1g} (A_2), $t_{2u}+h_g$ (A_3), $h_u+a_g+g_g$ (A_4) symmetries [5].

The C $1s$ absorption spectrum of Ti doped thin film shows less prominent π^* resonances as compared to C_{60} fullerene. The absorption peaks corresponding to A_3 and A_4 for C_{60} are visible in $Ti_{22}O_{59}C_{60}$ with less intensity and broader linewidth. The reduced peak height of the LUMO peak may indicate a charge transfer towards to the C_{60} molecule. The absorption peaks in the upper conduction band (σ^*) are less resolved in the $Ti_{22}O_{59}C_{60}$ film. The C $1s$ absorption of $TiC_{0.61}$ shows a broader π^* resonance at 285.2 eV and a σ^* resonance centered at 292 eV.

Figure 1. C $1s$ x-ray absorption spectra of C_{60} , $Ti_{22}O_{59}C_{60}$ and $TiC_{0.61}$.

Figure 2 shows O $1s$ XAS spectra of $Ti_{22}O_{59}C_{60}$ and a reference TiO_2 sample. As one can see, the spectra are divided into two regions below and above the ionization threshold (~ 536 eV), respectively. The first region is attributed to oxygen $2p$, weight-hybridized in states of predominantly Ti $3d$ character [6, 7]. The second region, above the threshold, is attributed to oxygen p character hybridized with Ti $4s$ and $4p$ states [8]. It is concluded that the large-energy spread (some 15 eV above E_F) of oxygen $2p$ states is an indication of strong covalency in the TiO_2 compound.

In a purely ionic model, oxygen has a configuration of O $1s^2 2s^2 2p^6$ and the $1s \rightarrow 2p$ channel would be closed in XAS. Covalency reduces the number of filled states with O $2p$ character, so that the strength of the O $1s$ signal at the threshold is related to the degree of covalency [9]. The decrease in intensity of the first-region bands, relative to the second-region bands is consistent with the observation in a O $1s$ XAS study going across the transition-metal series [6]. The main reason for this was the decrease in number of unoccupied $3d$ states available for mixing with O $2p$ states. In the O $1s$ absorption of $Ti_{22}O_{59}C_{60}$, the decrease in intensity of the first band may be caused by the interaction between Ti $3d$ and C $2p$ from C_{60} .

Figure 2. O $1s$ x-ray absorption spectra of TiO_2 and $Ti_{22}O_{59}C_{60}$.

At the Ti $2p$ edge of TiO_2 , the absorption spectrum contains four dominant peaks (Fig. 3). The first and second peaks are related to respectively the t_{2g} and e_g symmetries of the L_3 edge with an energy splitting of some 2.0 eV. The third and fourth peaks are related to respectively the t_{2g} and e_g symmetries of the L_2 edge [10]. Below the first absorption peak (at 456.7 eV) there are small leading structures that are related to a transition which is forbidden in LS-coupling, but it becomes allowed because of the multiplet $p-d$ interactions.

In the Ti 2*p* absorption spectrum of Ti₂O₅C₆₀, the absorption peaks are shifted towards low-energy, and the energy splitting (about 1.5 eV) and intensity ratio between *t_{2g}* and *e_g* become less as compared to TiO₂. The experimental observations can be explained as a superposition of two different titanium sites with the 3*d*¹ and 3*d*⁰ configurations. In the x-ray absorption study of La_{1-x}Sr_xTiO₃ perovskites [11], it was demonstrated that the metal (Ti) 2*p* x-ray absorption spectra of the La_{1-x}Sr_xTiO₃-series can be described as a superposition of *x* times the spectrum of SrTiO₃ (3*d*⁰ configuration) plus 1-*x* times the spectrum of LaTiO₃ (3*d*¹ configuration).

Figure 3. Ti 2*p* x-ray absorption spectra of TiC_{0.61}, TiO₂ and Ti_{2.2}O_{5.9}C₆₀.

The resonant and non-resonant C *Kα* XES spectra of C₆₀, Ti_{2.2}O_{5.9}C₆₀, and TiC_{0.61} are presented in Figure 4. The resonant C *Kα* emission of C₆₀ contains five resolved features, labelled E₁, E₂, E₃, E₄ and E₅. The sharp peak at 284.5 eV is the recombination peak which has the same energy as the incoming photons. According to *ab initio* Hartree-Fock calculations [12, 13] the first emission band E₁ corresponds to the highest occupied molecular orbital (HOMO) with 4*h_u* symmetry, while the second band E₂ represents a combination of the nearly degenerate 4*g_g* and 7*h_g* orbitals. The bands E₃ and E₄ contain more complicated molecular orbital combinations. The band E₅ contains the 2*h_u*, 3*t_{1u}* and 2*g_g* orbitals. A strong excitation dependence for all these features can clearly be discerned as comparing the resonant and non-resonant x-ray emission spectra in Figure 4.

The C *Kα* emission spectrum of the Ti_{2.2}O_{5.9}C₆₀ film is similar to pristine C₆₀ regarding the total emission bandwidth, peak energy positions and intensity ratio of different emission bands. On the other hand, the C *Kα* emission spectrum of TiC_{0.61} exhibits a single-band structure with much smaller bandwidth for both resonant and non-resonant excitations. This is a clear evidence that the buckyball structure is preserved in Ti_{2.2}O_{5.9}C₆₀. The small difference reflects the influence on the electronic structure of the C₆₀ molecule by the presence of titanium and oxygen atoms.

Figure 4. C *Kα* x-ray emission spectra of C₆₀, Ti_{2.2}O_{5.9}C₆₀ and TiC_{0.61}.

Figure 5 shows the O $K\alpha$ emission spectra of TiO_2 and $\text{Ti}_{1.2}\text{O}_{5.9}\text{C}_{60}$ with resonant and non-resonant photon excitations. Basically, all four spectra exhibit two sub-band structures. In the resonant case, the splitting between the two sub-bands is 3.2 eV in TiO_2 and only 2 eV in $\text{Ti}_{1.2}\text{O}_{5.9}\text{C}_{60}$. The full width at half maximum (FWHM) and the intensity of the low-energy peak of the O $K\alpha$ spectra vary with the energy of the incoming photons as shown in Figure 5. Due to strong Ti $3d$ - O $2p$ hybridization, the occupied O $2p$ states form a wide band, split into bonding and anti-bonding sub-bands [14]. The lower energy splitting of the sub-bands in $\text{Ti}_{1.2}\text{O}_{5.9}\text{C}_{60}$ in Fig. 5 may be caused by the chemical interaction between Ti and C_{60} .

Figure 5. O $K\alpha$ x-ray emission spectra of $\text{Ti}_{1.2}\text{O}_{5.9}\text{C}_{60}$ and TiO_2 .

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Spin-Density-Wave Band Gap in Chromium Thin Films

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INTRODUCTION

Magnetism and, especially, antiferromagnetism in thin films is a topic that has recently gained a lot of attention, the reason being twofold. For one, these magnetic layers can be arranged as multilayers that exhibit the giant magnetoresistance effect, such as in the ferromagnetic-antiferromagnetic FeCr multilayer system [1]. On the other hand, research into high transition temperature superconductors has revealed many material systems that exhibit antiferromagnetic phases [2], pointing towards a possible relationship between superconductivity and antiferromagnetic coupling. The analysis of such complex systems can be guided by the study of simpler materials, among which Cr metal has a special place in that it is not only an itinerant antiferromagnet, but also exhibits an incommensurate spin density wave (SDW), thus relating Fermi surface features to the magnetic properties [3]. Indication that the formation of the SDW below the Néel transition leads to a considerable reduction of the Fermi surface came originally from anomalous skin effect [4] and de Haas – van Alphen [5] measurements. A more direct determination of the electronic bandstructure from photoemission [6,7,8,9,10], however, encountered the problem of residual surface contaminants and was so far inconclusive, especially the formation of an energy gap or a transition temperature could not be established.

We have performed angle-resolved photoelectron spectroscopy (ARPES) experiments with high momentum and energy resolution on ultra-clean Cr(110) thin films that provide electronic bandstructure data. For the first time, direct evidence of the bandstructure backfolding as well as of the behaviour of the order parameter, i.e. the SDW energy gap that closes a function temperature, is presented.

EXPERIMENT

The ARPES experiments were carried out at beamline 7.0.1 at the Advanced Light Source. The energy resolution used was 50 meV, the momentum resolution was 0.05 ($2\pi/a$), with $a = 2.88 \text{ \AA}$, the lattice constant of Cr. The Cr(110) surface was prepared in ultra-high vacuum by evaporation of Cr onto a clean W(110) crystal and subsequent annealing. From a measurement of the size of the BZ, the film surface was strain-free. The crystal perfection of the Cr thin film was judged from a (1×1) LEED pattern as well as from the sharpness of the photoemission features.

EXTENT AND MAGNITUDE OF THE ENERGY GAP

From the previous experimental and theoretical work it is established that the nesting of the SDW wave vector, q_{SDW} , with respect to the bcc Brillouin zone Fermi surface occurs between the electron “octahedron” at Γ and the hole “octahedra” at the six H points. These Fermi surface structures are of very similar shape and curvature, as sketched in Fig. 1a. We chose the photon energy so that $k_{\perp}$ samples the bulk BZ (on which the surface BZ is superimposed) at Γ . Experimental bandmaps with this $k_{\perp}$ and with $k_{\parallel}$ varied along Γ –S were taken at temperatures above (panel b, $T = 490\text{K}$) and below (panel c, $T = 300\text{ K}$) the measured surface Néel temperature (440 K, see below). In comparing Fig 1b with Fig. 1c we observe (i) a second branch emerges at low temperature that is falling towards S, albeit weaker in intensity

FIG. 1. a) Schematic of the bulk and superimposed surface BZ. Below bandmaps along Γ -S taken at b) +190 °C and c) R.T. (Fermi distribution eliminated by division through background in a featureless region). In c) the upper branch can also be seen.

FIG. 2. Lower section of the SDW energy gap. The critical behaviour near the surface phase transition can be fitted with a power law

than the branch rising from Γ , and (ii) a band forms above E_F that exhibits a minimum in close vicinity to the maximum of the band below E_F , thus forming an almost direct gap which we determine to 120 meV. We associate this gap with the formation of a static spin density wave. We find that the gap is reasonably well matched in position, though not energy, by first-principles calculations, and that it extends with approximately constant magnitude over much of the electron octahedron. Moreover, using wider scans, we infer a nesting vector of $\mathbf{q}_{SDW} = 0.95 \pm 0.02 \Gamma$ -H, which is in excellent agreement with neutron scattering measurements [11].

CRITICAL BEHAVIOUR AT THE SURFACE PHASE TRANSITION

We monitored the order parameter of the phase transition by measuring the temperature-dependence of the energy gap. This implies acquisition of energy band maps like in Fig. 1 as a function of temperature and laying cuts at about 40% Γ -S in order to document the magnitude of the energy gap. From closer examination of numerous individual bandmaps, a surface transition temperature of $T_N^S = 440 \pm 10$ K is determined, considerably above the bulk Néel temperature of $T_N^B = 311$ K. The temperature dependence of the peak position of the lower branch is plotted in Fig. 2. The data can be represented quite well over a relatively wide temperature range by a power law $(1 - T/T_N)^\beta$ with $\beta = 0.38 \pm 0.05$. For comparison, the 3D Ising exponent is 0.325 and the mean-field exponent is 0.5. Given the long spatial range of the spin wave, an exponent intermediate between these two is quite reasonable.

However, in looking at the critical behavior of the magnetization, determined as a bulk quantity from neutron scattering [3], it is generally inferred that the transition, contrary to expectation for

a simple spin system, is of “weak” first order, with a small discontinuity at the critical temperature T_N^{Bulk} . The data shown in Fig. 2 are compatible with a small discontinuity to the first or second data point below the transition. To our knowledge, however, no other truly surface-sensitive measurement of the surface transition exists. Moreover, no surface phonon dispersion or surface magnetic moment determination at the (110) surface has been carried out. From W(110) it is known that a surface phonon anomaly exists [12], indicative of significant electron-phonon coupling at the surface. If this were also true for the homologous d-transition metal chromium, then such enhanced coupling could also lead to a weak first order transition.

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STXM Characterization of Crosslink Density in SAP

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INTRODUCTION

Customer demand for thinner diapers and other hygiene products has been leading manufacturers to decrease the amount of cellulose fluff and increase the proportion of superabsorbent polymer (SAP) used in their products. This increases the need for gel strength (weight bearing capacity) of the hydrated SAP so that they maintain their water absorption under load [1]. In order to meet the demands for the higher liquid absorption under load while maintaining liquid capacity, Dow and most other suppliers of superabsorbent polymers are using structured particle technology to enhance the strength of their material. These so called third generation superabsorbent polymers are crosslinked in a core-shell structure to improve liquid absorbence under load. Other than macroscopic tests to measure the liquid absorption capacity of the modified SAP, until recently there has been no method to determine the structure of these materials. In an effort to provide feedback for improvements in the process chemistry, we have been developing methodology to apply conventional and scanning transmission x-ray microscopy (CTXM and STXM) to examine water swollen experimental superabsorbent polymers which had been crosslinked in different ways. Since the relationship between degree of swelling and crosslink density is well established[2], we can determine the microscopic variation in crosslink density from the polymer density in the hydrated SAP. To date no other characterization method has been able to demonstrate sensitivity to the variations in crosslink density at the spatial scale available by STXM.

In work reported previously, we demonstrated that we could visualize the variation in crosslink density in core / shell type superabsorbent polymers using STXM [3]. These results can be very useful in understanding the effect of variations in crosslink chemistry and process parameters. Experiments performed during the last year have focused on quantifying the crosslink density on the submicron scale. The microscopic variation in the polymer density can be determined from the x-ray absorption intensity in STXM with a 50 nm spatial resolution.

RESULTS

The intensity of x-rays transmitted through a sample of thickness z is given by Beer's law:

$$I = I_0 \exp\{-\mu(E)\rho z\} \quad (1)$$

where $\mu(E)$ is the energy dependent mass absorption coefficient, ρ is the density and I_0 is the incident x-ray intensity. For multiple chemical species in the sample, the absorption by the different species is additive so that for the system of interest with water and polymer present at the same time equation 1 becomes:

$$\ln I/I_0 = \mu_{\text{poly}}(E)\rho_{\text{poly}}z + \mu_{\text{water}}(E)\rho_{\text{water}}z \quad (2).$$

By determining the energy dependent mass absorption coefficient and making the x-ray absorption measurements at two different energies, equation 2 can be solved to determine the polymer density. If images are recorded at two different energies, then the polymer density can be determined at every pixel of the image. Similar analytic methods have been used by Zhang et al. to map the DNA in sperm cells using STXM [4].

Figure 1. Mass absorption coefficient for superabsorbent polymer in the near edge spectral region (280-340 eV) compared to that for water at the same energy.

The x-ray absorption cross sections for all the elements have been tabulated as a function of energy by Henke, Gullikson and Davis, and are accurate for energies sufficiently far from an ionization threshold [5]. Near the threshold, the NEXAFS spectrum must be measured. Figure 1 is a plot of the mass absorption coefficient for water, and for superabsorbent polymer (80% neutralized sodium polyacrylic acid). The latter was determined by fitting a measured NEXAFS spectrum to the tabulated value of the mass absorption coefficient [5] below and above the near edge region (280 and 320 eV). The NEXAFS spectrum of SAP has an intense peak at 288.8 eV which is attributed to an electronic transition from a C(1s) orbital to the $\pi^*(\text{C}=\text{O})$ orbital on the acrylate C atom. This is the energy which provides the best contrast between water and polymer for STXM images (factor of 16 difference in cross sections). At 280.0 eV the photoabsorption cross sections for the two materials are similar.

In the example in Figure 2, we have examined a microtomed thin section of a spherical experimental SAP bead at 280.0 eV (below the C(1s) edge and at 288.8 eV (which is the peak absorption energy for the $\text{C}(1s) \rightarrow \pi^*(\text{C}=\text{O})$ transition of the acrylate carbon). The sample is completely hydrated in 0.9% salt water and there is excess salt water in the cell. In the 288.8 eV image the polymer section is clearly observable and the higher crosslinked shell can be seen near the edge of the sample as an arc across the top half of the image. Measurements of the swelling of these samples prior to crosslinking the surface, determined that the core of this SAP sample absorbs 68 times its' weight in water. Though the higher crosslinked shell will absorb somewhat less water, because of the similar absorption cross sections for water and polymer, and the excess water in the cell (up to 3 μm thick), at 280.0 eV, the polymer is invisible. From the latter image, a gradient in the water layer thickness can be discerned, with decreasing thickness from top to the bottom. Utilizing the known and measured x-ray absorption cross sections for water and

Figure 2. STEM images measured at 200.0 and 200.3 eV photon energy (top) and the polymer density calculated from these images (bottom left). At the bottom right is a plot of the polymer density extracted from the image at left along the indicated line to highlight the core / shell structure of the crosslinking in this sample of experimental SAP.

polymer and the additivity of the x-ray absorption cross sections, we can solve equation 2 to calculate (on a pixel by pixel basis) the image at the center of Figure 2 in which the intensity is in terms of polymer concentration. From this data and the Flory Rehner equation [2], the crosslink density can be also easily determined on a pixel by pixel basis.

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The electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_8$ studied by soft X-ray absorption and emission spectroscopies

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INTRODUCTION

Soft X-ray emission provides a means of elemental selectivity, chemical sensitivity to separate the partial contributions to the total density of states. This technique probes the bulk property of the matter owing to the large penetration depth of photons. Recently, synchrotron radiation sources producing intense tunable monochromatized X-ray beams have opened up new possibilities for soft X-ray emission spectroscopy (XES) [1]. The ability to tune the excitation with narrow bandpass allows one to discriminate the close lying core excited states, and thereby to separate e.g. chemical shifted species in the emission spectrum.

In the previous investigations, resonant SXES was used to study the electronic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ [3]. It has been demonstrated that the spectral shape of the O $K\alpha$ emission depends on the relative number of excited specific-site oxygen atoms. Tuning the excitation photon energy to the specific edges enhances the excitation of one particular chemically shifted species, such as separating in-plane oxygen from out-of-plane oxygen in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ cuprates. Thus, the features in the XAS spectrum related to the O unoccupied states can be characterized in terms of the density of states projected on individual oxygen sites [2-3].

In the present paper, we study the electronic structure of superconductors $\text{YBa}_2\text{Cu}_3\text{O}_8$ with a combination of XAS and XES. In the following, we will adopt the notation of O(1), O(2), O(3), and O(4) for, respectively, the oxygen sites between the Cu(1) atoms in the chain, those of the plane, and the apical sites.

EXPERIMENT

The $\text{YBa}_2\text{Cu}_3\text{O}_8$ [4] were prepared by solid-state sintering of the starting materials at 940°C for one week, annealing at 400°C in O_2 for two days to obtain a fully oxidized sample. The samples were characterized by X-ray diffraction and no impurities could be detected. The oxygen content was determined by iodometry.

The measurements were performed at beamline 7.0 at ALS, LBNL. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [5]. The XAS spectra were obtained by recording the fluorescence-yield with 0.3 eV resolution and normalized to the photocurrent of a clean gold mesh to correct the intensity loss of the excitation beam. The O $K\alpha$ emission was recorded using a high-resolution grazing-incidence grating fluorescence spectrometer [6]. The incidence

angle of the photon beam was about 20° to the sample surface in order to reduce self-absorption effect. The X-ray fluorescence was detected at the direction perpendicular to the incident photon beam in the horizontal plane. The resolution was set to 0.5 eV and 1.2 eV at the energy of 530 eV, respectively, for the monochromator and spectrometer. Zn $L\alpha$ and $L\beta$ emission lines were recorded in second order for energy calibration of O $K\alpha$ spectra.

RESULTS AND DISCUSSION

The O $1s$ XAS spectrum of $\text{YBa}_2\text{Cu}_4\text{O}_8$ are displayed in Figure 1. O $1s$ spectrum reflects the unoccupied O $2p$ states. We observe that an absorption pre-peak appears already at 528.5 eV which is an indication of induced O $2p$ holes upon oxygen doping. This is similar to that in the O $1s$ absorption edges of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [7-9], which was interpreted by a doping-induced shift of the Fermi level into the valence band, the creation of the holes in the valence band, and a transfer of spectral weight from states in the upper Hubbard band to the upper edge of the valence band [10-12]. The first absorption peak in the XAS spectrum of $\text{YBa}_2\text{Cu}_4\text{O}_8$ is considerably broader than expected from experimental resolution (0.5 eV) and the lifetime width of the O $1s$ state. It is most likely due to vibrational excitations and chemical shifts between different oxygen sites.

Figure 2. O $K\alpha$ XES and O $1s$ XAS spectra of $\text{YBa}_2\text{Cu}_4\text{O}_8$ which map occupied and unoccupied states close to the Fermi level, respectively.

Figure 2 shows the valence-core XES spectrum along with XAS spectrum. In the case of $\text{YBa}_2\text{Cu}_4\text{O}_8$, the absorption-emission spectra show the unbroken density of states crossing the Fermi level, reflecting the metallic character of $\text{YBa}_2\text{Cu}_4\text{O}_8$.

O $K\alpha$ profiles, similar to those of $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ [13], are also observed for $\text{YBa}_2\text{Cu}_4\text{O}_8$. This compound contains double Cu(1)-O(1) chains, thus having the larger number of O(1) atoms per unit cell. Same as for $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$, O $K\alpha$ spectra of $\text{YBa}_2\text{Cu}_4\text{O}_8$ do not show strong dependence on varying excitation energies (see in Figure 3). The spectra resemble that obtained with an electron beam in prior study [14]. Nevertheless, one can notice that the low-energy shoulder in 528.7-eV photon excited spectrum is less intense as compared to other spectra and extends somewhat more towards lower energies. Such a behavior is in agreement with band structure calculations for O(1) and O(4) (see for example, Ref [15]) and indicates a predominant contribution of these O atoms to the 528.7-eV peak of the O $1s$ absorption edge. Same as for $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$, this finding suggests a location of

Figure 3. O $K\alpha$ XES spectra of $\text{YBa}_2\text{Cu}_4\text{O}_8$ recorded at different excitation energies near O $1s$ threshold. The TEY spectrum at the O $1s$ edge is shown at the top panel.

an appreciable amount of doping-induced holes at O(1) and O(4) sites and an importance of O(1)-Cu(1)-O(4) ribbons for superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_8$.

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Transmission Magnetization Imaging Using the STXM

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INTRODUCTION

As nano-scale magnetic structures, including both ultrathin films and laterally confined structures, become more important in technology, so does the need to image their magnetization behavior. Many issues associated with magnetic structure, interactions between phases, and dynamics of reversal processes must be understood at relevant length scales in these structures [1]. Several common methods for imaging magnetization include visible magneto-optical techniques, magnetic force microscopy, and a variety of electron techniques including transmission, scanning, and imaging microscopy. Each has advantages and limitations, and together they should be considered as complementary and used to best advantage for specific problems. Following initial demonstration of magnetization imaging using the scanning transmission x-ray microscope (STXM) on beamline 7.0 we have continued to investigate these capabilities and how they complement other techniques to image magnetization.

Unique capabilities of magnetic microscopy using soft x-rays result from the strong contrast mechanisms inherent in large magnetic circular dichroism (MCD) [2] and magneto-optical rotation [3] at $L_{2,3}$ edges of the 3d transition metals. These large resonant magneto-optical effects lead to both elemental sensitivity and sensitivity to a relatively small number of spins. Photon-based soft x-ray microscopes (photon-in, photon-out) have advantages resulting from the ability of photons to penetrate well into samples to image magnetization in buried layers and at buried interfaces, as well as insensitivity to applied fields to allow for field-dependent imaging [4]. Two important capabilities of photon-based soft x-ray microscopes are illustrated below.

Direct contrast to magnetization is currently obtained in the STXM as absorption contrast through the MCD effect, by placing a saturated magnetized film upstream to create a circular polarizing filter [5, 6]. When tuned to the L_3 peak of Fe, Co or Ni the incident linearly polarized beam is converted to an elliptically polarized beam by preferential absorption of one of the two circular components with opposite helicity. Such circular filters are essentially Faraday effect modulators in the soft x-ray range. Reversing the magnetization in the filter reverses the helicity of the transmitted elliptical polarization. In both circular filter and magnetic sample the magneto-optical effects are proportional to $\mathbf{k} \cdot \mathbf{M}$ where $\mathbf{k}$ is the wave vector and $\mathbf{M}$ the magnetization.

VECTOR IMAGING OF MAGNETIZATION THROUGH TILTING

The relatively long working distance of the STXM allows sample tilting through large angles. Since most thin magnetic films have $\mathbf{M}$ in plane, tilting away from normal incidence is generally necessary to obtain magnetic contrast. Figure 1 demonstrates other advantages of tilting. All images are of the same region of a 33 nm Fe film containing a domain wall between 180°

Figure 1. Transmission magnetization images across a domain wall between 180° domains in a 33 nm thick Fe film. Images at left are obtained at 45° grazing incidence while those at right are obtained at normal incidence. The squares indicate what are believed to be the same location in the sample in the two different views.

domains having magnetization nominally along the arrows. At left are four images obtained from data taken at 45° from grazing and at right are corresponding images taken at normal incidence. The top two images show transmitted intensity obtained using incident + and – helicity elliptically polarized radiation, and the bottom contains the division and multiplication of these images. Divided images enhance magnetic contrast between regions with fixed magnitude of $\mathbf{k} \cdot \mathbf{M}$, while multiplied images enhance regions where $\mathbf{k} \cdot \mathbf{M}$ varies away from this average. Much structure in $\mathbf{M}$ is evident both along the domain wall and extending away from the wall into the domains. Normal incidence images reveal unambiguously that normal components of $\mathbf{M}$ are associated with domain walls in this film, and that these normal components form well-defined structures periodically positioned along the wall. Domain walls in soft magnetic films are of Bloch type ($\mathbf{M}$ rotates mostly out of film plane across wall) for large thickness and Néel type ($\mathbf{M}$ rotates mostly within film plane across wall) for small thickness. This specific sample is of intermediate thickness and shows both Bloch and Néel character; such hybrid wall structures are known as cross-tie walls. The ripple structure extending into the domains from the walls also shows normal $\mathbf{M}$ components and clearly originates at the Bloch lines that are spaced roughly 4 microns apart along the wall. These heterogeneities in magnetization structure relate directly to the magnetization reversal mechanism for this demagnetized film.

Many magnetic nanostructures may contain 3-dimensional components to their magnetization, like this simple system of a thin Fe film. While the origin of possible 3-dimensional magnetization may vary from system to system, the ability to image and quantify the full vector magnetization in small samples is generally important. The simple $\mathbf{k} \cdot \mathbf{M}$ contrast readily provides numerical algorithms to determine the vector components of magnetization along the different directions viewed. With three viewing angles the full vector dependence of $\mathbf{M}$ can be measured.

DIRECT IMAGING OF MAGNETIZATION IN EXCHANGE-COUPLED BILAYERS

A uniquely powerful capability of photon-out magnetization imaging with soft x-rays is the ability to penetrate overlayers that may be magnetic and image magnetization in buried layers. This is demonstrated in Figure 2. The sample in this case is a demagnetized sandwich structure consisting of Fe and Co films separated by a thin SiC spacer layer. The circular polarizer is a similar bilayer structure, providing MCD contrast at each elements L_3 edge. At left is a divided image taken at the Fe edge and at right a divided image taken at the Co edge. The large 180° domains of the single Fe film are absent in this bilayer structure, and instead we see much smaller, less regular features in the Fe magnetization. Similar features are seen in the Co magnetization. It is apparent that there exists partial but not complete spatial correlation of the magnetization distribution in the Fe and the Co layers. These images reveal that interactions between the two magnetic layers through the spacer layer can influence static magnetization distribution in each layer, as well as the magnetization reversal mechanism.

Figure 2. Transmission images of magnetization distributions in thin Fe and Co layers separated by a SiC spacer. Images obtained with opposite helicity elliptical polarization are divided to produce these images.

CONCLUSIONS AND FUTURE DIRECTIONS

The ability of photon-based soft x-ray microscopy techniques to study magnetic layers buried beneath other (possibly magnetic) layers offers important complementary capabilities to other magnetic imaging techniques. In particular, the ability to image non-destructively the magnetization in different, interacting layers of structures opens up many possibilities in the study of interactions between different magnetic phases in nano-scale structures. In the coming year we plan to implement an electromagnet that will enable field-dependent imaging of reversal processes at low fields. Alternatively we should be able to measure spatially resolved hysteresis loops from different parts of samples.

Clear limitations are evident in our scheme for magnetic imaging requiring polarizing filters to obtain MCD contrast. The Faraday effect filters function over only very limited bandwidths centered on strong white lines of ferromagnetic elements exhibiting MCD. The limited bandwidth precludes measurement of the full MCD spectrum of the sample that can provide important information regarding spatially varying chemical state effects and orbital and spin moment information from sum rules. The strong absorption in the filter reduces intensities by roughly an order of magnitude, thereby increasing the difficulty of imaging weak magnetization features. The implementation of a scanning x-ray microscope on an elliptically polarizing undulator would significantly enhance the capabilities of the current microscope. We are also considering how other contrast mechanisms, such as magneto-optical rotation, can complement current capabilities. A reflection (Kerr) microscope using polarization and/or intensity analysis of reflected beams for contrast would greatly increase the number of samples and scientific problems that could be addressed. Together with variable applied fields and control of sample temperature, these capabilities form the basis of a conceptual design for an advanced scanning x-ray microscope that would take maximum advantage of unique attributes of soft x-rays for imaging magnetization.

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X-ray Spectroscopic Studies of Low Dielectric Constant Parylene and Fluorinated Amorphous Carbon Films

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INTRODUCTION

Currently there are intense industry-wide efforts in searching for new low dielectric constant (low- k) materials for use in future generations of ultralarge scale integrated circuits (ULSI). The new low- k (< 2.5) materials are expected soon to replace silicon dioxide ($k = 4$) as the interlayer in multi-level interconnect scheme, reducing substantially the interconnect RC delay in ULSI circuits. There are a number of requirements for the new low- k materials, such as low dielectric constant, thermal stability (400°C or higher), being electrically insulating, high mechanical strength, and good adhesion to neighboring layers. These stringent requirements have reduced the candidates to porous silica and a few carbon-based materials. Among them fluorinated amorphous carbon (a-CF_x) [1-3] and parylene [4,5] polymer thin films showed significant promise. Since these materials are new in IC applications, a complete understanding of the properties of these films is essential before they can be reliably used in future ULSI circuits. Some high-resolution X-ray spectroscopy studies have been performed on a-CF_x and parylene polymer thin films [6].

EXPERIMENT

The experiments of C $1s$ absorption and $K\alpha$ emission were performed at beamline 7.0 at ALS, LBNL. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [7]. XAS spectra were obtained by measuring the total electron yield from the sample. The resolution of the monochromator was set to 0.15 eV at C $1s$ absorption edge. The XAS spectra were normalized to the incident photon current using a clean gold mesh to correct for intensity fluctuation of the photon beam. The XES spectra were recorded using a high-resolution grazing-incidence x-ray fluorescence spectrometer [8]. During the XES measurement, the overall resolution was about 0.5 eV for C $K\alpha$ emission.

RESULTS and DISCUSSION

Figure 1 shows the C $1s$ absorption spectra of Pa-N and three a-CF_x films grown at room temperature, 180°C, and 350°C. Detailed local bonding information of these new films can be obtained from comparing with existing literature on simple fluorocarbon molecules [MCI87,STO92].

Figure 1. C K -edge absorption spectra of Pa-N and a-CF_x films prepared at substrate temperature of room temperature, 180, and 350°C. These spectra were normalized at 297 eV.

In Figure 2 the C *K*-emission spectra of amorphous carbon, a-CF_x and Pa-N are shown. From comparing with a-C, the intensity centered around 275 eV is mostly due to C-C bands. More importantly, in the region of 282-285 eV there is little intensity in the spectra of Pa-N and amorphous carbon. The intensity in the spectra of a-CF_x is mostly due to F-induced states and due to the amorphous nature of the films. Since these states are at the top of the valence bands, this has important implications in the electrical properties of these a-CF_x films, it narrows the band-gap. Because the x-ray absorption spectra of a-CF_x and Pa-N films have similar threshold, we can argue that the band-gap of a-CF_x is about 2 eV smaller than that of the Pa-N. Again because the band edge is not well defined for amorphous films this conclusion is very qualitative. The effect of the core hole needs to be considered as well. Qualitatively this conclusion is supported by the fact that a-CF_x is not as good an insulator as Pa-N.

Figure 2. C *K*-edge emission spectra of Pa-N and a-CF_x films prepared at substrate temperature of room temperature and 350°C.

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Beamline 7.3.1 Abstracts

A Study of the Iron-Nickel Santa Catharina Meteorite Using X-PEEM And SEM Techniques.

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INTRODUCTION

The Santa Catharina meteorite is unusual in that it has previously been reported to contain an oxide, possibly spinel, phase within its structure^[1]. As the meteorite is metallic (rather than stoney), it is probable that it originated from within the core of an object of planetary mass that was forming in the early stage of the solar system. Determination of the oxide phase is important as it should provide information on conditions it experienced during its formation.

Previous work on other fragments of this meteorite (including another piece of this particular sample) have been conducted using electron microscopy techniques such as SEM (scanning electron microscopy), TEM (transmission electron microscopy), EELS, electron diffraction and the like. Whilst these techniques can provide excellent micrographs and information on the crystal structure and stoichiometry, it cannot provide the chemical state information available through x-ray absorption (XAS) techniques. Thus although the ratios of iron, nickel and oxygen can be measured by conventional electron microscopy, how the elements are chemically bonded together is not so straight forward to determine.

It has been demonstrated^[2] that XANES (x-ray absorption, near edge structure) measurements at the *L*-edges of the *3d* transition metals is a potentially powerful probe of valency and site occupancy. The development of X-ray PhotoEmission Electron Microscopy (X-PEEM) will allow this technique to be applied on structures exhibiting microgrowths of different phases such as this meteorite.

The newly commissioned PEEM2 beamline (7.3.1) at the ALS has been used in an attempt to determine the oxide phase present in the Santa Catharina meteorite. The data gathered using this technique is being combined with more conventional electron microscopy conducted using the SEM at Southampton Oceanography Centre in the UK.

RESULTS

Two key types of area within the Santa Catharina meteorite have been investigated. The first is a phosphorous rich grain which has apparently led to some form of condensation of nickel within the iron-nickel bulk of the meteorite. The second type of feature we have looked at are the 'islands' containing oxygen which occur in bands across the sample. Analysis of the latter is proving much more complex and is still ongoing, so our comments on these will be brief.

The phosphorous rich grain is illustrated in Figure 1 which shows a comparison between

XPEEM images taken at the iron & nickel L lines and that obtained from the SEM in backscattered mode of the same area. It should be noted that the energy calibration of the 7.3.1 monochromator was not completely correct at the time these data were taken and as yet we have not made the appropriate adjustments. Inset in Figure 1 is an outline sketch illustrating three key regions, A is the 'host' material and is comprised solely of iron & nickel, B is the boundary region, presumably left after condensation of the phosphorous rich grain and is almost devoid of nickel. Region C is the grain itself which contains a much higher nickel / iron ratio than that of the 'host' meteorite. SEM analysis of these three regions indicate a high phosphorous content in region C and no measurable quantities in A or B.

Figure 1: XPEEM images of phosphorous rich grain at Fe & Ni L resonances compared to SEM micrograph of the same area.

Comparison of the sharpness of features in the XPEEM and SEM images indicates a difference depending upon the physical structure in the top layers. A well defined boundary in the SEM image between regions A and B show that the SEM is operating with an overall higher spatial resolution than the PEEM2 instrument (although the latter was not fully optimised for these images). However the relative lack of clarity in the boundary between regions B & C in the SEM image can be attributed to the higher probe depth of the electron beam compared to the X-ray beam. The former being of much higher energy (typically 20kV) will penetrate upto a micron into the surface, revealing structure under the surface layer - in this case the 'shelving' of the grain. The X-PEEM technique in comparison is much more surface sensitive.

Deep penetration of the electron probe in the SEM also gives a relatively large probe size for elemental analysis using the SEM. The XPEEM technique by comparison can produce elemental maps very rapidly at the instruments normal operating spatial resolution.

An unexpected find is of magnetic domains in the almost pure iron boundary region (region B). This is illustrated in Figure 2 which shows the contrast between the maximum of the Fe L peak (the Fe^{2+} resonance at 721.5eV) and offset from this at 722.7eV (where the Fe^{3+} peak would be expected to be). The effect is to highlight the difference between the two domains. Figure 2 also shows the iron L -edge spectra for two of the larger domains, normalised to their pre-edge background levels and the difference spectra of these.

Our investigation of the oxide bearing phases is still ongoing. Three different regions have been investigated using XPEEM and SEM and all present a similar picture to each other. One compli-

Figure 2 . MCD Image and associated spectra of magnetic domains in boundary region of phosphorous rich grain obtained with PEEM2. Region B1 is one of the large bright bands in the boundary region to the immediate right of the almost black phosphorous rich grain. Region B2 is an adjoining dark band.

cation produced by XPEEM is due to the surface sensitivity. In order to ensure that we examined bulk oxides, rather than surface oxides of the cut face due to exposure to air, polishing lubricants *etc.* it was necessary to ion etch the sample in the PEEM2 sample preparation chamber. This was evidently successful at removing not only the oxygen at the surface, but also from within the top atomic layers of the sample. The deeper probe depth of the SEM has shown that oxide is concentrated in small islands (typically 20 microns in size) and is not evident in the main bulk of the meteorite. Iron *L*-edge spectra collected from these islands using PEEM2 shows an Fe^{3+} resonance in addition to Fe^{2+} . This Fe^{3+} peak is not present in the iron-nickel host. The presence of Fe^{3+} is a strong indicator of an iron oxide phase.^[2]

Whether or not the oxide phases in Santa Catharina are spinels it's hard to say at present. We need to complete our analysis of the data we have and compare it to other XAS measurements we have obtained from model mineral samples. However results obtained so far look promising.

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Photoemission electron microscope for the study of magnetic materials

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INTRODUCTION

Photoemission electron microscopy (PEEM) using ultraviolet (UV) radiation was first developed in the 1930's, and has since become a well-established technique. The resolution of modern PEEM instruments approaches 10nm, within a factor of two of the theoretical limit for uncorrected microscopes of 5nm [1, 2]. Our motivation in developing the instrument reported here was to construct a system for spectromicroscopic imaging of magnetic surfaces near the theoretical resolution limit for this type of microscope. One key target was to achieve sufficient positional stability so that the theoretical resolution could be achieved while acquiring spectroscopic data; as series of images are required high stability over tens of minutes is needed. A second goal was to provide this high level of performance in a beamline and endstation environment dedicated to microscopy.

PEEM PRINCIPLE

In PEEM photons incident on a sample cause photoelectron emission if the energy of the photons is larger than the work function of the sample. These photo-emitted electrons are extracted into an electron-optical imaging system by a large electric field that is applied between the sample and the first electrode of the electron optical system. This field is the first lens of the microscope. Several electron-optical lenses are used to form a full field image of the emitted electrons onto a detector such as a phosphor that converts electrons into visible light.

Two contrast mechanisms are available in UV-PEEM, topological contrast and workfunction contrast. Topological contrast is due to distortion of the electric field around surface topological features. The field distribution distortions disturb the electron trajectories which produces image contrast. Workfunction contrast is manifest in the intensity modulation of the photo-emission intensity due to the different emission probability in regions of different workfunction. Additional imaging modes are available when x-ray photons are used to stimulate photoelectrons. Elemental contrast is achieved by tuning the incident x-ray wavelength through absorption edges of elements. X-ray absorption and the resulting photo electron emission intensity is strongly enhanced at absorption edges. Areas on the surface containing the corresponding element emit more photoelectrons and thus appear bright in the PEEM image at a given absorption edge x-ray energy. The fine structure in the energy dependence of the x-ray absorption can be characteristic of the chemical bonding state of surface atoms. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy [3] can be applied to two-dimension image formation to obtain chemical contrast. Linearly and circularly polarized x-rays can be used to study the orientation of molecules. In orientation contrast linearly polarized x-rays are strongly absorbed when the electrical vector of the light and the orientation of a

bond in the molecule are parallel, and the absorption is weak for a perpendicular orientation [4]. Furthermore, x-ray magnetic circular dichroism (XMCD) can be utilized to study magnetic materials [5] since the absorption of left and right handed circularly polarized radiation varies with the relative orientation of the magnetic moment in the sample. XMCD permits the determination of spin and orbital moments using sum rules [6]. Finally, x-ray magnetic linear dichroism can be utilized to study the properties of antiferromagnetic materials.

BEAMLINE AND PEEM2 LAYOUT

The new instrument called PEEM2 is installed at the bending magnet beamline 7.3.1 which was specifically designed for XMCD microscopy. The spherical grating monochromator is entrance slitless and delivers monochromatic radiation in the energy range of 175-1300 eV. Since the vertical source size at the center of this bending magnet is less than 30 μm and corresponds to the typical field of view of the microscope, the source can be directly imaged onto the sample at unity magnification. The low line density of the grating (200 lines/mm) leads to a very slow variation of the focal length with the wavelength, therefore the monochromator can work with a fixed imaging distance [7]. As the magnification of the PEEM determines the required field of view and hence illumination, the sample is placed in the monochromatic focal plane, without the use of exit slits as typical for conventional systems. This results in an energy dispersed vertical line. Over the typical field of view however of 30 μm the wavelength is essentially fixed. The photon flux is very high for a bending magnet beamline because the minimum number of optical components are used, and the field of view and spectral resolution are optimized for XMCD-PEEM. The photon flux is 3×10^{12} photons/s in a 30 μm spot when the storage ring is operated at 1.9 GeV with a ring current of 400 mA in a design band pass of 1 eV at 1000 eV. A mask upstream from the monochromator is used to select above plane (left circularly polarized), in plane (linearly polarized), or below plane (right circularly polarized) radiation. The resolving power of the beamline is $E/\Delta E = 1800$.

The objective lens of PEEM2 is an electrostatic tetrode lens with a stigmator/deflector assembly located in its backfocal plane. A transfer lens produces a 1:1 image and a second objective backfocal plane outside the lens where an aperture is located. Four different apertures are mounted on a small flexure stage and can be easily exchanged in vacuum (2 mm, 50 μm , 20 μm , and 12 μm diameter). The intermediate lens (with another deflector) and projector lens form the final image on a phosphor screen deposited on a fiber optic plate. This fiber optic plate scintillator serves also as the vacuum interface, and is directly coupled through a second fiber optics taper to a slow scan cooled CCD camera. This detector arrangement is about 5 times more efficient than a lens coupling of the camera.

The typical distance between the objective lens and the sample is 2 mm, and the maximum operating voltage is 30 kV. The sample is held at high negative potential. The center electrodes of the lenses are biased to focus the electrons. All other electrodes and the detector are held at ground potential. The CCD camera can operate in two different modes with a maximum image acquisition rate of 4 images per second. This rate is

sufficient for focusing and adjustment of the microscope. The camera accommodates variable exposure times, with typical image acquisition times of a few to tens of seconds. The microscope is shown in Figure 1.

Figure 1: Drawing of PEEM2.

The theoretical resolution limit of PEEM2 was calculated by taking the complete angular and energy distribution of the photo-excited secondary electrons into account. The theoretical resolution limit considering all relevant aberrations is about 20nm obtained using an aperture of 10 μ m and a sample voltage of 30 kV. The transmission for such a small aperture is around 5 %. All these values depend on the work function of the sample material (we assumed 4 eV as a typical value for metals). The resolution of a PEEM using x-rays is dominated by the aberrations of the accelerating field.

EXPERIMENTAL RESOLUTION TESTS

PEEM2 has been in operation since December 1997. Most of the experiments have been dedicated to the study of magnetic materials. Here we demonstrate the spatial resolution of PEEM2. Figure 2 shows a low resolution and a high resolution image of a surface discharge track on a LaFeO₃ sample acquired at the La M₅ edge.

The operation voltage was 18kV, the 12 μm aperture was used, the exposure time was 60 s, and the estimated resolution is 20 nm. Magnetic imaging presents a greater challenge because the contrast based on the XMCD effect is typically only on the order of 5-30% whereas it can be up to factors of 5-10 for elemental contrast. Despite of the low contrast in XMCD imaging the highest resolution we have achieved so far for magnetic imaging is 25 nm. This result was obtained on Co stripes exhibiting stripe domains of a typical size of 100 nm. This resolution for imaging using x-rays is very close to the theoretical limit for x-ray operation. Better resolution can only be obtained by correcting for the aberrations of the microscope. The most promising approach to an aberration corrected PEEM seems to be the application of an electrostatic mirror. Aberration corrected PEEMs might achieve a spatial resolution in the few nanometer range.

Figure 2: Low resolution and a high resolution PEEM image of a discharge track on a LaFeO_3 sample acquired at the La M_5 edge. Estimated resolution 20 nm.

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The Antiferromagnetic Structure of Polycrystalline NiO Films

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INTRODUCTION:

An important but as yet poorly-understood phenomenon is the pinning (fixing) of the magnetization direction of a ferromagnet coupled to an antiferromagnet, an effect referred to as exchange biasing or exchange anisotropy. When a ferromagnet / antiferromagnet sandwich structure during growth is subjected to an external magnetic field along a specific direction in the interfacial plane, the ferromagnet remains pinned in that direction [1]. The exchange coupling is reflected by a hysteresis loop that is offset from zero field by the exchange field. Rotation of the magnetization direction from this preferred direction may require magnetic fields as high as several hundred Oersted. While it is clear, in general, that the exchange coupling effect across the ferromagnetic / antiferromagnetic interface must originate from symmetry breaking at the interface, the microscopic origin of the phenomenon has remained a mystery.

A complete understanding of exchange biasing is not only an interesting scientific problem but an important technological one, as well. It is used everyday in the manufacturing of magnetic recording heads. Of particular importance in the development of ever-more sensitive read heads, which sense the small flux changes arising from the magnetic domains on the spinning disk, is the so-called spin valve head. It is based on the giant magneto resistance effect and is currently being developed for tomorrows products. A necessary step to the understanding of exchange biasing is to determine the magnetic structures of both the antiferromagnet and the ferromagnet at their interface. The formation of antiferromagnetic domains is believed to be of particular importance to explain the experimental observation that the exchange anisotropy at the interface is in most cases quite weak, on the order of 1% of the maximum possible value, given by theory for an ideal single domain antiferromagnet [2, 3].

EXPERIMENT:

X-ray magnetic linear and circular dichroism (XMLD, XMCD) in combination with photoemission microscopy is a very powerful tool to study the magnetic and structural properties of complex surface and interface structures. Using this technique we can distinguish between elements in a composite or a layered structure by the different energetic positions of the core level absorption edges, a demand only met by x-ray based techniques. The magnetic structure of ferromagnetically ordered systems is accessible via the magnetic circular dichroism effect. The magnetic structure of antiferromagnetically

ordered systems can be investigated by the magnetic linear dichroism effect. These effects are based on a shift in the spectral weight of the multiplet split core level absorption edges depending on the relative orientation of the photon polarization and the spin orientation in the ferro- or antiferromagnet [4]. Together with the high spatial resolution that is achievable in electron microscopy, magnetic domains, areas of different orientation or magnitude of the magnetic moments, can thus be resolved. Imaging of ferromagnetic domains is a well established technique [5]. Here, we will demonstrate that photoemission electron microscopy is also able to detect and image the antiferromagnetic contrast due to antiferromagnetic domains at the surface of polycrystalline NiO, a material that is used in today's exchanged biased sensors.

PEEM2 is a full field imaging photoemission electron microscope that has been fully operational since summer 1998 at the bending magnet beam line 7.3.1.1 at the Advanced Light Source. PEEM2 uses the secondary electron yield upon illumination by x-rays for imaging. The beam line is optimized for high flux at the L absorption edges of the 3d transition metals around 700 eV and delivers linearly and circularly polarized soft x-rays into a focus of 30 μm . A spatial resolution of 25 nm has been achieved with PEEM2. It is possible to measure local absorption spectra with good statistics in reasonable times in areas as small as 100 nm [6].

Fig. 1: X-ray absorption spectrum of polycrystalline NiO measured with PEEM in an area of about 20 μm diameter. Shown is the Ni L_2 edge measured with linearly polarized light. The measurement geometry is shown to the right.

RESULTS:

We have investigated 200 nm thick polycrystalline NiO layers that are sputter deposited on Si and are then annealed in O_2 to increase the size of the crystalline grains. As a rule of thumb a maximum grain size of 200 nm is to be expected for 200 nm thick films. The sample was transported in air before introducing it into PEEM2. Due to the high inertness of NiO no change in the morphology and magnetic structure should occur. The sample was then capped with about 2 nm Cu to get the electrically conductive surface necessary for photoelectron-based imaging. A thicker contact layer, about 20 nm thick, was grown

using a masking technique, to achieve a good electrical connection. The capping was done in a separate preparation chamber connected with PEEM2.

Fig. 2. The images show the topography (left) and the antiferromagnetic contrast (right) of polycrystalline NiO at room temperature (top) and at 100°C (bottom). The field of view is 8 μm.

Figure 1 shows an absorption spectrum of the NiO L_2 edge taken at room temperature with PEEM2. Linear polarized light was used. The polarization direction lies in the sample plane. The inset shows the measurement geometry. Here, the absorption was measured in a large area of about 20 μm diameter, so we averaged over many domains. The multiplet split L_2 edge consists of a peak at 872.2 eV and a shoulder separated from the main peak by about 1 eV. This profile is known to be typical for a magnetically ordered NiO layer with an average magnetization oriented perpendicular to the photon polarization [4]. For a non-magnetic NiO layer both peaks would have almost the same intensity. The intensity ratio at the multiplet split L_2 absorption edge, which is very sensitive to the relative orientation of photon polarization and spin direction, is then used

to image with antiferromagnetic contrast, shown in figure 2. The four images were taken at the same spot on the sample at two different temperatures: room temperature (top) and at an elevated temperature of 100°C (bottom). The images showing the topography (left) result from averaging two images acquired on the two lines of the L₂ absorption edge. The images showing the antiferromagnetic structure result from dividing those two images. The image contrast is enhanced for better visibility.

The topography shows structures with a typical diameter of about 200 nm, visualizing the grain structure of the thin NiO layer. The topography does not change with temperature, demonstrating the stability of the NiO surface during modest heating in vacuum. The images on the right, acquired with antiferromagnetic contrast, show a very rich structure, demonstrating for the first time that x-ray absorption microscopy is suited to image the antiferromagnetic structure of ordered surfaces and interfaces through capping layers as thick as 2 nm. The decrease in magnetic contrast with increasing temperature results from the reduction of the NiO spin moment as its Néel temperature of 250°C is approached. This proves that the contrast arising from the peak ratio at the L₂ edge is of magnetic origin. We believe that these results are a major breakthrough in understanding exchange biasing, since application of dichroism techniques in x-ray absorption combined with spatial resolution will enable the investigation of the complex magnetic structures at ferromagnet - antiferromagnet interfaces as well as domains and domain walls in model and in realistic systems.

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Beamline 7.3.3 Abstracts

A Study of the Practicality of Using an ALS Bend Magnet as the X-Ray Source for Micro Protein Crystallography.

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INTRODUCTION

Using the technique of Protein Crystallography, synchrotron sources have played a growing role in solving the most difficult and important problems in structural biology. However, it is basically difficult to obtain large crystals (~200micron) of most proteins of interest that regular protein crystallography uses. It would be much easier if protein crystallography could be carried out with micro crystals as small as 20 micron. This would advance the progress rate of structural biology significantly. Diffraction from such small samples requires the development of x-ray microprobe tools. This work describes experiments underway to optimize camera designs and experimental protocols for x-ray diffraction studies with protein micro-crystals.

The ALS development beamline 7.3.3 has been used to carry out these baseline studies. These studies have shown :-

- (1) that a 40 micron x-ray beam gives acceptable background for protein crystals as small as 25 x 25 x 10 micron,
- (2) that the exposure times will be very acceptable when the ALS superbend sources become available, and
- (3) that radiation damage will require the use of only a few such crystals per complete data set.

Experimental

Micro Crystal Diffraction

A key objective of this work has been to establish what would be the smallest protein crystal that could be used to obtain high-quality diffraction data. Bacteriorhodopsin crystals were used for this purpose as they only rarely grow to a size as large as 100 micron; and abundant quantities of crystals in all size ranges below that are readily at hand.

Figure 1. Schematic layout of test beamline 7.3.3 used for micro protein crystallography.

Fig.1 shows the schematic layout of the ALS test beamline 7.3.3. The mirror at 16m collects 3×0.2 mrad of radiation and focuses the light to a 300×300 micron spot in the sample region. The radiation is monochromatized with a Ge(111) double crystal monochromator of bandpass ~ 1000 . The photon energy used was 11KeV. Within the hutch there is a vertical micro focus mirror just before the sample that is able to provide additional vertical focussing such that the vertical spot size is reduced to 40 micron with a 3 mrad convergence angle. Spot size reduction in the horizontal was not possible by mirrors as the light already has a 3mrad convergence angle and this represents a maximum for micro focus mirrors at 11KeV. Slits located just before the sample allowed controlled horizontal reduction of the spot size to 40×40 micron with 3 mrad convergence angle in both planes. This convergence angle is a standard value for protein crystallography

A one-degree rotation photograph was recorded for a bacteriorhodopsin crystal that was $25 \times 25 \times 10$ micron in size. The unit cell dimensions for this crystal are 6.2nm, 6.2nm and 10.8nm. Spots were seen out to 2.3Å. The exposure time was 600 seconds. The air-scatter background was at an acceptably low level, and this could be further reduced by operating with helium gas rather than nitrogen gas through the heat exchanger of the gas-stream sample cooler. For reasons of high thermal strain in the Ge(111) monochromator and the first mirror not being at the correct focus, the x-ray intensity available on this test setup at the time of these experiments was about 10-times less than it could be. Also of note is that the intensity with an ALS superbend magnet as the source will be higher by an additional factor of ~ 10 . This would indicate that on a superbend with a correctly engineered beamline and optics, diffraction patterns could be taken from bacteriorhodopsin crystals as small as $(20\mu\text{m})^3$ with 6 second exposures for 1 degree of rotation. This would mean that data collection times for micro crystals would no longer be a limitation.

Radiation Damage

In separate experiments with larger crystals and a larger x-ray beam, we have also examined the degree to which radiation damage limits the accumulated x-ray exposure that can be tolerated. Data were collected over a 10-degree wedge, in 1-degree steps; the goniometer was returned to the original setting and data were collected over the same 10-degree wedge. The process was repeated until substantial damage could be seen. The experiments used crystals that diffracted initially to about 2.1Å resolution. After an accumulated exposure of 10^{10} photons/micron², one could no longer see diffraction spots at a resolution higher than about 2.5Å, and reflections that remained at lower resolution were much weaker than in the first cycle. While measurements were not extended beyond an exposure of 10^{10} photons/micron², it is unequivocally clear that crystals would no longer be useful for data collection after a 10-fold higher exposure, i.e. 10^{11} photons/micron². This conclusion had already been drawn by Gonzales and Nave, using exposure of protein crystals to a white-source beam at Daresbury.

The 600-second exposure referred to earlier to record the diffraction pattern from the ~ 20 micron crystal corresponded to less than 10^{10} photons/micron². Thus we estimate that one could collect at least 10 degrees of data before radiation damage would require changing the crystal. A full data set, i.e. 90 degrees of data, could then be collected with fewer than 10 such micro crystals. More generally, the following rules-of-thumb are expected to apply to data collection from protein microcrystals:

CONCLUSIONS

1. Routine data collection will become possible on crystals that are 30 to 40 micron in size. This option should be especially valuable in those cases where efforts to improve crystal size are not immediately productive. The cost of prolonged efforts to increase crystal size will no longer be justified.
2. The small crystal size will allow one to diffuse a reactant (or small-molecule ligand) into the protein much more rapidly than would be the case for crystals of the "standard" size. The use of very small protein crystals will greatly increase the number of cases in which reactants can be loaded within the enzyme to relatively high occupancy at a rate faster than the reactant is processed by the enzyme. Also one will not have to use the extremes of low temperature that would otherwise be necessary to accomplish this.
3. The small crystal size may also make it possible to freeze crystals without the need to soak in a cryoprotectant, as is already known to be true for the micro crystals that are used in electron cryo-microscopy. Valuable time will be gained if one can bypass the search for conditions that preserve crystal quality and still allow crystal freezing.

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Development of a zone plate-based full field imaging microscope for hard x-rays

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Use of x-ray phase contrast in the hard x-ray region is among the most important developments in x-ray imaging techniques. The relative figure of merit of x-ray phase contrast to amplitude contrast may be approximately given by the square of the ratio of the real (f_1) and imaginary (f_2) part of the atomic scattering factor for "thin" samples. Because the real part of the atomic scattering factor is approximately equal to the number of free electrons in an atom while the imaginary part decreases with the cube of x-ray energy away from an absorption edge, the relative figure of merit can be significantly greater than unity. For example, the relative figure of merit is approximately equal to 3.6×10^5 for a sample consists of mainly carbon for 8 keV x-rays. For a "thick" sample, this relative figure of merit is multiplied by the inverse of the transmission of the sample. The superiority of phase contrast compared to absorption contrast for low-Z samples was dramatically demonstrated in the work of Cloetens et al (J. Appl. Phys., 81, p. 5878 (1997)). The measurements were made at the European Synchrotron Radiation Facility (ESRF) on cracks in polymers and in an aluminum-matrix-silicon carbide composite. An x-ray energy of 25 keV and a 150-meter source-to-sample distance was used to obtain highly coherent (collimated) x-rays to illuminate the sample. By placing a phosphor-CCD-based detector about 1 m beyond the sample, the intensity variations resulting from the phase curvature produced by such features as cracks and voids were recorded and used to reconstruct three-dimensional images of the features at 6-7 microns resolution. Cracks of sub-micron dimension were detected but not resolved due to the limited resolution. It should be noted that cracks and voids with micron dimensions were not detectable by simple absorption imaging (radiography) as they constituted such a small fraction of the total volume sampled.

In collimated-beam experiments, like those of Cloetens, and all others to date, the intrinsic resolution is that of the detector which is never better than a few microns. In order to circumvent the detector spatial resolution limitation, we are developing a zone plate-based x-ray full field imaging microscope capable of obtaining sub low micron spatial resolution. The microscope is a type of Zernike phase contrast microscope, which is an established technology in the soft x-ray region. The zone plate is used as the objective with a $\pi/2$ phase-shifting disk in the back focal plane in exact analogy to the visible light case. The magnification produced by the zone plate allows high resolution to be achieved even when a low-resolution detector such as a CCD detector is used. At an appropriate magnification, the spatial resolution is limited by the intrinsic resolution of the zone plate. The state of the art is about 0.15- μm resolution at high focusing efficiency for 8 keV x-rays and 0.08 μm at low efficiency and still improving.

An initial experiment was done using a prototype microscope on the beamline 7.3.3 with three days of beam time. The schematic of the experiment setup is shown in Fig. 1. The design allows us to use it either in a phase contrast mode or a dark field mode. In the dark field mode,

Fig. 1 Schematic of the full-field imaging microscope used in our experiment.

the image arises from the x-ray photons scattered out of the envelope of the incident beam as well as its corresponding image, and the image contrast is proportional to the scattering strength between two neighboring resolution elements, which is proportional to the square of the atomic scattering factor. Because of its low background, the dark field mode may be a preferred imaging technique for some special cases.

The key optical component in this setup is the phase zone plate and it was used as an objective in a light microscope. The phase zone plate used was developed in a long-term collaboration between Argonne National Laboratory, University of Wisconsin at Madison, and Istituto di Electronica dello Stato Solid, Italy. Its key parameters are given below:

Diameter	145 μm
Outermost zone width	103 nm
Thickness of Au	900 nm
Focal length @ 8 keV	10 cm

In theory, the theoretical spatial resolution of the phase zone plate is about 0.12 μm and an experimental value of 0.15 μm was demonstrated. The focal length becomes 9.375 cm at 7.5 keV x-ray energy that was used in the experiment. The zone plate was used to a magnifying objective as a lens is used in the optical region. In order to achieve high spatial resolution with a CCD detector with a 24 μm pixel size, a large sample-detector distance was used to obtain a large x-ray magnification by the phase zone plate, and a scintillator/lens system was used to further magnify an image before it was recorded by the CCD detector. The x-ray and optical magnification were 21 and 14 respectively and the combined total magnification is therefore 294. Each pixel of the CCD detector, therefore, represents a spatial size of 0.081 μm on the objective plane.

In our first experiment, only the dark field imaging was done because of its relative simplicity and the time limitation. In the dark field mode, the pinhole was used to define a field of view to be imaged. In principle, the field of view can be as large as the area of the zone plate in an optimized setup and is limited in our present setup to an area with a linear dimension approximately equal to the radius of the zone plate. A pinhole of 50- μm diameter was used in our experiment and it defined the field of view. With each pixel of the CCD representing of 0.08 μm on the object plane, the corresponding image field at the CCD detector was an area of 625 x 625 pixels.

This setup was used to obtain full field imaging of several samples, which include a human hair, a Cu mesh grid, a pyrolytic carbon piece of about 2 mm thick, and a piece of grass. The exposure time required was about 100 seconds. It was found that once the imaging microscope is aligned, imaging of different samples could be easily done. Fig. 1 shows two images obtained using the imaging microscope in the dark field mode. Because of time limitation, we could not complete a plan of using the setup in the phase contrast mode. A phase shifter made by drilling a 20 μm on a 6.5- μm thin Al foil was prepared before the experiment. We believe it should be straightforward to use this setup to develop the phase contrast imaging technique in the hard x-ray region. We are now developing a more optimized version of this system.

Fig 2 Image of a part of a Cu mesh grid (2000 mesh/inch) (a) and a human hair of 38- μm in diameter (b) The field of view is about 50 μm .

In summary, an x-ray tomographic facility with 0.1- μm spatial resolution can be developed using a bending magnet source at the ALS. This feasibility has been confirmed by a preliminary experiment done on beamline 7.3.3. Such a facility would be a very important tool for materials and engineering research.

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Implementing Time-Resolved EXAFS in a Laser-Pump SR-Probe Experiment

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INTRODUCTION

Over the last ten years there has been a tremendous development aimed at probing in "real-time" photoinduced structural modifications for various types of systems. This has been possible thanks to the advent of pump-probe femtosecond spectroscopy. In these studies, an ultrashort optical pulse (the pump pulse) initiates a dynamical process in the system and dynamics is subsequently inspected by a delayed optical probe pulse. Both the excitation and the probing rely on an *a priori* knowledge of the spectroscopy (energy, intensity and lineshape of bands) of the system under study. Unfortunately, spectroscopic data are not easy to translate to atomic coordinates, except in a few rare cases. In addition, the spectroscopic properties of a system become less and less system-specific when the latter grows in size (e.g. biological molecules or condensed phases). On the other hand, crystallographic techniques such as x-ray or electron diffraction and x-ray spectroscopic techniques such as EXAFS (Extended X-ray Absorption Fine Structure) or XANES (X-ray Absorption Near-Edge Structure) have proven to be powerful techniques for structural determination of biomolecules and condensed matter with high spatial resolution. Diffraction techniques probe long range order in a periodic structure, while X-ray absorption techniques (EXAFS and XANES) or diffuse scattering (in liquids) probe local environments around a given atom. Inversion of the data to atomic coordinates is in addition possible. Therefore, in this project we aim at combining the direct inversion advantages of these x-ray absorption techniques and their high spatial resolution with the high temporal resolution of ultrafast pump-probe techniques [1]. This necessitates a tunable source of intense ultrashort x-ray pulses, which is provided by synchrotron radiation. In order to demonstrate the feasibility of this technique, we have decided to single out a system that has a kinetic process resolvable with the pulse duration of synchrotron x-rays (tens of picoseconds): molecular iodine in liquid solvents.

EXPERIMENT AND INITIAL RESULTS

Last November, we performed a laser-pump x-ray probe experiment at beamline 7.3.3. of the ALS, which delivers x-ray photons in the 2-12 keV region. The fs laser system of the beamline is synchronized to one single bunch in the camshaft mode, which enables laser pump x-ray probe performance at 1 kHz. The single camshaft pulse of interest is detected with a fast avalanche photodiode behind the sample and is electronically singled out via a 1 kHz triggered and gated boxcar integrator.

With this set-up we have chosen I₂ in solution as our test system. The strategy is to excite I₂ into the predissociative B state (Fig. 1) and monitor its stabilisation in the weakly bound A state, before the system relaxes back into $v''=0$ of the ground state. The L₁ 5p hole (pre-edge) resonance was chosen as the probe, since we expect the 2s→5p overlap conditions to change in a sensitive manner with varying internuclear separation.

Figure 1: Relevant potential energy surfaces of iodine in the condensed phase. The vertical arrow indicates the photoexcitation process, and the dotted arrows show the main relaxation pathways back to $v''=0$ of the ground state: 1) predissociation, 2) caging, 3) electronic relaxation and, 4) vibrational cooling.

The laser system delivers pulses at the fundamental around 800 nm and the frequency-doubled output around 400 nm. The latter corresponds to an extremely weak I_2 optical absorption cross section of ca. $6 \times 10^{19} \text{ mm}^2$ in the gas phase and in non-polar solvents (2-3 orders of magnitude weaker than at the Franck-Condon maximum at 530 nm). However, in polar solvents the Franck-Condon maximum is blue shifted down to ca. 430 nm, which enhances the I_2 cross section at 400 nm by ca. 3 orders of magnitude. We have therefore used ethanol as I_2 solvent, although the time scales for relaxation back to the ground state were unknown for this system.

In our test run white light from the bend magnet penetrates the sample and is monochromatized by a Ge(111) crystal into an avalanche photodiode. Absorption spectra are derived by measuring the photodiode signal with and without sample (a 0.3 mm thick liquid jet in He atmosphere), and normalisation yielded spectra such as shown in Fig. 2.

Fig. 2: Left : Static X-ray absorption spectrum of I_2 /ethanol taken via a gated boxcar (15 μs gate width) and triggered with the laser repetition rate of ca. 1 kHz (bottom) compared to an EXAFS spectrum (top). Right : L3 edge of iodine, a) EXAFS from Filippini et al., b) 10 μs gated spectrum, c) and d) 50 ns gated spectra (all at 1 kHz). c) with laser pump pulse (delay 0), d) without laser pulse (delay -550 ns).

In these experiments we employed our electronic chopping capabilities, which allows selection of a single bunch at the laser repetition rate of 1 kHz. The quality of these spectra can still be improved, but are in principle limited by the x-ray flux. Spectra b), c) and d) in Fig. 2 (right) were taken simultaneously in the laser pump-SR probe experiment by running the APD signal in parallel through 3 boxcar integrators. Spectrum b) was obtained by setting the gate width to 10 μ s, while both c) and d) only accepted the camshaft single pulse (via a 50 ns gate width). c) was synchronized to the laser, and the gate in d) was shifted to the single camshaft pulse 550 ns *before* the laser enters the sample. With these devices we have ample control over the experiment. In a next step, we will introduce a Lock-In amplifier referenced to an additional laser chopper at ca. 100-400 Hz, which should aid in reducing the noise.

Even though we managed to have both laser and x-ray pulse on the sample, we did not detect photo-induced changes. A possible reason is a relaxation process much faster than the x-ray pulse width. To check the latter, we have performed a one-colour laser-only pump-probe experiment to measure the relaxation time of photoexcited I_2 back to the ground state in ethanol (see Fig. 1). While our attempt to observe the stabilisation within the A state with its much larger internuclear separation via EXAFS is feasible for nonpolar solvents due to their well known longer relaxation times (in the 100 ps to several nanosecond time scales, depending on the solvent), we had to determine the time scales for I_2 /ethanol experimentally. Fig. 2 shows that the very fast recovery of ground state I_2 occurs within picoseconds, which explains our failure to observe a photoinduced absorption change. Improvements underway include a new double crystal monochromator at 7.3.3., an improved dye circulator for different I_2 solvents (e.g., hexane), and optimized data acquisition electronics.

Fig. 2: Pump probe experiment of a 0.3 mm sample I_2 /ethanol (5g/l concentration) with 400 nm pump (25 μ J) and 400 nm probe (10 μ J).

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Picosecond Structural Dynamics Probed by Time-resolved X-ray Diffraction

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INTRODUCTION

Phase transitions and lattice dynamics in solids, structural changes in proteins, and chemical reactions occur on timescales of femtoseconds to picoseconds. Time-resolved x-ray diffraction offers a direct probe of these processes on the atomic scale. In this ongoing experiment, we investigate laser-induced structural dynamics in the semiconductor Indium Antimonide¹. We report the direct observation of laser-induced coherent acoustic phonons, and probe in real time the transition from an ordered to a disordered state.

EXPERIMENT

The experiment was performed at beamline 7.3.3. The white beam is monochromatized to 5 keV by a Si (111) crystal and then diffracted off an asymmetrically-cut InSb (111) crystal onto the detector. The detector is a streak camera with 3 picosecond time resolution running in averaging mode². A 1 kHz Ti:Sapphire laser system produces 150 femtosecond, 800 nm laser pulses, at 2.5 mJ/pulse. The laser is synchronized to the synchrotron RF with 2 ps jitter. One part of the laser pulse is split off to trigger a photoconductive switch which drives the sweep plates of the streak camera. A second part of the laser pulse is overlapped temporally and spatially with an x-ray pulse on the InSb crystal and initiates a structural change in the material. The crystal structure is then probed at later times by measuring the time-resolved diffracted intensity on the detector.

RESULTS

X-ray diffraction measurements were made at different rocking curve angles (the angular deviation from the Bragg condition) and at different laser fluences. In fig. 1, the normalized time-resolved diffraction efficiency is shown at an angle of +40 arcseconds, at a fluence of ~10 mJ/cm². It is observed that along with an initial drop in the diffracted intensity, the reflectivity oscillates with a period of ~15 picoseconds, indicative of fast, large-amplitude, coherent lattice oscillations.

Figure 1. Normalized x-ray reflectivity on the large angle side of the rocking curve following ultrafast laser excitation.

We interpret this result in the following manner: On a timescale faster than the lattice can relax, an impulsively generated stress develops through either thermal heating of the lattice or direct acoustic deformation potential coupling of excited carriers to the lattice. This results in the excitation of coherent acoustic phonons across a range of wave vectors near the Brillouin zone center. Off the peak of the rocking curve, the wave vector of an acoustic phonon compensates for the mismatch between the reciprocal lattice vector and the scattering vector. This is similar to diffuse scattering experiments, except that the scattering is due to coherent rather than incoherent thermal vibrations, so that the intensity oscillates at the acoustic phonon frequency.

The acoustic phonon dispersion relation near the zone center is measured by recording the oscillation frequency for different angles relative to the Bragg peak (Fig. 2).

Figure 2. Oscillation frequency for different rocking curve angles, a measure of the phonon dispersion relation. The slope is proportional to the longitudinal acoustic sound velocity in the material.

From the slope of the above plot, we find the longitudinal acoustic sound velocity along the 111 direction to be 3 ± 1 km/sec in agreement with the known value of 3.7 km/sec.

The atomic displacements due to the coherent phonon oscillations can be estimated from the observed oscillation amplitude. We estimate an amplitude on the order of 10% of a lattice spacing, consistent with the incoherent acoustic phonon amplitude one would expect for InSb near its melting transition.

At higher laser fluences ($>15 \text{ mJ/cm}^2$), near the damage threshold of the material, the diffracted intensity follows the lower fluence data for the first half period of an oscillation, but does not recover (Fig. 3). In effect, the atoms are impulsively excited out of the harmonic potential in which they normally reside, into a disordered state.

Figure 3. Normalized diffracted intensity on the larger angle side of the rocking curve, at a laser fluence $\sim 15 \text{ mJ/cm}^2$.

CONCLUSION

In this work, an ultrafast laser-induced phase transition in InSb was investigated using the method of time-resolved x-ray diffraction. We directly observe the excitation of large amplitude coherent lattice motion, and a transition to a disordered state. In addition, it is demonstrated that x-ray diffraction may be used in the time domain as a probe of phonon dynamics.

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Shape Effect Related to Crystallographic Orientation on Deformation Behavior in Copper Single Crystal

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INTRODUCTION

The deformation behavior of single crystals is influenced by several factors, such as purity, crystallographic orientation, temperature, size, shape, and surface condition, etc.[1,2]. The size and shape of the crystal can especially have a significant influence on the deformation behavior. Many studies on crystals of similar orientation and purity show distinct differences [3,4], which can only be accounted for by the variation of glide path-length due to changes in size and shape of the sample. But it has been commonly believed that the initial operative slip system depends only on the initial crystallographic direction of the tensile axis and not on the glide path-length in samples [5-7].

This paper describes an investigation of the shape effect related to crystallographic orientation on deformation behavior in pure Cu single crystals by scanning electron microscope and an *in-situ* reflection Laue method using synchrotron radiation. The changes in crystallographic orientation of the single crystals during deformation were measured by the reflection Laue method that is suitable for *in-situ* observation. We examined two types of samples having the same orientation of tensile axes and an alternate crystallographic orientation in the direction of width and thickness of the sample. The two samples show different characteristics of deformation behavior, such as activated slip systems, movement of tensile axis, and mode of fracture.

EXPERIMENTAL PROCEDURE

The material used in the present study was 99.999% single-crystal copper. A tensile sample having a gauge length of 12 mm and a cross-section of 4.6-mm width and 1.0-mm thickness was prepared by spark-erosion cutting. After mechanical polishing, the sample was annealed in vacuum at 800 C for 72 hours and chemically polished to remove the damaged and oxidized surface layer formed during the mechanical polishing and heat treatment. From the procedure for sample preparation above, two tensile samples were prepared. The two samples had the same crystallographic orientation of tensile axis but had an alternate crystallographic orientation in the direction of width and thickness of the sample.

The synchrotron radiation source of the beamline 7.3.3 at the Advanced Light Source was employed for the *in-situ* reflection Laue experiment. The sample was elongated in steps of 0.45 mm by a tensile device mounted on a 2-circle goniometer. The focused x-ray beam size on the sample was 300 μm $\times$ 300 μm . Laue patterns were collected at each elongation step using white radiation and a x-ray CCD camera. The exposure time for each Laue frame was 1 sec. Two load cells attached to the left and right side of the sample grips measured the applied load on the sample. The strain rate was $3.7 \times 10^{-4} \text{ sec}^{-1}$.

Figure 1. Tensile axis movement in the standard triangle. (a) sample A; (b) sample B.

RESULTS AND DISCUSSIONS

Stereographic projections of copper single crystal are shown in Fig. 1 where the initial orientation and the following rotations of the tensile axis were determined for each sample. All samples were uniaxially elongated until the point of fracture. According to classical deformation theory, the initial operative slip system is determined only by the initial crystallographic orientation of crystal relative to the tensile axis. The Schmid factor is the main item to determine the initial operative slip system in single-crystal tensile experiments [5]. If the crystallographic orientation of the tensile axis is located near the symmetry line connecting the $[001]$ and $[111]$ axes on the stereographic projection, then the classical theory predicts that two slip systems, BIV and CI, can be operating simultaneously. Here the BIV and CI slip systems represents $(111)[\bar{1}01]$ and $(\bar{1}\bar{1}1)[011]$, respectively.

With the exception of alternative crystallographic orientations in the directions of width and thickness, the samples A and B are in the same deformation condition from the viewpoint of the

Figure 2. Schematic diagram of the crystallographic orientations of samples and the slip plane and slip direction before deformation. (a) sample A; (b) sample B

Figure 3. Photo image of deformed Cu single crystal. (a) sample A; (b) sample B.

classical deformation theory. However despite the similarity of initial crystal orientations of the samples, vastly different deformation behaviors were observed. In sample A, the rotation of tensile axis showed an oscillatory motion (Fig. 1a) as the classical theory predicted. The oscillatory motion means that the BIV and CI slip systems were activated simultaneously as initial operative slip systems. But the tensile axis of sample B moved in the opposite direction, which indicated that the operated slip systems were different between the samples A and B despite the similarity of initial crystal orientations of the two samples. To explain this unexpected result from the sample B, we took into account glide path-lengths of all the slip systems as well as the Schmid factor. Figs. 2 (a) and (b) show the expected operating slip systems in the samples A and B, respectively. The Schmid factors for BIV and CI slip systems are the largest in all the 12 possible slip systems of the sample. The Schmid factors of the AII and AIII slip systems are about 95% of those of the BIV and CI slip systems. Here the AII and AIII slip systems are $(\bar{1}11)[101]$ and $(\bar{1}11)[0\bar{1}1]$, respectively. If the AII and AIII slip systems are activated simultaneously as initial operative slip systems, the predicted movement of tensile axis can result in the Fig. 1(b). The calculated glide path-lengths of the AII and AIII slip systems are about 2 times larger than those of the BIV and CI slip systems in the early deformation stage of the samples examined. Therefore it is concluded that the Schmid factor does not solely determine the initial operative slip systems: the glide path-length may be another important factor to determine the initial operative slip systems.

Figure 4. Slip line Images of scanning electron microscope. (a) sample A; (b) sample B in the centered region; (c) sample B in the boundary region.

Figs. 3 (a) and (b) show optical micrograph of sample A and B, respectively. The fracture mode of the sample A is shear with shearing angle of about 73 degrees (Fig. 3a). This shearing fracture of the sample A occurs as the result of extensive slip on the active slip systems, BIV and CI. The fracture mode of the sample B is not clear, as shown in Fig. 3(b). There are two possibilities: one is the shearing fracture due to AII and AIII slip systems and the other is necking due to multiple slip. When fracture occurs, the tensile axis is near the $[001]$ direction. Therefore it is still unclear which is the origin of fracture.

Fig 4 shows scanning electron microscope images of the samples. It should be mentioned that the method of slip line measurements suffer from the disadvantage that they are essentially surface observations and describe the slip pattern at the surface only. However, since the height

of slip lines is proportional to the number of escaped dislocations, these slip lines may be thought to describe adequately the behavior of the operated slip systems inside the bulk [2]. The observed slip lines of sample A show the characteristic shapes and agree with previous prediction in Fig. 2(a). The two different slip lines have an intersection angle of less than 10 degrees. The measured angle of the slip lines is slightly larger than that calculated result from the initial orientation. In sample B, we can observe the characteristic slip lines that result from different slip systems. The shape of slip lines in the central region accords with the result of Laue diffraction. But the shape of slip lines in the boundary region displays another feature. Because of the shape effect of sample, the glide path-length in the boundary region is much shorter than that in the central region. The measured angle between two slip lines is 65 degrees and is nearly the same as the calculated value. Therefore it is concluded that these slip lines are caused by the BIV and CI slip systems.

CONCLUSIONS

The deformation behavior of pure copper single crystals has been investigated by scanning electron microscope and an *in-situ* reflection Laue method using synchrotron radiation. Although the samples have the same orientation of the tensile axes besides the alternative crystallographic orientation in the directions of sample width and thickness, they show very different deformation behavior. In sample A, the BIV and CI slip systems are activated and shearing fracture occurs. In sample B, the AII and AIII slip systems are mainly operated in the central region but the BIV and CI slip systems are activated in the boundary region due to change of glide path-lengths. The first operative slip system should not be necessarily the one with the highest resolved shear stress. The condition of a minimum glide path-length through single crystal should be taken into account as one of the factors to determine the operative slip system.

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The Practicality of an ALS Bend Magnet as the X-Ray Source for solving Structural Biology problems.

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INTRODUCTION

Significant progress in structural biology is occurring at present with the maturation of the technique of protein crystallography carried out at synchrotron radiation sources worldwide. Access to bright, tunable X-ray beamlines limits the pace of progress in structural biology. We have a program to establish the practicality of carrying out structural biology studies on a regular bending magnet at the local ALS synchrotron. Building such a beamline on a low power, high brightness ALS bending magnet source is viewed as being a very cost-effective solution to improving rapid access to local protein crystallography facilities. To this end we have carried out a Multiple Anomalous Dispersion (MAD) experiment at the Co edge and also studied the diffraction data set from weakly diffracting crystals.

EXPERIMENTAL

We carried out experiments on Beamline 7.3.3 to demonstrate the feasibility of data collection and structure determination by multiwavelength anomalous diffraction (MAD) analysis using an ALS bend source. The optical configuration included a channel-cut, germanium monochromator operating with a band pass of $\sim 1/1000$. Optimized optics in the new beamline are expected to increase brightness by over fifteenfold over the prototype configuration used on 7.3.3. Several crystalline samples were analyzed, including a designed, α -helical coiled coil and a eukaryotic, transcriptional coactivator/activator complex.

RH3, a designed, trimeric α -helical coiled coil with an engineered metal binding site (Harbury et al., 1998) was used to demonstrate that the bend magnet source and optics can meet the rigorous demands of MAD analysis. The trigonal crystals have unit cell dimensions of 25 x 25 x 141 Å, with a single 12 kDa trimer in the asymmetric unit. The metal binding site, consisting of paired γ -carboxyglutamate residues, offers the flexibility to incorporate different metal ions for phasing. Crystals grown in the presence of Co^{2+} , which has four anomalous electrons, were analyzed. Complete data sets were collected to 1.9 Å resolution at eight energies across the cobalt edge (~ 7709 eV) and processed in an automated mode with a SMARTfilm routine developed at UCB (James Holton and T.A., unpublished). Data collection was completed in ~ 10 hours, and processing yielded merging R values of 5-9% and overall $I/\sigma I$ values of 11-20. The data were of average quality, reflecting the rapid collection speed (Table 1).

Data collected at the energies of the maximum anomalous and dispersive signals (Fig. 1) were used in concert with the low energy reference data to identify the Co^{2+} binding sites with the program SHELX (Sheldrick, 1990). Initial phases were calculated using MLPHARE (CCP4, 1994), resulting in excellent phasing statistics including phasing powers above 2.0 (Table 1). These phases were subsequently improved by solvent flattening with DM (CCP4, 1994), yielding electron density maps that were extremely clear and readily interpretable (Fig. 2). Automated model building and refinement with wARP (van Asselt et al., 1998) produced initial R and free R-values of 0.239 and 0.320, respectively, prior to any manual adjustment of the model. The entire process, from data collection to preliminary refinement of the model, was completed in 36 hours.

Figure 1. Dispersive (D_{iso}) and anomalous differences as a function of data collection energy for RH3. The dispersive difference was calculated versus the low energy reference energy of 7700 eV. The dispersive difference was maximized at 7720 eV and the anomalous difference was maximized at 7730 eV. Significantly, the maximum dispersive difference did not occur at the apparent midpoint of the anomalous signal.

ALS Beamline 7.3.3, 12/98, 50-1.9 Å resolution, Co ²⁺ complex							
Energy	R _{sym}	R _{anom}	I/σI	Completeness (%)	Multiplicity	Phasing power ano/disp	Cullis R ano/disp
7000	0.058	0.043	14.2	80.1	3.1	0.14/2.38	0.99/0.54
7710	0.062	0.048	11.6	93.2	3.1	0.17/1.14	0.98/0.79
7715	0.051	0.043	13.3	93.6	3.3	0.26/0.82	0.97/0.88
7720	0.079	0.050	18.0	84.7	7.2	1.02/-	0.68/-
7730	0.068	0.086	12.8	94.4	4.9	1.36/2.05	0.59/0.59
7740	0.052	0.077	12.6	93.8	3.3	1.21/2.26	0.63/0.56
7750	0.055	0.061	12.7	94.2	3.3	0.82/2.17	0.75/0.57
8000	0.094	0.102	20.1	92.8	3.2	0.46/1.82	0.89/0.66
Mean figure of merit (25-1.9 Å): 0.776							
Crystallographic R/R _{free} (25-1.9 Å): 0.239/0.320 (824 atoms built and refined with wARP 5.0)							
SSRL Beamline 1-5, 50-2.0 Å resolution, Ni ²⁺ complex							
8342.0	0.084	0.036	20.8	86.6	8.1	1.01/4.37	0.70/0.35
8348.2	0.081	0.076	21.4	86.6	8.2	1.69/2.22	0.51/0.58
8900.0	0.084	0.049	16.4	84.5	7.0	1.30/-	0.60/0.35
Mean figure of merit (25-1.9 Å): 0.831; after solvent flattening: 0.899.							
Crystallographic R/R _{free} (25-1.9 Å): 23.3/26.9 (Δbonds = 0.007 Å, Δangles = 1.07°; refined with CNS (Brunger, 1998))							

Table 1. RH3 data collection and phasing statistics. Space group P3₁, a=b=25, c=141 Å.

Figure 2. MAD-phased, experimental electron density map of RH3 (25-1.9 Å resolution) contoured at 1σ clearly shows helical trimer and the core isoleucines packing in a knobs-into-holes arrangement. View is along the pseudo-three-fold axis of the trimer showing a cross section through the parallel helices.

As a comparison, data were collected from a comparable, isomorphous crystal of RH3 complexed with Ni^{2+} at Beamline 1-5 at SSRL. Data collection at four energies required four full days of beam time. The quality of the data collected on ALS Beamline 7.3.3 compares favorably with the data collected at SSRL (Table 1), and clearly the ALS bend source offers superior brightness and speed.

To explore the feasibility of using ALS Beamline 7.3.3 for data collection on a more weakly diffracting experimental system, we analyzed crystals of a complex between the transcriptional coactivator DCoH and the dimerization domain of its cognate activator, HNF-1. The crystals have the symmetry of space group $P2_1$, with 62 kDa in the asymmetric unit. Data collected at a single energy required ~10 hours of exposure, compared to four days on a laboratory source or three hours at Beamline 7-1 at SSRL. The resolution and accuracy of the data were better than data from a laboratory source (not shown), but slightly worse than the data collected on the same crystal at SSRL Beamline 7-1 (Table 2). Although the reduced data quality directly reflects the comparably lower flux of Beamline 7.3.3, it is important point out that SSRL 7.1 is a wiggler beamline, while 7.3.3 is an ALS bend magnet.

	ALS Beamline 7.3.3, 12/98		SSRL Beamline 7-1	
Resolution (Å)	R _{merge}	I/σI	R _{merge}	I/σI
50 - 7.39	0.030	37.9	0.020	46.7
5.87	0.027	34.1	0.023	59.8
5.13	0.029	30.6	0.022	63.6
4.66	0.028	32.8	0.021	66.8
4.33	0.030	32.4	0.023	64.6
4.07	0.032	28.6	0.025	64.1
3.87	0.034	27.4	0.027	63.3
3.70	0.040	24.5	0.030	59.2
3.56	0.046	21.6	0.035	54.7
3.43	0.054	18.9	0.038	50.9
3.33	0.060	16.5	0.041	47.6
3.23	0.088	11.9	0.050	39.9
3.15	0.088	10.1	0.055	36.1
3.07	0.106	8.7	0.066	31.6
3.00	0.129	7.2	0.075	27.4
Overall	0.041	24.0	0.030	54.4

Table 2. DCoH/HNF-p1 data collection statistics. Space group: P2₁, a=49.4, b=83.0, c=70.4 Å, β= 97.4°.

These results demonstrate the feasibility of solving structures rapidly using an ALS bend magnet source. In particular, both energy resolution and intensity are sufficient for MAD analysis and for weakly diffracting crystals. Proposed enhancements to the optical system over the current 7.3.3 configuration would be expected to provide over an order of magnitude increase in brightness and a commensurate increase in data quality and throughput. Taken together, this data clearly shows that an inexpensive ALS bend magnet can readily compete with far more costly wiggler facilities.

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Beamline 8.0.1 Abstracts

Band-structure and core-hole effects in resonant inelastic soft-x-ray scattering: Experiment and Theory

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INTRODUCTION

Resonant soft-x-ray fluorescence spectroscopy (RSXF) refers to the study of the changes in x-ray emission spectra as the excitation energy is varied near a core-level absorption threshold. It has been the application of RSXF to solids in the soft-x-ray regime that has garnered most of the interest in the past decade [1]. Although the description of the scattering in terms of purely delocalized states [2, 3, 4, 5] is appealing in its simplicity, serious questions have arisen concerning the validity of this picture [6, 7]. In core-level absorption spectroscopy (XAS or NEXAFS), core-hole effects and core excitons are clearly observed, and have long been known to dramatically affect the interpretation of absorption spectra [8]. Since the final states in XAS are the intermediate states in RSXF, it has been argued that an interpretation which omits excitonic effects is intrinsically suspect [6]. In fact, it has been asserted in at least one work that the inclusion of such effects is necessary in order to correctly account for the experimental data [7].

In this work, we will focus on the possible role core-hole effects have on the RIXS in a particular system: graphite. This will be accomplished by examining, at higher resolution than previously attainable, the changes in the scattering near the σ^* and π^* absorption thresholds in this material. Comparisons will then be made to simulated spectra that include or exclude core-hole effects. Our conclusion is that core-excited states have only minor effects on the emission features, even though they clearly have a pronounced effect on the total fluorescence yield. However, other spectral features are not fully accounted for by the inclusion of core excitons in the scattering.

RESULTS AND DISCUSSION

Due to recent advances in the storage ring at the ALS, Beamline 8.0 now delivers, by more than an order of magnitude, more flux in the 100-1000 eV range ($\approx 1.3 \times 10^{13}$ photons/sec for $\Delta h\nu \approx 60$ meV). This affords us the opportunity to examine, with much higher resolution than in previous studies, the crystal momentum conservation and selectivity during RIXS, for intermediate state energies near well-known core-excited states, while retaining data acquisition times around ten minutes. This can be accomplished by narrowing the bandwidth of the excitation energy $\Delta h\nu$ down to ≈ 60 meV. This reduction of the bandwidth narrows the widths of the iso-energy contours in the BZ that are summed over during the RIXS process (i.e. the spread of crystal momenta in the BZ is reduced). Figures 1 & 2 show RSXF data collected near the π^* (Fig. 1) & σ^* (Fig. 2) absorption edges in graphite, using both narrow- and wide-band excitation ($\Delta h\nu \approx 60$ meV or 500 meV).

Through comparison of Fig. 1(A) and 1(B), it is clear that narrow-band excitation has an marked effect on the measured spectra. Features in Fig. 1(B) are sharper than in Fig. 1(A). As the excitation energy increases, the transition from emission around the K point ($h\nu' \approx 272$ eV) to emission around M ($h\nu' \approx 276$ eV) occurs over a narrower range of excitation energies. Note carefully the upper π -band emission ($h\nu' = 281$ -283 eV) in Fig. 1(A) versus Fig. 1(B). Whereas in Fig. 1(A) there is a range of energies for which emissions from both the K and M branches of the upper π bands are observed simultaneously, reduction of the excitation bandwidth leads to a much more smooth transition in Fig 1(B).

Fig. 1. (A,B) Experimental RIXS spectra for HOPG collected for excitation energies near the π^* absorption threshold of 284.5 eV, but using different excitation energy bandwidths ($\Delta h\nu$). The excitation energies are given to the left of each spectrum. The width of the incident radiation for these spectra is approximately (A) $\Delta h\nu \approx 300$ meV and (B) 60 meV. Note the abrupt onset of emission at $h\nu' = 276$ eV. (C) Simulated RIXS in graphite near the π^* threshold. Solid lines correspond to simulated spectra obtained with core-hole effects included, whereas dashed lines are spectra obtained without inclusion of these effects.

Simulated emission spectra for excitation energies near the π^* threshold, generated with (solid lines) and without (dashed lines) the inclusion of core-hole effects, are shown in Fig. 1(C). Note that the dashed and solid curves nearly overlap each other, and that the agreement between theory and experiment is very good throughout the range of energies near the π^* threshold. Clearly, momentum conservation and selectivity are very much in force for all the excitation energies above, equal to, and below the π^* energy. In fact, careful comparison with the simulated spectra in Fig. 1(C) shows that using the narrower bandwidth enhances the agreement between theory and experiment in the K-to-M transition region.

The apparent absence of core-hole effects can be qualitatively explained as follows. Core-hole effects are strong in XAS since the core-hole is present the final state. However, in RIXS, the core-hole is present only in an intermediate state. Although the corresponding exciton can be more localized in real space, and thus more delocalized in momentum space, the final momenta which participate in the scattering are determined by the projection of the excitonic state onto the RIXS final state, which contains an electron in the conduction band and a hole in the valence band. These final states are almost certainly not as localized as the core excitonic states. Thus, momentum selectivity is for the most part the same as one would expect based on a one-electron or non-interaction picture.

The above explanation is sensible for excitons whose binding energies lie within the continuum of conduction band states, as for the π^* exciton above. However, at the σ^* edge, there is a well known exciton that is well-separated from the bottom of the σ^* bands near the M-point in the graphite band structure, with a binding energy estimated to be 0.1 to 0.2 eV [4, 9]. Fig. 2(A) shows RSXF spectra obtained near the σ^* absorption edge using $\Delta h\nu \approx 500$ meV, and Fig. 2(B) show similar spectra obtained using $\Delta h\nu \approx 60$ meV. As opposed to data acquired near the π^* edge, the spectra obtained using the narrower bandwidth have several additional features, highlighted by the dotted line and arrows in Fig. 2(B). The feature located at $h\nu' \approx 281$ eV does not move with excitation energy, and is detectable over a narrow energy range (~ 0.5 eV). Note that its appearance and disappearance corresponds exactly with the σ^* absorption energy ($h\nu \approx 291.6$ eV). Two other, weaker, features also rise and fall with the appearance of the 281 eV feature, located at roughly 276 eV and 269 eV.

Inspection of the graphite band structure indicates that these features are derived from states at the M-point in the BZ. Apparently, in this range of excitation energies k -selectivity is present to a significant degree, and the portion of the BZ selected is near M. This data strongly suggests that a highly localized intermediate state exists near the bottom of the σ^* bands at M, and that this state slightly influences the scattering for a narrow range of energies centered on the M-point.

Note carefully that these emission features do not move in energy as the excitation energy is varied. In a non-interacting picture, we would observe an M-to- Γ cross-over, similar to the K-to-M cross-over discussed above. For instance, we should observe a very rapid dispersion, to lower emission energy, of the 281 eV feature, as $h\nu$ varies from roughly 291 eV to 292.5 eV. The fact that they do not move suggests that a highly localized, excitonic state (comprised of a narrow range of k -values near M) dominates the RIXS in this narrow intermediate state energy range.

Fig. 2. (A,B) Experimental RIXS spectra for HOPG collected for excitation energies near the σ^* absorption threshold of 291.6 eV, but using different excitation energy bandwidths ($\Delta h\nu$). The excitation energies are given to the left of each spectrum. The emission near 281 eV (dotted line) is consistent with final states corresponding to a $\pi \rightarrow \sigma^*$ promotion near M. This feature does not move with the excitation energy. Note also the absence in (A) of the emission feature at 281 eV and at other energies highlighted by the arrows in (A). (C) Simulated RIXS in graphite near the σ^* threshold. There are significant differences between the simulations, and that the agreement between theory and experiment is improved via the inclusion of core-hole effects.

The assignment of these features to excitonic effects is further supported by the simulated spectra shown in Fig. 2(C). RIXS spectra have been generated for excitation energies corresponding to the σ^* exciton region, with the solid and dashed lines representing spectra obtained with and without excitonic effects as before. As opposed to Fig. 1(C), there are now clear qualitative differences between the dashed and solid curves. Note too that the agreement between theory and experiment is improved by the inclusion of core-hole effects. Thus, based on the experiments and the comparison with simulated spectra generated without core-hole effects, we conclude that excitons have only minor effects on the detailed line-shape of the resonant emission spectra in graphite. This conclusion can be extended to a number of other systems [1].

SUMMARY

To summarize, we have demonstrated that the RIXS present in resonant fluorescence spectra above a core-level absorption threshold may be utilized to probe the band structure of a material, as first put forward by Ma [2]. We have probed, using narrow-band excitation, the role core-hole effects play in the RIXS process. In graphite, core-hole effects result in only minor changes to the resonant emission spectra. The ability of RIXS to examine the $\mathbf{k}$ -resolved electronic structure, coupled with the intrinsic strengths of soft-x-ray fluorescence for probing the bulk-sensitive and element-resolved electronic structure of materials, demonstrates the great potential of this technique for probing the electronic structure of novel materials systems which are often inaccessible to other techniques.

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Breakdown of the Dipole Approximation in Soft-X-Ray Photoemission

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A mainstay of angle-resolved photoemission is the (electric-) “dipole approximation,” which ignores all higher-order photon interactions, such as electric-quadrupole and magnetic-dipole effects, and predicts simple electron ejection patterns as a function of angle. In the dipole approximation, a single parameter, β , completely describes electron angular distributions as a function of the angle, θ , relative to the polarization, $\mathbf{E}$, of the ionizing radiation (Figure 1). The solidly colored regions in Figure 2 represent angle-dependent photoemission patterns (with the ejection probability in any direction proportional to the distance from the origin) for different values of β in its range from -1 to 2 . For these dipole-approximation patterns, the angular distribution is always symmetrical around $\mathbf{E}$ and is isotropic for the special case of $\beta = 0$ (Figure 2a).

In the first step beyond the dipole approximation, higher-order photon interactions lead to nondipole effects in these patterns, described by two new parameters, δ and γ . A second angle, ϕ , relative to the propagation direction, $\mathbf{k}$, of the ionizing radiation (Figure 1), also comes into play, permitting forward-backward asymmetry. To demonstrate how significant nondipole effects can be for angular-distribution patterns, the dotted curves in Figs. 2b and 2c and all three curves in Fig. 2a exemplify extreme values for δ or γ . All curves show the same ejection probability along the y axis and in the y - z plane and also show large differences in the forward and backward directions.

To probe the limits of the dipole approximation, soft x-ray photoemission measurements on neon were made at Beamline 8.0. Two-bunch operation was necessary because electron kinetic energies were determined via time of flight (TOF), an efficient technique in which nearly all kinetic energies can be measured simultaneously. The extremely high flux from an ALS undulator was necessary

Figure 1. In the dipole approximation, β alone describes electron angular distributions as a function of the angle, θ , relative to the polarization, $\mathbf{E}$, of the radiation. Higher-order photon interactions lead to nondipole effects, described by two new parameters, δ and γ , and a second angle, ϕ , relative to the propagation direction, $\mathbf{k}$, of the radiation.

Figure 2. Angle-dependent photoemission patterns, with the ejection probability in any direction proportional to the distance from the origin. Solidly colored regions represent dipole-approximation patterns for different values of β . For these, the angular distribution is always symmetrical around E and is isotropic for the special case of $\beta = 0$ (a). The solid curves in (b) and (c) represent nondipole angular-distribution patterns for 2p (b) and 2s (c) photoemission inferred from Figure 3.

to obtain sufficient signal for precise measurements of δ and γ . Two analyzers, placed at the “magic angle” ($\theta = 54.7^\circ$), where β has no influence, but at different angles ϕ to be sensitive to forward–backward asymmetries, sufficed to measure nondipole effects as a function of photon energy.

Figure 3 superimposes two neon photoemission spectra taken with the “magic-angle” analyzers, one in the y - z plane (light color), the other not (black). The spectra are scaled to each other by using neon *KLL* Auger lines, which must have isotropic angular distributions ($\beta = \delta = \gamma = 0$). Obvious intensity differences between the 2s and 2p photoemission peaks are due to nondipole effects. The solid curves in Figs. 2b and 2c represent nondipole angular-distribution patterns for 2p (b) and 2s (c) photoemission inferred from Figure 3. Other spectra show that intensity differences occur at energies as low as 250 eV. Changes in ejection probability as a function of angle are observable well below 1 keV, at photon energies much lower than generally expected for effects beyond the dipole approximation.

Figure 3. Superimposed neon photoemission spectra taken with the “magic-angle” analyzers, one in the y - z plane (light color), the other not (black). The spectra were scaled to each other by using neon *KLL* Auger lines. The intensity differences between the 2s and 2p photoemission peaks are due to nondipole effects.

More significantly, measurements on other atoms and molecules demonstrate that “low-energy” breakdown of the dipole approximation is a general phenomenon. It is likely that many applications of angle-resolved photoemission (e.g., most studies of atoms and molecules, band mapping in solids, photoelectron diffraction and holography, orientational studies of adsorbates, etc.) need to include nondipole effects in their analyses. More work to determine the range of validity of the dipole approximation is under way.

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C-Functional Group Chemistry of Humic Substances and Their Spatial Variation in Soils

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Organic molecules derived from biological processes and the biochemical alteration of plant and animal residue are common in soils and natural aquatic systems and their concentration ranges from <1 ppm to as high as 4×10^5 ppm. Their composition varies widely with location and origin (e.g. soil, marine), and consists of small chain molecules (e.g. acetate, citrate), organic macromolecules (e.g. proteins), and polyfunctional humic substances (HS)¹. Of these, humic substances exist at high concentrations, and are stable to biochemical alteration with long lifetime. In addition, HS can form strong complexes with both inorganic and organic contaminants and mineral surfaces, and thus play a major role in geochemical processes². At least for a century, research has been focused on understanding the HS functional group chemistry and the macromolecular structure - the properties of HS that control their behavior in the environment.

Traditionally researchers have been isolating humic substances from soils and water using various methods (e.g. alkalies, resins), and evaluate their functional group chemistry using different techniques such as nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy (IR), and pyrolysis³. Although these methods have provided important information on the functional groups of HS of different origin, very little is known about their chemistry in their native state⁴. Low C-concentration of several natural samples, and the presence of other interfering elements/molecules of HS and the mineral matter limit the applications of conventional laboratory techniques in *in-situ* characterization of HS functional group chemistry. Hence HS isolation, purification and preconcentration are necessary for their characterization⁵. However, the recent technological developments in soft X-ray spectroscopic tools, and the construction of third generation synchrotron sources, have made the *in-situ* examination of organics possible. In addition, element-specific chemical information for molecules present in water or on mineral surfaces can be obtained under ambient conditions. We have initiated a research program to understand the chemistry of HS in their native state, and to explore the applications of soft X-rays in probing their functional group chemistry and metal complexation patterns. Several soft X-ray beamlines at the ALS (B.L 8.0, 7.0, 6.3.2, 9.3.2) and other complimentary facilities at the Lawrence Berkeley National Laboratory (NCEM), and the Stanford Synchrotron Radiation Laboratory have been used for this study. In this report, the C-functional group chemistry of isolated and pristine HS is discussed here.

EXPERIMENTAL METHODS

In-situ functional group chemistry of HS of different origin (fluvial, soil, peat) and several other structural models (e.g. carboxylic acids, amino acids) is evaluated using SXEER (soft X-ray Endstation for Environmental Research) on beamline 8.0, and the STXM endstation on beamline 7.0. At this stage of the investigation, we focused on the HS C-NEXAFS features and their relation to the different HS functional groups. In addition, this C-functional group information obtained from the NEXAFS can be compared and correlated with the published NMR data. Excepting for the studies on SXEER (in transmission and fluorescence), the C-NEXAFS spectra

of all aqueous/precipitate samples were collected in transmission mode. Several of these solid samples were also analyzed at beamlines 6.3.2, and 9.3.2 in vacuum (using electron yield detection). For examining liquid samples in transmission mode, liquid droplets/soil suspensions were sandwiched between 1600 Å thick windows.

RESULTS AND DISCUSSION

C-Functional Groups of Humic Substances

Previous NMR (C, N, proton) spectroscopic studies of HS indicate that these molecules primarily contain aliphatic C-H, C-N, methoxyl, carbohydrate, carboxyl, alcohol, and ketonic groups, and aromatic C-H, C-N groups^{4,5}. The C-NEXAFS spectra of humic substances also exhibit several sharp peaks below 291 eV, which correspond to the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions of different C moieties in humics. Since the energies of these electronic transitions are characteristic of different functional groups⁶, several HS functional groups can be identified from their C-NEXAFS spectral features (Fig. 1). The spectral region above 291 eV is broad without any sharp features, which may be due to the overlap of broad peaks corresponding to the $1s \rightarrow \sigma^*$ transitions of several HS functional groups. Humic substances isolated from different sources indicate that they contain the same functional groups, but at different concentrations. For instance, the fulvic acids contain high carboxylic to aromatic carbon when compared to the humic acids, and these results are in agreement with that of NMR studies. Although peak intensities in the NEXAFS spectra vary with the orientation of molecules on substrate surfaces⁶, the HS in powdered form and in aqueous solutions do not exhibit any specific orientation, and hence their peak intensities can be used to obtain the relative concentrations of different functional groups.

Figure 1. C-NEXAFS spectra of fulvic and humic acids. The peak positions shown in the table (on right) are obtained from curve-fitting. The peaks corresponding to cyanide groups overlap with those of C=C, and C=O and hence they can not be interpreted unambiguously from the C-NEXAFS spectra of the mixture. However, the N-NEXAFS spectra of HS can provide that complimentary information.

Our studies also indicated that the NEXAFS spectra of air dried HS collected in vacuum and at atmospheric pressure conditions exhibit the same spectral features, which suggests that vacuum conditions do not alter the chemistry of solid HS. However, aqueous humic substances exhibit significant changes in the spectral features of HS functional groups due to their protonation,

changes in molecular conformation, and/or metal complexation. Although the total number of C-functional groups that can be identified by the NMR are greater than that of C-NEXAFS, some of the functional group information can only be obtained from the NEXAFS alone (e.g. on polyaromatics). Unlike the NMR signal, the C-NEXAFS features do not have interference from other elements in soils. In addition, more (either new or complimentary) information can be obtained from the N-, O-, P-, and S-NEXAFS spectral features. Altogether the NEXAFS features of these different functional groups can offer significantly more information on humics in their native state, and for their metal/mineral complexed HS than the other spectroscopic techniques.

Spatial Heterogeneity of Humic Substances in Soils

As mentioned earlier, HS are commonly isolated from soils and aquatic systems using various techniques, before they are analyzed. Otherwise the C concentration of original samples is not sufficient enough for most of the spectroscopic methods. In addition, other elements and soil minerals that associate with HS can interfere with the HS analysis^{e.g.7}. To evaluate the influence of isolation procedures on the functional group chemistry of humic substances, we examined the C-functional groups of a pine ultisol (collected from Puerto Rico, USA), and the HS isolated from this soil sample. The C-NEXAFS spectra of organic molecules present in this soil sample is collected from different locations in the sample.

Figure 2. Spatial heterogeneity of C in pine ultisol. The picture on left shows a transmission X-ray microscopy image of soil aggregates in pine ultisol. The soil sample contains Fe-oxides and clays, and the organic carbon concentration in soil is about 4.5 % as C, and a pH of 5.0. The NEXAFS spectra shown on the right are for different locations in the soil aggregates. The sharp peaks at ~ 288.5, 290.5, and the doublet at 300 eV correspond to the carboxylic, carbonate and the potassium L₂ & L₃ edges, respectively. The low-energy shoulder at 287 eV corresponds to the ketonic, and aliphatic C-H groups.

When compared with the NEXAFS spectra of isolated soil humic substances (Fig. 1), pristine soil organic molecules (i.e. soil organics not subjected to isolation procedures) exhibit spectral features representative of carboxylic, carbonate, and ketonic groups with no distinct spectral features of aromatic C. Only one (location 4 in Fig. 2) of the several locations in the soil sample examined (10 μ x 10 μ area) showed a broad feature around 285 eV in the C-NEXAFS spectrum, which may correspond to the aromatic C. This spectrum is noisy, which may be because of high sample thickness and/or low C-concentration. However, based on these results one can conclude that carboxylic, carbonate (inorganic, organic) and ketonic groups predominate the C-NEXAFS spectrum of pine ultisol, and the aromatic content is at extremely low concentration. This may

suggest that the HS isolation procedures may be causing the enrichment of organic molecules rich in aromatic unsaturated C, relative to the carboxylic and other groups.

The concentration of organic molecules in aquatic systems are typically very low (< 50 ppm), and it is not feasible to obtain C-NEXAFS spectra in transmission or fluorescence mode for these samples. We are currently testing different solid state detectors to improve the sensitivity of fluorescence detection of dilute aqueous samples. However, high fluorescence yield at high energies permitted the examination of S-functional groups of organics present in fluvial samples and their HS isolates at the SSRL. These studies also indicate that the isolation procedures modify the sample chemistry. Experiments are in progress to characterize the *in-situ* fractionation of metals and contaminants into HS, and their specific interactions with different functional groups of HS.

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Correlating Electronic Structure with Cycling Performance of Substituted LiMn_2O_4 Electrode Materials – A Study Using the Technique of Soft X-ray Emission

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INTRODUCTION

Rechargeable batteries based on LiMn_2O_4 cathodes have been suggested as an attractive alternative to the current nickel and cobalt based systems due to their relatively high energy density, low toxicity, and low cost [1]. Unfortunately, they exhibit a high degree of capacity fading [2]. Partial substitution of small quantities of metal cations for the Mn can significantly improve the cycling behavior of these electrode materials [2-6] – but at the expense of a decrease in initial capacity. For a given nominal oxidation state of Mn, data from W. Liu et al. [5] indicate that electrodes that have been substituted with Co cycle more efficiently than those that have been substituted with Ni. However, the relationship between the type and amount of metal substitution and the cycling enhancement has not been adequately explained.

L-edge x-ray emission spectroscopy (XES) of transition metals is a highly sensitive probe of covalency. As has been observed by these authors in Mn systems [7] and earlier by other groups studying Cu compounds [8], the higher the degree of covalency, the larger the ratio of L_α/L_β in transition metal complexes. In order to probe the covalency of these systems and to obtain a better understanding of the correlation between electrode performance and electrode composition, we have measured soft x-ray emission spectra on a series of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials (Me = Co, Ni, Li and $0 \leq y \leq 0.5$).

EXPERIMENTAL

Manganese L-emission spectra were recorded using the University of Tennessee soft x-ray fluorescence endstation on Beamline 8.0 at the Advanced Light Source [9]. A 925 l/mm grating was used to monochromatize the above threshold excitation energy for the emission measurements (Mn: ≥ 670 eV, Co: ≥ 825 eV, Ni: ≥ 900 eV) and a 1500 l/mm grating was used in the fluorescence spectrometer. With an entrance slit of 50 microns, the resolution of this detector corresponds to approximately 1.1 eV in the Mn fluorescence region. Mn Emission spectra were calibrated relative to the L_β emission of MnO [10] and the spectra were normalized to unit intensity at the L_β peak.

The LiMn_2O_4 and $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ (Me = Co, Ni, Li) samples were prepared as has been previously described [11] and the structures were confirmed by x-ray powder diffraction measurements. The dry powders were pressed into pellets for the XES measurements.

RESULTS AND DISCUSSION

Figure 1. Mn L-emission Spectra of $\text{LiNi}_y\text{Mn}_{2-y}\text{O}_4$ Electrode Materials. Three different amounts of Ni-substitution ($y = 0.00, 0.175, 0.25$).

The L-edge XES spectra from a series of $\text{LiNi}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($y = 0.00, 0.175, 0.25$) are presented in Figure 1. The L_α and L_β emission are centered here at 637.5 and 648.5 eV, respectively. Upon increasing the nominal Mn oxidation state by a higher level of Ni substitution, the intensity of the L_α peak (with respect to the intensity of the L_β peak) increases. The larger L_α/L_β ratio for the sample with a higher Mn oxidation state indicates an increase in the covalency of the Mn, as is expected. In order to correlate the dependence of this increase in covalency with the type of metal substitution, the spectra of a series of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($\text{Me} = \text{Co}, \text{Ni}, \text{Li}$) were simulated with four Lorentzian components.

The dependence of the relative covalence (the L_α/L_β ratio normalized to the L_α/L_β ratio of a sample of LiMn_2O_4 which was recorded under the same experimental conditions) on partial metal substitution of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($\text{Me} = \text{Co}, \text{Ni}, \text{Li}$) is shown in Figure 2. As the manganese oxidation state is increased by increased substitution with Co, the covalency of the Mn is increased. A similar trend is observed for Ni substitution. In addition, for a given average nominal Mn oxidation state, a sample substituted with Co is more covalent than one substituted with Ni which is in turn more covalent than a sample with Li-substitution.

This increase in covalency of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials with $\text{Me} = \text{Co}$ as compared to $\text{Me} = \text{Ni}$ mirrors the increase in cycling efficiency as seen by W. Liu et al. It is logical that greater covalency would be beneficial to electrode performance. The more covalent the Mn-O bond, the stronger the bond, making the spinel structure more resistant to the destructive expansion and contraction observed for LiMn_2O_4 electrodes.

As the cycling efficiency and covalency increase (for a given nominal Mn oxidation state), the crystal radius of the substituent is decreasing (effective crystal radius: $\text{Li}^+_{\text{oct}} = 0.90 \text{ \AA}$, $\text{Ni}^{2+}_{\text{oct}} = 0.83 \text{ \AA}$, $\text{Co}^{3+}_{\text{oct}} = 0.69 \text{ \AA}$ [12]) while the oxidation state of the substituent is increasing ($\text{Li}^+ < \text{Ni}^{2+} < \text{Co}^{3+}$). Further experiments with different types of metal substitutions will help to determine the driving force for the differences in covalency to allow further feedback for battery development.

We have shown that Mn L_{α}/L_{β} emission can be used to determine the relative covalency of potential $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials. The positive correlation observed between covalency and cycling efficiency provides an explanation of improved cycling properties as a function of metal substitution and should allow identification of promising candidates for high performance rechargeable batteries with quick turnaround time.

Figure 2. Dependence of the Relative Covalence of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ Electrode Materials (Me = Co, Ni, Li and $0.00 \leq y \leq 0.25$) on the Nominal Mn Oxidation State.

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Double photoionization of F in CaF_2

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INTRODUCTION

In inner shell photoionization of low atomic number elements, multiple excitation processes occur with significant probability. Double ionization processes for inert gas atoms such as He, Ne and Ar have well been investigated experimentally¹⁾⁻⁴⁾ and have been understood theoretically⁵⁾⁶⁾, based on three mechanisms, i.e. (1) the absorption of a photon by a single electron followed by the interaction of the photoelectron with the remaining orbital electrons, (2) the shake off, and (3) the ground state correlation. However, the double ionization probabilities in solids are less prominent⁷⁾, and have dependency on change in chemical environments⁸⁾⁹⁾. Representative solids to show such a dramatic change in the multiple ionization probabilities are fluorides, and then CaF_2 was chosen here for a test material whether or not the ratio of double to single ionization can be determined with enough measurement accuracy at the 8.0.1 beam line within a few hour experiment.

EXPERIMENTAL RESULTS AND DISCUSSIONS

F $K\alpha$ emission spectra of CaF_2 shown in Fig. 1 were measured using a grating monochromator at B.L.8. Excitation energies are written at the right hand side of Fig. 1, where K^1L^0 and K^1L^1 denote initial states of X-ray emissions, i.e. one vacancy in K and no vacancy in L, and each one vacancy in K and L, respectively. Namely F $K\alpha$ X-rays, noted as K^1L^0 and K^1L^1 , are emitted from singly and doubly ionized initial states of F in CaF_2 . Energy calibration for the reported emission spectra was obtained by assuming the energy of K^1L^0 to be 677.2eV¹⁰⁾. The intensity ratio of the K^1L^0 line to the K^1L^1 line versus the excitation energy is plotted in Fig. 2. By assuming constant fluorescence yields for the K^1L^0 and K^1L^1 states, one can interpret Fig. 2 as a plot of the ratio of the double ionization cross section to that of single ionization. Increasing tendency of the ratio versus the energy is the same as that for the ratios for He, Ne and Ar, where the latter ratios reach their maximum between 100 and 250 eV above their threshold energies. Such experimental results obtained here indicate that a series of F $K\alpha$ emission spectra taken from fluorides by changing the excitation energies are to be good candidates for explaining electron-electron correlation in solids.

Fig.1 F $K\alpha$ X-ray spectra of CaF_2 . Energies of incident X-rays are indicated at the right hand side.

Fig.2 Relative intensity (K^1L^1/K^1L^0) of Fox X-rays emitted from CaF_2 .

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Electronic Structure of Boron Oxides Measured by Soft X-Ray Emission Spectroscopy

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INTRODUCTION

Boron oxides (B_2O_3) are important materials especially in the ceramic and glass industries, and are also interesting materials from the viewpoint of materials science. Generally, they have rather complex crystal structures, which result in a variety of optical characteristics. Therefore, it is important to understand the fundamental chemical bonding structure in B_2O_3 . The characterization of B_2O_3 and borate glasses has been investigated mainly by optical spectroscopy [1], and many theoretical studies [2, 3] have been intensively conducted. However, there has been little study of characterization using soft x-ray spectroscopy. Soft x-ray spectroscopy using monochromatized highly brilliant synchrotron radiation has become a powerful tool for electronic structure analysis [4]. We therefore measured the soft x-ray emission/absorption spectra and photoelectron spectra of B_2O_3 to elucidate the electronic structure and band structure. In this paper, high-resolution soft x-ray emission spectra in the B *K* and O *K* regions and photoelectron spectra are described to reveal the valence structure. Selectively-excited B *K* and O *K* x-ray emission spectra are also described to study the band structure.

EXPERIMENT

Commercially obtained bulk B_2O_3 samples were used for spectral measurements of soft x-ray emission and absorption. Soft x-ray emission measurements of B_2O_3 were performed using a grating x-ray spectrometer at BL-8.0. The excitation energy of the incident beam was varied from the threshold to the continuum in both the B *K* and O *K* regions to elucidate the radiative decay process of the inner-shell excitation. X-ray absorption measurements were performed at BL-8.0 using a fluorescence yield (FY) method and at BL-6.3.2 using a total electron yield (TEY) method. Photoelectron spectra of B_2O_3 thin films were measured at the Photon Factory [5].

RESULTS AND DISCUSSION

(1) Valence Band Structure: Figure 1 shows the soft x-ray emission spectra of bulk B_2O_3 in the B *K* and O *K* regions, and the photoelectron spectrum of the B_2O_3 thin film. These spectra were taken in the “off-resonance” excitation. The excitation energy in the x-ray emission measurements was tuned to about 20 eV higher than the threshold (209.6 eV for B *K* and 550 eV for O *K*) and that in the photoelectron measurements was tuned to about 20 eV lower than the B *K* threshold (175.6 eV). In the figure the energy scale of these spectra is normalized and aligned from the Fermi edge. The density of states (DOS) spectra of B_2O_3 calculated by Li et al. [2] using a first-principles calculation with a local-density approximation (LDA) were superimposed on the soft x-ray emission spectra: the s- and p-portions of the boron DOS were superimposed on the B *K* spectrum and those of the oxygen DOS on the O *K*.

In the B *K* x-ray emission spectrum, a main peak was observed at 181 eV with a high-energy tail and low-energy satellite at 167 eV. In the O *K* x-ray emission spectrum, a sharp main peak was observed at 525.5 eV with a small peak at 520 eV. These measured spectral features of the B *K* and O *K* x-ray emission are approximately in agreement with the p-portion in the calculated

DOS spectra. Therefore, the main peak with the high-energy tail in the B *K* XES can be assigned to B2p, and the low-energy satellite to hybridized B2p-O2s. The two-peaked structure of the O *K* XES can be assigned to O2p. In the photoelectron spectrum, three peaks were observed at the binding energy of -8 eV (denoted as E_1 in the figure), -12 eV (E_2), and -26 eV (E_3). The spectral feature of this photoelectron can be assigned by comparing the B *K* and O *K* x-ray emission spectra as follows: E_1 is due to O2p, E_2 is mainly B2p and slightly O2p, and E_3 is B2p, B2s, and O2s. The tail near -15 eV is mainly B2s.

(2) Radiative Decay Process: Figure 2 shows the excitation-energy-dependence of the B *K* x-ray emission spectra. The excitation energy was varied from 191.6 eV below the threshold to 224.6 eV on the continuum. In the 224.6-eV excitation, we observed a main peak at 181 eV assigned to B2p, a low-energy satellite at 167 eV assigned to B2p-O2s, a high-energy satellite at 194 eV, and a small peak at 175 eV. The 175-eV peak can be assigned to the third-order diffraction of the O *K* x-ray emission peak, because this peak energy corresponds to one-third of the peak energy of O *K* x-ray emission, and the peak shape is independent of the excitation energy from the B *K* threshold to the continuum. Both the main peak and low-energy satellite shifted about 2 eV toward lower energy during the π^* -excitation at 193.6 eV. This peak shifting can be explained by the change in initial- and final-state screening effects produced by the absence of the electron excited to the bound excitonic π^* orbital [4], which is the “spectator” resonant inelastic x-ray scattering (RIXS). The intense emission peak near 194 eV in the 193.6-eV excitation is the “participator” resonant elastic x-ray scattering (REXS) due to the π^* -B1s transition of the participator electrons [6]. The positions of the main peak and the low-energy satellite were almost independent of the excitation energy above 193.6 eV of the π^* state. This suggests that the band structure of B₂O₃ is fairly non-dispersive in the B2p valence and conduction band, which is consistent with the theoretically calculated band structure [2].

Figure 3 shows the excitation-energy-dependence of O *K* x-ray emission spectra and the FY-absorption spectrum. The excitation energy was varied from 532 eV below the threshold to the continuum at 560 eV. In the absorption spectrum, a prominent peak observed at 536.5 eV may be assigned to the π^* state. In the x-ray emission spectra, the main peak assigned to O2p slightly shifted depending on the excitation energy. This slight peak shifting at the π^* -excitation is due to the spectator RIXS. However, no REXS via π^* -state was observed in the O *K* region. These slight shifts of the main peak and the absence of REXS show that the bound electron state of the π^* -orbital in O *K* threshold is weaker than that in B *K*. The lack of any shifting of the main peak in the higher-energy excitation above π^* -state also shows that the band structure is non-dispersive, which is consistent with theoretical band calculations [2].

CONCLUSION

Soft x-ray emission spectra in the B *K* and O *K* regions of B₂O₃ were measured, and the valence band structure of B₂O₃ was revealed from the hybridized B-O bondings by comparing these spectra with the photoelectron spectrum of B₂O₃ thin films and theoretical DOS spectra. Although resonant radiative decay processes such as “spectator” RIXS and “participator” REXS were strongly observed at the π^* -excitation in the B *K* threshold, weak resonant radiative decay phenomena were observed in the O *K* threshold. This shows that the bound electron state at the π^* orbital in boron atoms is stronger than that in oxygen atoms. No significant peak shifts were observed in the selectively-excited x-ray emission spectra in the B *K* and O *K* thresholds, which shows that the band structure is fairly non-dispersive. These spectral features are in agreement with the theoretically calculated band structure.

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Figure 1 The upper two spectra show the B *K* and O *K* x-ray emission of bulk B₂O₃, and the lower one shows the photoelectron spectrum of B₂O₃ thin film (dotted lines). All spectra were off-resonance spectra: the excitation energies were 209.6 eV for B *K* x-ray emission, 550 eV for O *K* x-ray emission, and 175.6 eV for the photoelectron spectrum. Theoretical DOS spectra (solid lines) of valence orbitals in boron and oxygen atoms, calculated by Li et al. [2], are superimposed on individual B *K* and O *K* x-ray emission spectra.

Figure 2 B K x-ray emission spectra of bulk B_2O_3 in which the excitation energy was varied from 191.6 eV to 224.6 eV. The O K x-ray emission spectrum, in which the horizontal axis shows the third-order diffraction energy, is superimposed.

Figure 3 The upper panel shows the FY x-ray absorption spectrum of bulk B_2O_3 . The excitation energy positions are marked with bars. The lower panel shows the O K x-ray emission spectra of bulk B_2O_3 , in which the excitation energy was varied from 532 eV to 560 eV.

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Electronic structure of KNbO_3 : Nb $M_{4,5}$ X-ray fluorescence measurements

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Mixed oxides of perovskite-type structure, depending on their composition, give rise to a variety of electric, magnetic and optical effects. Among these perovskite oxides, potassium niobate provides multiple electro-optical and catalytic applications [1], making the study of its electronic structure very important. Besides the typically used X-ray photoelectron spectroscopy (XPS), the X-ray emission spectroscopy (XES), which is an element- and partial state-sensitive technique, provides important experimental information about the spatial- and energy-resolved distribution of electronic states in the compound. For the study of dielectric materials, XES has certain advantages over XPS because it is not affected by charging effects, and the quality of the surface preparation is not so crucial. The measurements of the X-ray fluorescence while scanning the excitation energies below and beyond the excitation threshold of particular core states, which are possible at the ALS Beamline 8.0, open new opportunities for the study of soft x-ray resonant inelastic spectra (XRIS). It has been shown that these spectra may reveal some momentum-resolved information regarding the valence band dispersion [2-5].

We measured the Nb $M_{4,5}$ emission spectra in KNbO_3 over the range of excitation energies 206.5 to 240.6 eV. The interpretation of our data has been done based on first-principles calculations of the electronic structure, emission and absorption spectra by the all-electron full-potential linearised augmented plane-wave method.

Figure 1. Nb $M_{4,5}$ emission spectra of KNbO_3 . The excitation energy is tuned through the Nb 3d-threshold from 206.5 to 212.3 eV (a) and from 212.3 to 240.6 eV (b).

In Fig. 1 (a-b) the Nb $M_{4,5}$ emission spectra of KNbO₃ are shown for various excitation energies near the Nb 3*d* threshold. Four features are observed and labeled A through D. The most dramatic changes in the shape of the fine structure of Nb $M_{4,5}$ emission spectra are found for excitation energies between 206.5 and 212.3 eV where new features (D and B) appear with changes in excitation energy. It is suggested in Ref. [6] that in Nb, $M_{4,5}$ emission reveals only the M_5 ($3d_{5/2}$) emission features because the M_4 ($3d_{3/2}$) is filled by radiationless transition. Therefore it was unexpected when we found the excitation energy dependence of Nb $M_{4,5}$ to be distorted by the spin-orbit splitting of the Nb 3*d*-levels and not revealing the band dispersion.

Fig. 2 displays a full calculation of the Nb $M_{4,5}$ emission spectra based on the Nb 5*p* and Nb 4*f* DOS modulated by the transition probabilities. In the calculation, the resulting spectrum has been simulated by shifting the two identical contributions by the value of the spin-orbit splitting in the Nb 3*d* shell, which amounted, according to our full-electron calculation, to 2.88 eV. These two contributions, corresponding to individual M_4 and M_5 spectra, were then summed up with relative weights of 2:3. It is found that the contribution of the Nb 4*f* states to the emission is negligible and only 5*p*→3*d* transitions are important for the interpretation of Nb $M_{4,5}$ XES. The O 2*s* states contribute to the Nb M_5 XES due to the O 2*s* - Nb 5*p* hybridization. The corresponding features in the Nb M_4 and M_5 XES near -16 eV and -13 eV are broadened in the experimental spectra but still recognizable in Fig. 1 as peaks A and B.

Going back to the discussion of the energy dependence of the Nb $M_{4,5}$ emission spectra in KNbO₃ (Fig. 1), we note that according to our XPS measurements the Nb M_5 ($3d_{5/2}$) and Nb M_4 ($3d_{3/2}$) binding energies are 207.2 and 210 eV, respectively (relative to the vacuum level). Conclusively the emission features in the spectra excited between 206.5 and 209.6 eV are generated by the refill of the Nb M_5 ($3d_{5/2}$) hole as excitation of Nb M_4 is not possible below 210 eV. In the excitation energy range between 210.5 and 216.9 eV additional features B and D appear as a result of contributing transitions to Nb M_4 ($3d_{3/2}$). The sharp increase in intensity in the emission spectra at excitation energies from 216.9 eV to 221.1 eV can be attributed to the threshold of the 3*d*→5*p* absorption. This is illustrated by the calculated Nb M_4 -absorption spectrum in Fig. 3. The 3*d*→5*p* absorption starts to contribute at an excitation energy of about 218 eV. The onset for the 3*d*-4*f* absorption occurs around 235 eV. The strong enhancements of the emission (see Fig. 1) occur when the excitation energy exceeds the M_5 threshold ($E_{\text{exc}}=208.5$ eV), M_4 threshold ($E_{\text{exc}}=211.5$ eV), the 3*d*-5*p* threshold ($E_{\text{exc}}=221.1$ eV) and the 3*d*-4*f* threshold ($E_{\text{exc}}=240.6$ eV) as displayed in the absorption spectrum (Fig. 3). We note that the spectrum excited at the 3*d*-4*f* threshold ($E_{\text{exc}}=240.6$ eV) is divided by 4 in order to display all spectra on the same scale.

Figure 2. Calculated Nb $M_{4,5}$ XES of KNbO₃ broadened for instrumental distortion (0.2 eV), core level life-time (0.35 eV) and valence life-time (2.0 eV). The contributions of unbroadened M_5 and M_4 spectra are also shown.

The emission spectrum corresponding to the excitation energy of 221.1 eV in Fig.1 exhibits, as compared with that for $E_{\text{exc}} = 216.9$ eV, strongly enhanced M_5 but relatively unchanged M_4 intensity. Therefore, this specific selective excitation of Nb M_5 XES can be also used to receive experimental information about the Nb $5p$ DOS undistorted by overlapping with Nb M_4 XES. Starting from $E_{\text{exc}} = 222.5$ eV, the resonant emission gets enhanced for the M_4 component as well, so that the original shape of the spectrum (for smaller excitation energies) is roughly restored, but with much higher intensity.

To summarize, we have measured soft x-ray emission spectra excited through the Nb $3d$ threshold. The spectra show dispersion and are explained by the calculations (based on DOS and full band structure calculations). The changes in the spectra occur at the $3d_{5/2}$, $3d_{3/2}$, $3d-5p$ and $3d-4f$ thresholds of the absorption. Tuning the excitation energy to the corresponding thresholds of the absorption spectrum allows us to attribute contributions from the decay of the $3d_{5/2}$ holes (peaks C and A) and the $3d_{3/2}$ holes (peaks D and B) via valence emission. The overlap of these two spectra complicates the analysis of the excitation energy dependent trends in the resonant emission which otherwise would be able to provide key information about band dispersion, as shown by studies of other materials [2, 3].

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Figure 3. Calculated and measured partial fluorescence yield at the Nb $3d$ threshold.

Electronic Structure of Transition Metal Oxides Studied by X-ray Fluorescent Spectroscopy

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The new results are presented of the experimental study of ferroelectrics (KNbO₃ and KTaO₃) by means of X-ray fluorescence spectroscopy. In particular, *Nb* *M*_{4,5} (5p4f→3d_{5/2,3/2} transition), *Nb* *M*₃ (4d5s→3p_{3/2} transition), *Ta* *N*₃ (5d6s→4p_{3/2} transition) and *O* *K*α (2p→1s transition) X-ray emission spectra (XES) have been measured over a range of near-threshold excitation energies [1-2] at Beamline 8.0 of the ALS. The emission spectra are explained by the calculations (based on DOS and first-principle band structure calculations taking into account the dipole transition matrix elements). The changes in the spectra occur exactly where we see structure in the absorption spectrum, at the 3d_{5/2, 3/2}, 3d-5p and 3d-4f thresholds. The emission is due to refill of the 3d_{5/2} (peaks C and A) and 3d_{3/2} (peaks D and B) holes via valence emission. It was suggested [3] that *Nb* *M*_{4,5} XES only reveals the *M*₅ (3d_{5/2}) features because the *M*₄ (3d_{3/2}) is filled by radiationless transition. However, we found that the excitation energy dependence of *Nb* *M*_{4,5} XES is distorted by the spin-orbit splitting of the Nb 3d-levels and hence the band dispersion effects to be blurred. The *Nb* *M*_{2,3} and *Ta* *N*_{2,3} XES have not been, to our knowledge, measured before, they were not listed in the Bearden tables [4]. These spectra lie in a convenient energy region for the synchrotron study to be well separated by selective excitation and can be used for study of d-states distribution in 4d and 5d-transition metal compounds.

Excitation energy dependence of *Ti* *L*_{2,3} XES of TiO₂ is measured near the *Ti* 2p threshold at E_{exc}=458.2-476.9 eV [5]. It is found that *Ti* *L*_{2,3} XES of TiO₂ contains the normal X-ray emission (NXES), which is insensitive to the excitation energy and similar to the spectrum excited far from the threshold and spectrum of resonance X-ray emission (RXES), spectral features of which strongly depend on the excitation energy. We have used a band approach for the discussion of the excitation energy dependence of *Ti* *L*_{2,3} RXES of TiO₂. The RXES process is described as convolution of d-states of intermediate and final states under fulfillment of the *k*-conservation rule. The curves of restricted joint density of states (*rJDOS*) are calculated using *FP LMTO* method and found to be in a reasonable agreement with experimental *Ti* *L*_{2,3} RXES of TiO₂ measured at different excitation energies.

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Inelastic scattering at the 3d- and 4d-4f thresholds of Lanthanides

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We have used soft x-ray inelastic scattering based on excitation with monochromatic synchrotron radiation to elucidate the role of 4f electrons in recombination processes at the 3d-4f and 4d-4f thresholds of Nd₂O₃ [1] and LaAlO₃ [2]. The experiments are performed at the undulator beamline 8.0.1 of the Advanced Light Source utilizing the spherical grating monochromator and the Rowland circle endstation.

1. Nd₂O₃

At excitation energies above the M_{IV} (3d_{3/2}) threshold, we observe Coster-Kronig (3d_{3/2}→3d_{5/2}) enhanced fluorescence from the refill of the M_V (3d_{5/2}) hole via the 5p and 4f channel. Fluorescence occurs mainly due to transitions in which charge-transfer provides additional 4f electrons. Resonant inelastic scattering dominates the emission process and we observe two energy loss features at 21 and 2.3 eV, which are due to net transitions 5p to 4f (5p⁶4f³ → 5p⁵4f⁴) and 4f-inner shell excitations [3] 4f³ → (4f³)^{*} respectively.

When comparing the emission spectra excited through the 3d-4f and the 4d-4f threshold, we note some aspects that are different:

- The contribution of non-dipole transitions (⁴I → ²G, ²H) to the inelastic scattering is stronger at the 3d than at the 4d threshold.
- Only the 3d-4f spectra exhibit charge-transfer and Coster-Kronig processes.
- While the main inelastic process at both thresholds is the excitation of the electrons within the 4f shell (2.3 eV energy loss), the 5p-4f energy loss (21 eV) is not apparent at the 4d threshold.
- At the 4d threshold, radiationless processes such as Auger-electron emission and autoionization suppress fluorescence from the decay of the vacancy in the d-shell via the 4f channel.

Our calculations of the emission spectra make use of the Kramers-Heisenberg formula and are in excellent agreement with the experimental results emphasizing the localized character of the 4f electrons.

2. LaAlO₃

At excitation energies above the M_{IV} edge of La we also observe Coster-Kronig enhanced fluorescence that refills the 3d hole via 5p and 4f electrons. We find a new delayed onset of the fluorescence as the 7.5 eV inelastic scattering evolves into 3d-4f emission about 8 eV above the absorption threshold which we attribute to the energy required to produce a charge-transfer hole. Raman scattering with a net energy loss between the initial and the final states of 7.5 and 16.3 eV is observed. We suggest that the 7.5 eV inelastic scattering feature whose excitation energy is about 8 eV higher than the 3d-4f absorption feature arises from a 4f L charge-transfer. According to our calculations, the 16.3 eV loss is due

to the promotion of a 5p electron into a 4f orbit. Due to the high degree of localization of the 4f electrons, calculations based on a purely atomic model provide a consistent interpretation of the observations. One of the surprising outcomes of these measurements has been the observation that inelastic scattering provides the major contribution to the x-ray emission between the M_V and the M_{IV} absorption thresholds. This is due to the fact that the M shell fluorescence yield is of the order of 0.5%. Secondly it is surprising to see how C-K transitions “switch on” fluorescence once the threshold energy has been achieved.

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Investigation of slider surfaces after wear using Photoemission Electron Microscopy

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INTRODUCTION

The trend of increasing storage density of magnetic storage media at the high rate of 60% annually places very high demands on the materials systems used in these devices. The head/disk interface is one of the key focal points for increasing the storage density further, and this requires improved slider performance, increasingly reduced head disk spacing, and increasingly thinner protective disk overcoats and lubricant thicknesses.

We have applied Photoemission Electron Microscopy (PEEM) to study the elemental and chemical structure and modification of slider surfaces after wear.

PEEM STUDIES OF SLIDERS WORN IN A TRIBOCHAMBER USING LUBRICATED DISKS

A tribochamber consisting of a spindle, an actuator, and a quadrupole mass spectrometer in UHV (base pressure $< 10^{-6}$ Pa) was used for the wear tests [1]. Supersmooth-textured 65 mm disks were coated with 5 nm cathodic arc deposited amorphous hard carbon and lubricated with 0.85 nm of perfluoropolyether (ZDOL) lubricant. Uncoated and coated sliders made from $\text{Al}_2\text{O}_3/\text{TiC}$ were used for the test where the coating was a sputter deposited hydrogenated diamond-like carbon (CH_x) of 6 nm thickness. The continuous drag tests were performed at a drag speed of 0.2 m/s, a load of 30 mN, and a sliding time of 600s.

Substantial scratch marks were found at the surfaces of both, the coated and uncoated slider, after the wear. These areas were studied using the PEEM microscope.

The PEEM microscope used for these studies is located at the undulator beamline 8.0, which is equipped with a spherical grating monochromator having three different gratings to cover the energy range from 200-1500 eV with a resolving power of $E/\Delta E=10,000$. A two-lens, electrostatic microscope operating at a nominal voltage of 10 kV was used for these studies. The microscope is equipped with an aperture at the back focal plane of the objective lens to limit the pencil angle of the electron trajectories and thus increase the resolution. The microscope has a spatial resolution of 200 nm, and it is described in detail in [2].

Figure 1 shows a PEEM image of a scratch we found on a coated slider which was obtained in the following way. An image was acquired at an X-ray energy of 280 eV, which is below the carbon K absorption edge. This image showed mainly topological contrast. Another image was acquired at 300 eV which is the energy of the carbon σ resonance at the K absorption edge [3]. This image showed features due to a superposition of topological and chemical contrast of carbon. Figure 1 is a subtraction of these two images showing contrast only due to the presence of carbon. It shows that there is less carbon in the scratch than the surrounding area which was CH_x coated before the wear.

Figure 1: PEEM image of scratch on surface of CH_4 coated slider. The boxes mark the areas where local NEXAFS spectra were acquired

Figure 2. Carbon K edge spectra taken in the areas indicated in Figure 1 of the CH_4 coated slider

Using PEEM we can obtain taking local NEXAFS spectra by selecting small areas of interest on the sample and taking images at incrementally increased X-ray energies. The areas from which local NEXAFS spectra were taken at the surface of the CH_4 coated slider are indicated in Figure 1. The carbon K edge spectra shown in Figure 2 are normalized to the incident X-ray flux, and their relative intensity reflects the relative amount of carbon present at the sample surface. The spectrum outside the scratch is a typical diamond-like carbon spectrum with the π^* resonance at 285 eV corresponding to sp^2 bonded carbon atoms, and the broad σ resonance around 300 eV [3-5]. The small peak at 286.4 eV can be attributed to $\text{C}=\text{O}$ bonds [3, 4], and this small oxygen contamination is probably due to the fact that the slider was exposed to air for a long time after the coating. The striking new feature found in the scratch is the strong peak at 288.5 eV which indicates carboxylic bonds ($\text{O}=\text{C}-\text{OH}$) [3, 4, 6]. This is remarkable because the spectrum obtained in the scratch is very similar to the spectra taken in wear tracks of hard disks. It was observed that the carbon K edge spectrum in wear tracks of disks lubricated with ZDOL showed the additional carboxylic peak, which was not present in the undisturbed lubricant/hard carbon overcoat of the disks [7, 8]. The spectrum containing the additional carboxylic bond was interpreted as the characteristic feature of degraded lubricant. Unlubricated disks did not show additional peaks or any other variations of the shape of the spectrum of the wear tracks, just a reduction of the total carbon signal [8]. The shape of the carbon spectrum in the scratch indicates that degraded lubricant has been transferred to the slider surface and accumulated in the scratch. It can be seen that a total reduction of the carbon signal was also observed here, the signal is reduced by about 20% in the scratch. Since the carbon signal is a superposition of the CH_4 coating on the slider and the lubricant transferred from the disk to the slider, the CH_4 thickness is probably reduced considerably.

Figure 3 shows a PEEM image of a scratch on the surface of the uncoated slider. The same procedure was applied as described for Figure 1 (subtracting an image acquired at 280 eV from an image acquired at 300 eV) to obtain contrast only due to the presence of carbon.

Figure 3: PEEM image of scratch on surface of uncoated slider. The boxes mark the areas where local NEXAFS spectra were acquired.

Figure 4: Carbon K edge spectra taken in the areas indicated in Figure 3 of the uncoated slider.

From the carbon K edge spectra (Figure 4) acquired in the areas indicated in Figure 3 and from Figure 3 itself one can see that there is almost no carbon at the surface of the slider except in the scratch. The carbon K edge spectrum in the scratch shows the same signature as the spectrum in the scratch of the CH_x coated slider (Figure 2) and the spectra found in wear tracks of disks lubricated with ZDOL. The carboxylic peak is higher with respect to the π^* and σ resonances because the spectrum is not a superposition of CH_x and degraded lubricant as it was on the coated slider. The oxygen K edge spectra inside and outside the scratch indicated the formation of carboxylic bonds [3, 4, 6] confirming the results from the carbon K edge spectrum. The titanium $\text{L}_{2,3}$ edge spectra showed a much stronger titanium signal than the coated slider. The intensity is reduced in the scratch compared to the area outside which shows that material (degraded lubricant) has been deposited at the surface. The reduction is about 60%, therefore the thickness of the deposited degraded lubricant is of the order of the electron escape depth of this material.

DISCUSSION AND CONCLUSIONS

Both carbon coated and uncoated sliders exposed to a wear test in a UHV tribochamber using lubricated disks showed the appearance of scratches at the rail surfaces. It was found that degraded lubricant was transferred from the disk to the sliders and accumulated in the scratches. Local NEXAFS spectra of the degraded lubricant showed the formation of carboxylic bonds, which was also observed in other experiments studying the chemical modification of the lubricant in the wear tracks of disks. It was found that the CH_x slider coating was removed locally during the wear test.

Sliders used in another wear test on unlubricated disks [9] showed no carboxylic bonds in the local NEXAFS spectra. They were also not observed in another experiment in which the wear

tracks of unlubricated disks were investigated [8]. Only a reduced thickness of the CH_x coating was found locally on those sliders.

It was found under all conditions studied that tribochemical modifications occur only when a lubricant is present at the disk surface. Without lubricant only a mechanical reduction of carbon coating thickness on the slider surface was found. In the presence of a lubricant the lubricant was altered chemically (oxidized) during the wear and this chemically modified lubricant was transferred to the slider surfaces.

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Probing Interlayer Exchange Hardening Interactions With The X-Ray Magneto-Optical Kerr Effect

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INTRODUCTION

Exchange hardening refers to interactions between two magnetic phases to yield a superior composite, and provides one route to new hard (permanent) magnet materials with increased stored energy product [1], a figure of merit roughly proportional to the saturation magnetic moment times the coercive field. Because permanent magnets are ubiquitous in the technology that generates and utilizes electricity, improved permanent magnets can lead to substantial efficiencies in energy usage. Typically materials with high magnetic moment have low coercivity (low magneto-crystalline anisotropy) while high coercivity (anisotropy) materials often have low saturation moment. The goal of exchange hardening is to utilize interfacial exchange interactions between finely dispersed (nano-scale) hard and soft phases to realize these improved properties.

Most experimental techniques that measure the magnetic response of composite exchange hardening systems measure the net or aggregate response of the entire sample. A more complete understanding of these heterogeneous systems would be obtained by utilizing techniques that can follow the magnetization reversal of the hard and soft phases individually. By resolving the response of the individual phases, important details of how magnetic exchange interactions and microstructural changes affect each phase and thus contribute to the aggregate response of the composite can be learned. The element-specificity of resonant magneto-optical effects near core levels in the x-ray range offers numerous opportunities to study the magnetism in different phases.

HARD/SOFT EXCHANGE SPRING BI-LAYER SYSTEMS

We have begun to apply our newly developed magneto-optical Kerr and Faraday rotation techniques to study the responses of individual phases in model exchange hardening systems known as exchange-spring magnets [2,3]. These quasi-epitaxial layered structures grown by sputter deposition consist of bi-layer exchange couples. Typically a textured polycrystalline soft layer, Fe in our case, is grown on top of a hard Sm-Co layer that exhibits a significant degree of epitaxy and also some disorder in the form of some chemical heterogeneity. Exchange coupling at the Sm-Co/Fe interface results in significant changes in the properties of both the hard and soft layers, and by adjusting the thickness of each layer the composite response can vary widely between that of the two layers individually.

In a certain range of Fe and Sm-Co thickness interesting magnetic behavior is observed leading to the term exchange-spring structure. For Fe thickness comparable to or greater than the exchange stiffness length, as a demagnetizing field is applied along the easy axis, the top region of the Fe layer reverses magnetization first while the bottom of the Fe layer remains pinned in the opposite direction by the exchange coupling at the interface. While this situation persists a domain wall exists in the soft Fe layer parallel to the interface. Across this domain wall Fe spins rotate coherently by 180° parallel to the wall (Bloch wall) to form a spiral or twisted spin

structure in depth. As the demagnetizing field increases this domain wall is compressed and pushed toward the Sm-Co layer until at some high value this twist is pushed through the interface into the hard layer as the entire structure reverses. At fields below this irreversible switching of the hard layer, the magnetization spiral in the soft Fe layer is entirely reversible, leading to the term spring magnet because the moment will spring back to the original direction over a considerable range.

A simple one-dimensional model of this exchange spring behavior has been developed and shown to fit measured magnetometry data quite well [2,3]. Since most of the magnetic moment in these samples results from the soft Fe layer, the measured data and success of the model in fitting the data primarily apply to the reversal of the soft Fe layer. Indeed some discrepancy exists at the irreversible field where the hard layer reverses, with measurements showing a broader range of reversal than does the model. Thus measurements of the reversal in both the soft Fe and hard Sm-Co layers are of interest to better understand the applicability of this simple one dimensional theoretical model. Of interest is the extent to which the reversal of each layer conforms to the predictions for that layer, and especially how spins in each layer near the interface are influenced by the presence of the layer across the interface having very different anisotropy. Questions of interest include, for example; how many hard layer spins reverse at fields below the irreversible field in response to Fe spins above, and likewise how many Fe spins remained pinned until the hard layer switches?

XMOKE STUDIES OF THE MAGNETIZATION TWIST IN THE FE LAYER

We are using element-resolved soft x-ray magneto-optical Kerr effect (XMOKE) hysteresis loops to follow the reversal of each layer individually [4]. By tuning near the Fe $L_{2,3}$ edges XMOKE loops measure the response of just the Fe in the soft layer, while tuning near the Co $L_{2,3}$ edges yields the rotation of the Co in the hard layer. Measurements effectively utilize the intensity of linearly polarized undulator beamline 8.0 to measure Kerr rotation (in reflection) at different grazing incidence angle θ to vary the penetration depth into the sample.

Figure 1 shows the geometry of the measurement and some calculations simulating the intensity of the total electric field in the sample for a series of θ values. These calculations are made using realistic values of optical constants just below the Co L_3 edge, and reveal that only at relatively

Figure 1. A spring-magnet structure is shown schematically at left consisting of a 20 nm Fe layer grown atop a 20 nm Sm-Co layer. The Cr cap layer prevents oxidation of the magnetic structure while the Cr underlayer seeds epitaxial growth. At right are calculations of the total electric field intensity vs. depth into this structure for a series of grazing incidence angles θ .

high grazing incidence angle does a significant field penetrate into the hard Sm-Co layer. Likewise these simulations show that by varying θ the field in the Fe layer can be varied so that just the top of this layer is sensed at small θ , and deeper regions of the Fe layer contribute to measured signals increasingly with θ . Thus one approach to obtaining depth-resolved information about magnetization is simply by varying incidence angle and measuring magneto-optical signals.

Early XMOKE data taken near the Fe L_3 edge at $\theta = 5^\circ$ are shown in Figure 2. A longitudinal field varied along the easy axis yield these data from the reflected (Kerr) intensity and the rotation intensity measured after a linear polarizer placed in the reflected beam. The top of the Fe layer begins to switch at roughly 0.1 T while the irreversible field corresponding to the switching of the Sm-Co layer is roughly 0.6 T. At intermediate demagnetizing fields a reversible spin spiral structure exists in the Fe layer, as revealed in these data. The top panel shows the measured intensity after the linear polarizer that is sensitive both to polarization and intensity changes in the reflected beam. The middle panel shows the Kerr intensity measured before the polarizer that is insensitive to polarization changes on reflection. Dividing the top by the middle intensity yields the bottom panel showing the Kerr rotation angle. This Kerr angle is primarily sensitive to changes in the longitudinal component of the Fe moment, while the Kerr intensity signal is sensitive to changes in Fe moment transverse to the propagation direction. Such transverse components are necessarily associated with the coherent rotation of Fe spins that exist within the domain wall formed in the reversible field region. Data collected at different angles show systematic trends with θ .

Figure 2. XMOKE hysteresis loop data measured several eV below the Fe L_3 edge for the model exchange spring structure depicted in Figure 1. Intensity measured after the linear polarizer (top), divided by Kerr intensity measured before the linear polarizer (middle), yields the Kerr angle (bottom).

By careful analysis of these XMOKE data we can thus learn about the three dimensional vector behavior of magnetization vs. depth within the Fe layer. We are implementing the magneto-optical formalism of Zak, *et al.*, [5] to calculate the magneto-optical Kerr response from an arbitrary magnetization structure in depth into the sample. We expect to be able both to test the model predictions of magnetization in this structure, and possibly determine a best experimental profile for the depth-variation of magnetization into the Fe layer.

Initial efforts to measure Co XMOKE loops in this sample were unsuccessful because of its large roughness resulting from the MgO substrate [6]. This sample's roughness is greater than the x-ray wavelengths used and reduces the reflected signal by several orders of magnitude compared

to that observed for relatively smooth samples at the large θ values needed to ensure penetration into the Co layer. Indeed from smoother bi-layer structures of Fe on Co having similar thickness to this exchange spring sample we clearly see the reversal in the buried Co film, confirming that it is roughness of this specific sample that limits study of its hard layer reversal. Indeed roughness may be one source of discrepancy between the simple one-dimensional model and behavior of real samples. We have several ideas to obtain hard layer data on this and similar samples.

CONCLUSIONS AND FUTURE DIRECTIONS

It is clear from these and other data that by combining element-specificity and depth-penetrating capabilities of XMOKE and related soft x-ray magneto-optical techniques we can study magnetic interactions in nano-phase composite magnets through their effects on the constituent phases. These unique capabilities should impact our understanding of many important problems in heterogeneous magnetic structures of increasing interest from fundamental and applied perspectives.

These model exchange spring structures, whose magnetization reversal is complex yet thought to be reasonably well understood, are ideal systems to study as we move from the development of new x-ray magneto-optical techniques into their application to study important problems in magnetic materials. With continued effort we expect to be able to more rigorously test existing models describing magnetic exchange interactions in these structures than can current experimental techniques. By developing an understanding of the reversal in the hard and soft layers of model spring magnet systems, we will be well-positioned to apply these techniques to systems that may be less structurally perfect and whose behavior is less easy to predict and also less easy to understand experimentally. Exchange hardening composites exhibiting more disorder are important because they are more easily produced than epitaxial structures, and hence are good candidates for practical materials based on the exchange-hardening concept.

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Probing intermixing and impurity localization at a buried interface: the CdS/Cu(In,Ga)Se₂ thin film solar cell heterojunction

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INTRODUCTION

The investigation of interfaces in layered systems is one of the most important and challenging fields of solid state physics. For example, nearly all electronic devices are based on, or contain, buried interfaces. Consequently, a detailed quantitative knowledge about the atomic and electronic structure at buried interfaces is of general importance. This calls for an experimental probe sensitive to the location of the interface, sensitive to the electronic and chemical structure at the interface, and atom-specific to discern the various elements involved. In addition, the probe should be non-destructive to rule out any obscuring influence of the measurement technique on the information that is being obtained.

Unfortunately, no single such probe exists today. Several techniques such as X-ray diffraction and scattering, X-ray standing waves, X-ray absorption, electron microscopy, second-harmonic and sum-frequency generation, and Raman spectroscopy have been used to address a few of these demands. It is the purpose of this report to demonstrate that the complementary techniques X-ray Emission Spectroscopy (XES) and Photoelectron Spectroscopy (PES) can be combined to unambiguously identify both interfacial intermixing and the localization of a particular atomic species (Na) at a buried CdS/Cu(In,Ga)Se₂ thin film solar cell heterojunction.

SCOPE

Thin film solar cells based on CdS/Cu(In,Ga)Se₂ heterojunctions are one of the most promising and efficient systems in their field. Photovoltaic conversion efficiencies up to 17.7 % on a laboratory scale [1] and up to 11.8 % for full size modules (1.2 kW) have been achieved [2]. Despite the importance of the Cu(In,Ga)Se₂ (CIGS) based solar cell, however, the microscopic mechanism of how the photon-excited charge carriers are separated and transported to the electrodes is far from being fully understood. All existing models explain the electronic properties of the heterojunction based on an abrupt interface between the CdS buffer layer and the CIGS absorber material. In contrast, we will demonstrate that the buried interface is clearly non-abrupt with a graded distribution of S, Se, and In across the heterojunction. Moreover, the potential role of Na impurities at the CdS/CIGS interface is poorly understood. It is generally accepted that Na impurities have an extremely beneficial influence on the solar cell performance over a wide range of Na concentrations [3], and several chemical models have been proposed [3-5]. To date, however, the enhancing mechanism and the microscopic Na location have not been understood. There is some evidence that for thermally treated CIGS films the Na is mostly

located at the surface [6], but it has been assumed that Na at CIGS surfaces does not play a role for the complete solar cell device, because a CdS layer is deposited onto the CIGS film by an aqueous dip, and because water can remove Na from the CIGS surface [5,7]. It is the purpose of this report to demonstrate that Na is in fact not only located on the free CIGS surface, but that a significant fraction remains localized at the buried CdS/CIGS interface.

EXPERIMENTAL

The experiments were performed at the undulator Beamline 8.0 of the Advanced Light Source employing the Soft X-Ray Fluorescence spectrometer [8] and the Ellipsoidal Mirror Analyzer [9]. The samples were prepared by Rapid Thermal Processing (RTP) technology from elemental layers of Cu, In, Ga, and Se deposited on Mo-coated sodalime glass substrates. CdS was deposited using chemical bath deposition (CBD) in aqueous solution. The CdS overlayer thickness was controlled by the duration of immersion; the absolute thickness values are accurate only within 30 %, the relative values within about 10 %. Immediately after preparation, the samples were sealed under dry-nitrogen ambient conditions. One CIGS film was treated by ion-sputtering to remove the Na surface content. A single sputter step was performed on this sample with 2 keV Ar⁺ ions at about 1 $\mu\text{A}/\text{cm}^2$ for 30 minutes.

RESULTS

In Fig. 1, XES spectra of the Na K_{α} transition ($2p \rightarrow 1s$) are presented. The excitation photon energy was set to $h\nu = 1075$ eV in order to maximize the Na signal. The spectra were normalized and energy calibrated with respect to the Cu L_{α} transition ($3d \rightarrow 2p_{1/2}$) which was measured simultaneously with the Na signal. The entire spectrum for the pristine CIGS surface is shown in the inset of Fig. 1. The location of the Na signal under investigation is marked as well. The main part of Fig. 1 shows the Na $2p \rightarrow 1s$ and the Cu $3p \rightarrow 2s$ transitions for the pristine CIGS surface (spectrum a), after a short ion-sputter treatment (spectrum b), and after deposition of 5 nm CdS (spectrum c) and 100 nm CdS (spectrum d) on the pristine CIGS film. The Na peak for the pristine CIGS surface is completely removed by the sputter treatment, as seen both in XES and PES. This demonstrates that Na is (within the detection limits of XES) entirely located at the CIGS surface and not, as commonly believed, in the bulk (e.g., at defects or grain boundaries). Note that the Na saturation content at RTP-produced CIGS surfaces was previously determined to be about 1 % of a monolayer [7], so that the peak in spectrum a) corresponds to about a hundredth of a surface monolayer. Consequently, even about 1 ppm Na should be resolvable in the CIGS bulk, i.e., in

Figure 1. X-ray emission spectra of the CdS/Cu(In,Ga)Se₂ interface formation: (a) pristine Cu(In,Ga)Se₂; (b) after short sputter treatment; and after chemical bath deposition of (c) 5 nm CdS and (d) 100 nm CdS.

the ion-sputtered sample, which is apparently not the case (Fig. 1 b). Remarkably, the Na content of the pristine CIGS surface (spectrum a) is only slightly reduced upon deposition of 5 nm CdS (spectrum c), while the corresponding PES experiment (not shown) detects only a very weak Na signal, in accordance with the signal attenuation expected for a 5 nm overlayer. In XES, we were able to observe Na signals for overlayer thicknesses up to 50 nm, well beyond the common buffer layer thickness in CIGS solar cell devices. Apparently, the Na atoms are localized at the buried interface and the Na content is reduced, but not removed by the aqueous CdS dip. Note that due to the normalization with the Cu signal all influences due to the differences in X-ray attenuation from the buried regions are removed. We do detect a reduction of the Na content due to an interaction between water and Na, as reported previously [7]. However, significant amounts of Na remain present and are localized at the CdS/CIGS interface.

Moreover, we find that the CdS/CIGS interface is strongly intermixed. From a signal attenuation analysis of PES spectra (not shown) we derive that both Se and In segregate into the CdS overlayer. In the case of Se segregation, we find a significant Se peak for CdS overlayer thicknesses of 50 nm and above, while in the case of In no PES signal could be observed above 15 nm. Because typical CdS film thicknesses in industrial solar cell applications lie between 15 and 50 nm, we conclude that the so called “CdS buffer layer” is in fact an In-containing sulfoselenide layer.

Analogous to a diffusion of Se into the overlayer, a simultaneous diffusion of S into the CIGS substrate is to be expected. We did in fact find direct spectroscopic evidence for such behavior in the XES spectra shown in Fig. 2. In this experiment, the S 2p core levels are ionized and the X-ray emission due to electronic transitions from the valence band region into these core holes is monitored. In particular, emission lines representing the S 3s→2p transitions, the Cd 4d→S 2p transitions, and the Cd 5s→S 2p transition from the upper valence band (UVB) can be identified, as marked in Fig. 2, spectra d) and e). In spectrum e) the exciting photon energy was tuned to 162.7 eV so that only the S 2p_{3/2} core level was ionized. The presence of a Cd-S cross-over transition is an interesting finding in itself, because it demonstrates a wavefunction overlap between the S 2p and the Cd 4d orbitals.

Spectra a) - d) in Fig. 2 were multiplied by appropriate scale factors for ease of comparison. While spectra b) - d) are essentially identical to each other and to the CdS reference spectra [10], this is not the case for the 5 nm CdS overlayer sample, for which the Cd 4d→S 2p transitions are almost entirely absent. Apparently, no overlap between the S 2p orbitals and the Cd 4d orbitals exists for a thin CdS overlayer, i.e., Cd and S atoms do not form the usual Cd-S bond, but are

Figure 2. XES of the electronic transition between valence band states and ionized S 2p core levels, for various CdS thicknesses (a - d, excitation energy $h\nu = 208$ eV) and excited between the ionization thresholds of S 2p_{3/2} and S 2p_{1/2} (e, $h\nu = 162.7$ eV).

most probably separated. This is again interpreted as the formation of an additional sulfoselenide, namely $\text{CuInS}_x\text{Se}_{2-x}$, at and below the surface of the CIGS substrate. In addition, a chemical bond between In and S such as in In_2S_3 seems possible, both within the CIGS substrate and the CdS overlayer. Independent of the details of the interpretation, the experimental data clearly demonstrate that the chemical and atomic configuration of the S atoms is completely different from what one would expect for an abrupt CdS/CIGS interface.

CONCLUSIONS

In summary we find that (a) the buried CdS/CIGS interface is strongly intermixed and that (b) Na impurities, which are usually found at the free surface of CIGS films, are localized at the buried CdS/CIGS heterojunction after the interface formation. Both findings are of great importance for the understanding of the solar cell performance. In the former case, all existing interface models (especially the band offsets) have to be reconsidered in view of the intermixing results. In detail, the formation of sulfoselenide compounds by interdiffusion leads to a graded electronic structure at the interface with unexpected values for band gaps and band offsets.

Moreover, the localization of Na impurities at the interface is expected to play an important role in terms of interface dipoles, electron donation, and chemical reactions involving oxides at the buried heterojunction. The present results show that a combination of photoelectron spectroscopy and X-ray emission spectroscopy constitutes a powerful tool to investigate the atom-specific structure of buried interfaces and their intermixing behavior, and demonstrates that the availability of intense soft X-ray sources is of crucial importance for exploring the hidden secrets of buried interfaces with such techniques.

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Resonant Elastic X-Ray Scattering in Graphite and Diamond

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INTRODUCTION

Resonant soft x-ray emission spectroscopy, using highly brilliant monochromatized synchrotron radiation as excitation probes, has become an exciting focus of current spectroscopic methods for materials science, because it can provide a new experimental way to analyze the electronic structure of materials in relation to the band structure [1]. Resonant radiative-decay can generally be categorized into two processes: One is resonant inelastic x-ray scattering (RIXS) caused by the correlation of the “spectator” electrons, excited in threshold localized states, with valence electrons, and the other is resonant elastic x-ray scattering (REXS) caused by the radiative transition of the “participator” electrons to the inner core-holes. The “spectator” RIXS has been intensively studied by many researchers, and interesting phenomena concerning the radiative-decay process have been observed in many materials [2, 3]. On the other hand, the study of the “participator” REXS is less advanced: intense REXS has been observed only in boron compounds [4-6]. However, we believe that participator REXS should be observed in other compounds and it should also provide significant information about the radiative-decay process and electronic structure. We first focused on graphite and diamond because the electronic structures and RIXS of these typical carbon materials have already been well investigated. In this paper, we demonstrate the energy spectra of elastic x-ray scattering of graphite and diamond at the C *K* threshold and discuss REXS in carbon materials in relation to the electronic structure characterized by sp^2 - and sp^3 -carbon atoms.

EXPERIMENT

Commercially obtained powder samples of graphite and diamond were used for the REXS measurements. The average particle size of the graphite powder was 45 μm and that of the diamond powder was 36 μm . X-ray scattering and x-ray emission spectra were measured using a grating x-ray spectrometer with a position sensitive detector (PSD) installed in beamline BL-8.0. Fluorescence yield (FY) absorption spectra were also measured using this spectrometer. Energy spectra of elastic x-ray scattering were measured by varying the window width of the PSD in the FY-absorption measurements. Total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2.

RESULTS AND DISCUSSION

Figure 1 shows the elastic x-ray scattering spectra of (a) graphite and (b) diamond powders. The upper panels show the C *K* x-ray emission spectra of graphite and diamond, observed with the PSD in the grating x-ray spectrometer in BL-8.0. In these measurements, the PSD was aligned to detect x-rays from 263 to 298 eV. Elastic x-ray scattering should be observed in the energy region above 283 eV, and RIXS or fluorescent x-ray emission should be observed below 284 eV. To distinguish the elastic x-ray scattering from RIXS, we measured FY-absorption spectra by varying the window width of the PSD. We could detect RIXS in (B) the narrow window of 263–283 eV and could detect both RIXS and elastic x-ray scattering in (A) the wide window of 263–298 eV. Thus, we could obtain the energy spectra of the elastic x-ray scattering by subtracting the FY-absorption spectrum obtained with the narrow window from that obtained with the wide window, (A) - (B), as shown in the lower panels. In the elastic x-ray spectra of the graphite, an intense peak was observed near 284 eV and small bumps were observed in the

energy region from 285–292 eV. In diamond, few significant peaks, except for a small peak at 288 eV, were observed in the elastic x-ray scattering spectrum.

Figure 2 shows the elastic x-ray scattering spectra of graphite and diamond superimposed on the individual TEY-absorption spectra. In graphite, the intense 284-eV peak approximately corresponds to the π^* -absorption peak and the broad bumps in the range from 285–292 eV correspond to the region between the π^* - and σ^* -absorption peaks. No significant scattering structure was observed above the σ^* -peak region. Therefore, this elastic x-ray scattering in graphite corresponds to the threshold unoccupied electronic structure of $p\pi^*$ states in sp^2 -carbon atoms and it should be attributed to REXS. This REXS transition via $p\pi^*$ states agrees with the intense REXS observed in trigonally coordinated boron compounds [4, 5]. In diamond, the small peak at 288 eV corresponds to the threshold peak due to an exciton in the TEY-absorption. This small scattering peak may also be REXS via exciton states, which was also explained with the vibronic coupling effects of core excitons by Ma et al. [7]. However, this REXS in diamond is negligible compared with that in graphite. This agrees with the above-mentioned REXS mechanism, because there are no $p\pi^*$ states in the sp^3 -carbon atoms of diamond. This means that we may experimentally distinguish the $p\pi^*$ states from the complicated hybridized-electronic-structure in unoccupied states of carbon compounds by using REXS spectroscopy.

Figure 3 shows the FY-absorption spectra of graphite taken with the wide and narrow windows, superimposed on each other by normalizing the x-ray scattering intensities. The spectral height at 284 eV in the narrow-window absorption spectra shows the probability of the spectator RIXS process, and that in the wide-window absorption shows the sum of the spectator RIXS and participator REXS. We can therefore quantitatively determine the transition probability ratio between the spectator RIXS and participator REXS by comparing these peak heights. From the figure, the transition probabilities of the spectator RIXS and participator REXS in graphite can be determined to be 66% and 34%, respectively.

CONCLUSION

REXS was observed at the C K threshold of graphite. It is caused by the transition of the participator electrons via $p\pi^*$ states in sp^2 -carbon atoms. This shows that REXS spectroscopy can identify the $p\pi^*$ orbitals in the unoccupied hybridized orbitals of carbon atoms. The transition probability ratio between participator REXS and spectator RIXS in the resonant radiative-decay process can be determined from REXS spectroscopy, confirming that REXS at thresholds provides significant information about the radiative-decay process and about the electronic structures of materials.

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Figure 1 Upper panels show the C K x-ray emission spectra of (a) graphite and (b) diamond. Lower panels show the fluorescence-yield (FY) absorption spectra taken with (A) wide and (B) narrow windows, and the subtracted spectra of (A) - (B). The subtracted spectra give elastic x-ray scattering spectra at the threshold.

Figure 2 Elastic x-ray scattering spectra of (a) graphite and (b) diamond, superimposed on total-electron-yield (TEY) absorption spectra.

Figure 3 FY-absorption spectra of graphite taken with (A) wide and (B) narrow windows.

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Resonant Soft x-ray emission investigation of Be-chalcogenide thin films and superlattices

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INTRODUCTION

Since the first demonstration of blue-green laser diodes on the basis of ZnSe [1], II-VI heterostructures have attracted considerable interest in view of potential applications in optoelectronics. Recently, the new class of Be-chalcogenides with novel and interesting properties have obtained remarkable attention. Significant improvements are expected from the use of Be-based heterostructures, since these materials are harder as compared to conventional II-VI materials. Thus the dislocation density is much lower than for, e.g., ZnSe/ZnTe heterostructures, which in turn improves the lifetime of the devices drastically.

Despite the technological relevance of BeTe very little is known about its band structure, as well as about the stability, abruptness, and atomic intermixing of the BeTe/ZnSe interface. Using molecular beam epitaxy or atomic layer epitaxy techniques the termination of the heterointerfaces can be tailored appropriately, i.e., it is possible to prepare both Zn-Te or Be-Se bonds at the interface. Recent photoemission (PES) investigations [2] of thin BeTe overlayers on ZnSe indicate intermixing over several layers for a BeSe interface and a sharp heterointerface for the ZnTe interface.

The inherent disadvantage of PES is the low probing depth which is limited to a few atomic layers. Therefore the influence of intermixing and interdiffusion in a real heterostructured laser device cannot be determined. Soft x-ray emission spectroscopy (XES), in contrast, offers several advantages for probing buried interfaces of real device heterostructures, for instance bulk sensitivity, elemental and chemical sensitivity and non-destructive depth analysis.

RESULTS AND DISCUSSION

We present results of our ongoing studies (BL 8.0, SXF endstation) of excitation-energy dependent resonant XES measurements of thick BeTe(100) and BeSe(100) layers as well as heterostructure superlattices with different period lengths and interface terminations. The transition from the valence band to the Be 1s core level probes the local partial density of states of the valence band at the Be site. By probing the spectral variations with various excitation energies, band structure information can be extracted, in particular at high symmetry points of the Brillouin zone (BZ). Fig. 1 shows excitation-energy dependent XE-spectra of BeTe(100). To obtain the coherent fraction of each spectrum a high energy spectrum was subtracted from the closer-to-threshold excited spectra with the restriction that the remaining intensities must be positive [3]. The two first coherent spectra of BeTe for $h\nu = 113.5$ eV and $h\nu = 113.7$ eV show maxima at about 3.5 eV and 6 eV below the valence band maximum (VBM). These peak intensities correspond to transitions at the X-point, which is the only k-value with unoccupied states which can be reached with the lowest excitation energy. This can be seen in the band structure plot in Fig. 2, which shows a first-principles calculation of the BeTe band structure obtained within the framework of the density-functional formalism in the local density

approximation [4]. The spectrum for $h\nu = 115.5$ eV shows the highest observed emission energy, which can be associated with transitions at the Γ -point of the BZ: at this k-value of the BZ the conduction bands are flat, which corresponds to a high density of states. Thus the emission observed in this spectrum is dominated by transitions at the Γ -point. The spectra between these two high symmetry points represent an intermixing of different k-values, and a detailed analysis for an exact determination of the corresponding k-values is still in progress.

Fig. 1 Excitation-energy dependent XE-spectra of BeTe(100). The spectrum for $h\nu = 113.7$ eV corresponds to transitions at the X-point. The spectrum for $h\nu = 115.5$ eV corresponds predominantly to the Γ -point (highest emission energy).

Fig. 2 First-principles calculation of the BeTe(100) band structure obtained within the framework of the density-functional formalism in the local density approximation.

Fig. 3 shows the corresponding valence band XE-spectra of BeSe(100). The excitation energy dependence is weaker for BeSe than for BeTe as is confirmed by band structure calculations, which also show a smaller dispersion of the valence bands. Again the first spectra ($h\nu = 114.1$ eV) correspond to transitions at the X-point, and the spectrum for $h\nu = 116.2$ eV predominantly to transitions at the Γ -point of the BZ. These two sets of excitation-energy dependent valence band spectra of BeTe and BeSe serve as reference spectra for comparison with heterostructure superlattices (SL). We have investigated BeTe(6ML)/ZnSe(8ML) SLs with 20 periods and different interface termination (Be-Se interface and Zn-Te interface). Fig. 4 shows valence band spectra near threshold for the two heterostructures with different interface terminations with spectra of the bulk reference samples. The spectra for the SL with a ZnTe interface and the BeTe bulk sample are very similar. In this heterostructure the Be atoms should be surrounded only by Te atoms, which indeed seems to be the case. However, the difference between BeSe interface and BeTe sample is obvious. In this heterostructure there should be a ratio of BeTe to BeSe layers of 5:1. Thus, a spectrum dominated by the BeTe lineshape would be expected. The comparison of the spectra of the SL with BeSe interface and the BeSe bulk sample indicates a strong intermixing at the BeSe interfaces. In contrast, the ZnTe interface seems to be more abrupt, as it resembles the BeTe reference spectrum much more closely.

Fig. 3 Excitation-energy dependent XE-spectra of BeSe(100). The transitions for lowest excitation energy (114.1 eV) occurs at the X-point. The transitions with the highest emission energy (116.2 eV) correspond predominantly to the Γ -point.

Fig. 4 Valence band spectra near threshold for two SLs with different interface termination. The spectrum of the ZnTe-interface superlattice is similar to the BeTe reference sample. This indicates an abrupt interface. For the BeSe interface also spectrum with a BeTe-lineshape like is expected. The comparison with the BeSe reference sample shows a strong intermixing.

CONCLUSION

The experimental results confirm that XES can be used as a bulk-sensitive method to study the electronic bulk band structure of solids in detail. Moreover, using XES spectra as (bulk) reference allows a “fingerprint-approach” to the electronic and chemical structure of buried superlattices and thin interfaces. In the present experiment this approach could be utilized to investigate the atomic intermixing of BeTe/ZnSe-superlattices, and it could be derived that superlattices with BeSe interface show strong intermixing, while ZnTe-terminated interfaces are identified to be more abrupt.

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Satellite free F K α from CaF₂ and SrF₂

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INTRODUCTION

A characteristic X-ray is emitted from an atom whose inner shell electron has been ionized by bombardment of electrons, ions and photons with sufficient energies. The fine structure of the characteristic X-ray resulted from a transition between an inner shell and a valence band has been utilized to understand a partial density of state of the valence band which is responsible for revealing various types of physical and chemical properties of atom-aggregates. However, under the excitation conditions mentioned above, multiply ionized states are produced together with a singly ionized state, which emit X-rays with higher energies, named satellites, than the energy of the characteristic X-ray from the latter state. Coexistence of these two kinds of X-rays make explanation of the fine structure complicated and ambiguous.

Monochromatized synchrotron radiations can well be used to eliminate the satellites emitted from the multiply ionized states¹⁾. In this report we compare observed satellite free F K α emissions with the partial density of states estimated from the DV-X α molecular orbital calculations²⁾. Here CaF₂ and SrF₂ were employed for investigating the partial density of state of occupied F 2p in the valence bands.

EXPERIMENTAL RESULTS

F K α emission spectra of CaF₂ and SrF₂ shown in Fig. 1(a) and (b) were measured using a grating monochromator at B.L.8. Excitation energies were 704 and 703 eV for CaF₂ and SrF₂, respectively, which were chosen, referring to a series of excitation-energy dependent F K α spectra emitted from CaF₂³⁾, from the following stand point; photon energies to be large enough for F K shell single ionization but too small for K¹Lⁿ multiple ionization. Here K¹Lⁿ denotes a state with one and n vacancies in K and L shells, respectively. Energy calibration for the reported emission spectra was obtained by assuming the energy of K¹L⁰ of F K α from CaF₂ to be 677.2 eV⁴⁾.

The F K α peaks of CaF₂ and SrF₂ can be deconvoluted into two components with 1.8 eV in FWHM, whose centroid energies, their energy separations and relative intensities are summarized on table 1.

Fig.1 Observed F K α emission spectra free from doubly ionized satellites, which are emitted from CaF₂ (a) and SrF₂ (b).

Table 1 Molecular orbital components of F K α emitted, and theoretically estimated from CaF₂ and SrF₂.

		Observed	Calculated	MO
CaF ₂	Centroid	676.4 eV	Relative	30t ₂
	Energies	677.7		33t ₂
	Peak separation	1.3 eV	1.4 eV	
	Relative Intensities	42 %	41 %	30t ₂ 33t ₂
SrF ₂	Centroid	676.7 eV	Relative	51t ₂
	Energies	677.6		53t ₂ 54 t ₂
	Peak separation	0.9 eV	1.0 eV	
	Relative Intensities	34 %	37 %	51t ₂ 53t ₂ 54 t ₂

MOLECULAR ORBITAL CALCULATIONS AND DISCUSSIONS

Molecular Orbital (MO) calculations at the ground state were performed using the discrete-variational (DV)-X α method²⁾. The basis functions for CaF₂ and SrF₂ were 1s-3p for F, 1s-4p for Ca and 1s-5p for Sr. Sample points of 10000 for numerical integration were distributed three-dimensionally in a manner described elsewhere²⁾. A diameter and depth of the potential to confine wave functions were chosen to be 0.67a₀ and -3.0 Hartree, respectively, where a₀ is an interatomic distance between F and Ca or Sr atoms. In the present study, a cluster model of (F⁻ M²⁺₄F⁻₆F⁻₁₂M²⁺₁₂)¹³⁺ with Td symmetry was employed, as shown in Fig. 2.

Fig. 2 A cluster model (F M²⁺₄F⁻₆F⁻₁₂M²⁺₁₂)¹³⁺ for CaF₂ and SrF₂, where M denotes Ca and Sr. A central F is surrounded by four M²⁺ as the first neighbors, six F⁻ as the second, twelve F⁻ as the third, and twelve M²⁺ as the fourth neighbors.

Calculated F 2p partial density of states (PDOS) for CaF₂ and SrF₂ are shown in Fig. 3 (a) and (b), respectively, which are responsible for F K α emissions if assuming the dipole approximation for the K α transition to be used. Here two and three components of PDOSs for CaF₂ and SrF₂, respectively, were convoluted using FWHM of 1.8 eV, and are drawn by full lines, where relative intensities and their energy separations between two main components are summarized on Table 1.

The calculated PDOSs of F 2p for CaF₂ and SrF₂ reproduce the F K α spectra of the fluorides observed here satisfactorily. In addition, the above PDOSs can well be used to explain shapes of

photoelectron spectra of F 2p and F K α emission spectra already reported⁵⁾⁶⁾ for CaF₂ and SrF₂, though the latter are contaminated with the doubly ionized K¹L¹ satellites.

Fig. 3 Calculated F K α emission spectra emitted from CaF₂ (a) and SrF₂ (b).

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Soft x-ray emission and absorption study of boron carbides.

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Boron carbide is a solid with a structure based on B_{12} icosahedra and 3-atom linear chain forming units,^{1,2} which exhibits very interesting physical properties: B_4C is a light, hard, semiconductor and refractory material.³ Although the stoichiometric compound is nominally B_4C , the boron to carbon ratio can vary over a broad range by partial substitution of B by C atoms both in the chains and in the icosahedra. Near the carbon rich limit, i.e. 20 at. % carbon and B_4C stoichiometry, the solid is composed of $B_{11}C$ icosahedra and CBC chains. As the composition becomes more boron rich, CBB chains replace the CBC ones. With further carbon reduction the $B_{11}C$ icosahedra are replaced by B_{12} units.^{4,5} Figure 1 sketches the structure of boron carbide.

Figure 1. Structure of boron carbide.

The electronic structure of this solid is poorly known, due to the large number of atoms in the unit cell, the complexity of the atomic structure and the lack of experimental results available so far for comparison. Among the problems to perform

angle resolved photoemission are the difficulty to grow single crystals and obtain clean surfaces, and the small size of the Brillouin zone that poses problems of angular resolution. Moreover, calculations of the electronic structure of boron carbide show a complicated dispersion of the multiple bands with momentum, indicating that it can be difficult to extract useful information from angle resolved experiments.⁶

An interesting question is how much of the electronic structure of the boron icosahedra remains in the solid. Boron carbide is not a molecular solid, since it is a hard and refractory material, but its atomic structure is based on the B_{12} unit. It is interesting to compare the density of states in different solids based on B_{12} icosahedra, like boron carbides with different stoichiometries, with molecules based on B_{12} cages like boranes and carboranes.⁷

X-ray absorption spectroscopy (XAS) and soft x-ray emission spectroscopy (SXF) can be used to obtain information on the partial density of unoccupied and occupied electronic states corresponding to the different elements, respectively. Since the signal is not restricted to the surface area, surface cleanliness is not a limiting factor. This allows the study of polycrystalline and amorphous specimens in the form of bulk samples, powders, and thin films. A complete study of the electronic structure, with a comparison of theoretical and experimental results is being performed.⁸ Some experimental results are described below.

Figure 2 shows from bottom to top, the x-ray absorption spectra at the $B(1s)$ edge from: (a) a polycrystalline B_4C -bulk sample, (b) a B_4C powder, (c) a non-stoichiometric B_xC ($x > 4$) thin film grown by sputtering, (d) a B_xC film grown by pulsed laser deposition, (e) an amorphous boron powder and (f) a crystalline boron powder. Curve (a) is used as a reference for comparison purposes.

Figure 2. X-ray absorption spectra at the boron edge from: (a) B_4C -bulk sample, (b) B_4C -powder, (c) B_xC film grown by sputtering, (d) B_xC film grown by pulsed laser deposition, (e) amorphous B, and (f) crystalline B

Figure 3. Left panel: soft x-ray emission spectra from the same samples considered in Fig. 2. Right panel: difference spectra obtained from subtraction of the bulk- B_4C spectrum.

A first observation is the position of the absorption edge, at 189 eV for stoichiometric B_4C and at 187 eV for boron and non-stoichiometric boron carbide. Also, there are additional peaks in the non-stoichiometric and boron samples compared to the B_4C reference, that cannot be assigned to B_2O_3 contamination.

Regarding the density of occupied states, Figure 3 (left panel) shows the soft x-ray emission spectra out of resonance from the same set of samples. The overall lineshape is very similar, suggesting that the density of occupied states is given mostly by the B_{12} units present in all the samples. However, there are small changes in the density of states that are evident in the difference spectra presented in the right panel. Here, the x-ray emission signal corresponding to the reference B_4C sample (a) have been subtracted from all other spectra. The extra features appear consistently in the two non-stoichiometric films, and in the two boron powders, and are not present in the B_4C powder. This shows that there is a clear relationship between the density of states and the B to C stoichiometry, and that the presence of long range order is only a secondary effect.

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Soft X-ray Emission Spectra of Crystalline Carbon Nitride Deposited by Electron Cyclotron Resonance (ECR) Sputtering

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INTRODUCTION

Carbon nitrides, especially β -C₃N₄, have been theoretically predicted by Cohen et al. [1-3] to be as hard as or even harder than diamond. This has stimulated many material scientists to try to deposit crystalline carbon nitride films by various methods. The characterization of carbon nitrides and investigation of their electronic structure have also become important in understanding how atomic bonding affects the calculated hardness. However, most experimental work on characterization has been done using electron diffraction or transmission electron microscopy (TEM) for identifying carbon nitride crystals; few x-ray spectroscopic studies have been done for electronic structure analysis because of the difficulty of obtaining crystalline films with sufficient crystalline purity for x-ray spectroscopy.

Recently, Tani et al.[4] succeeded in depositing high-purity crystalline carbon nitride films using electron-cyclotron-resonance (ECR) plasma sputtering methods. The crystal structure of these ECR-deposited carbon nitride films was confirmed by x-ray diffraction (XRD) and several chemical stoichiometric analysis methods to consist mainly of α - and β -C₃N₄ crystals, which may be spectroscopically high-purity crystalline films. We therefore measured high-resolution soft x-ray emission spectra of these ECR-deposited carbon nitride films to obtain information about the electronic structure of the carbon nitride crystals. In this paper, we describe the high-resolution C K and N K x-ray emission spectra, including selectively-excited and absorption spectra, of these ECR-deposited carbon nitride films and present information about their electronic structure.

EXPERIMENT

Carbon nitride films were deposited on Si(100) substrates by ECR sputtering, using a carbon target in a nitrogen atmosphere. The atomic ratio of nitrogen to carbon (N/C) was determined to be approximately 1.35, which agreed well with the stoichiometric composition of C₃N₄, according to x-ray photoelectron spectroscopy (XPS), heavy ion elastic recoil detection (ERD), and Rutherford backscattering (RBS). The crystal structure was analyzed by XRD, and a clearly observable XRD peak structure confirmed that the ECR-deposited carbon nitride films contained sufficient crystalline phases for x-ray spectroscopic measurements. Although an unknown diffraction peak was observed, the rest of the XRD pattern approximately agreed with the lattice constants theoretically predicted for α - or β -C₃N₄. The deposition process and chemical analysis of the ECR-deposited carbon nitride films are reported in detail elsewhere [4].

X-ray emission spectra in the C K and N K regions were measured using a grating x-ray spectrometer installed in beamline BL-8.0. Fluorescence-yield (FY) absorption spectra were also measured using this spectrometer. Total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2.

RESULTS AND DISCUSSION

Figure 1 shows (a) C *K* x-ray emission spectra of the ECR-deposited carbon nitride films and the reference carbon samples taken with 320-eV excitation and (b) the N *K* x-ray emission spectrum of the carbon nitride films with 430-eV excitation. In the C *K* spectra, the spectral shape of the carbon nitride consisted of a sharp main peak at 278.5 eV, a low-energy satellite at 266.5, and a high-energy-side tail near 282 eV. This spectral feature was completely different from those of the reference carbon samples. It is well known that the spectral shapes of graphite and diamond arise from sp^2 and sp^3 carbons respectively, and that the spectral shape of ion-beam-sputtered amorphous carbon may essentially arise from a mixture of sp^2 and sp^3 carbons. Therefore, the spectral shape of the carbon nitride suggests that carbon atoms in the film take up C-N bonding rather than sp^2 - or sp^3 -structured C-C bonding. The full width at half maximum (FWHM) of the symmetrical main peak of the carbon nitride is 2.8 eV, which is narrower than those of reference carbon compounds. This shows that the C2p electronic structure of the ECR-deposited carbon nitride films is more degenerated than that of the reference carbon samples. In the N *K* x-ray emission spectrum of the carbon nitride, two dominant peaks were observed at 392 eV and 388 eV.

In order to assign the spectral features of the C *K* and N *K* x-ray emission spectra of the carbon nitride, we tried to calculate C2p- and N2p-density of states (DOS) of carbon nitride clusters using discrete-variational (DV)- $X\alpha$ molecular orbital calculation methods [5]. A cluster model of $C_8N_{12}H_{28}$, which involves one unit cell structure of β - C_3N_4 , was used for the calculations. The C2p-DOS consists of three segments: the main segment is due to C2p, the low-energy segment is hybridized C2p-N2s, and the high-energy small segment is hybridized C2p-N2p. The N2p-DOS consists of roughly two segments: the high-energy segment is due to N2p and the low-energy segment is due to hybridized N2p-C2p. Using the calculated DOS spectral shapes as an analogy, we may therefore assign the spectral features of the ECR-deposited carbon nitride films as follows: the main peak (A) was caused by C2p, the low-energy satellite (B) by the hybridized C2p-N2s, and the high-energy tail (C) by hybridized C2p-N2p in the C *K* x-ray emission spectrum, and the 392-eV peak may be assigned to N2p and the 388-eV peak to hybridized N2p-C2p in N *K*. It is also confirmed that chemical bonds in the ECR-deposited carbon nitride film should be C-N bonds.

Figure 2 shows the selectively-excited C *K* x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY absorption spectra are also shown in the upper panel. The emission peak intensities of both the 278.5-eV main peak and the 266.5-eV low-energy satellite were enhanced in the 288.6-eV excitation. However, no significant peak shifts or new peak appearances were observed for other energy excitations. This therefore suggests that the band structure of C2p in the ECR-deposited carbon nitride films is fairly non-dispersive.

Figure 3 shows the selectively excited N *K* x-ray emission spectra and absorption spectra. The high-energy emission peak at 392 eV was enhanced in the case of 407.5-eV excitation tuned at the higher-energy absorption peak. In comparison, the low-energy emission peak at 388 eV was enhanced and a small peak appeared at 390 eV in the case of 399.5-eV excitation tuned at the lower-energy absorption peak. Aside from these emission peak intensity enhancements and the appearance of a small peak, no other significant peak shifting was observed. This indicates that the band structure of N2p may also be fairly non-dispersive.

CONCLUSION

High-resolution soft x-ray emission spectra of ECR-deposited crystalline carbon nitride films were measured in the C *K* and N *K* regions. From the DV- $X\alpha$ molecular orbital calculations, the spectral features of the C *K* and N *K* x-ray emission can be assigned to the C2p- and N2p-DOS in

the hybridized C-N bonds. The narrow spectral shape observed in the C *K* x-ray emission suggests that the carbon nitride films have a highly degenerated electronic structure in their C-N bonds. Selectively-excited x-ray emission spectral measurements indicate that the band structure of the carbon nitride films should be fairly non-dispersive. These results also confirm that soft x-ray emission spectroscopy is a useful method for characterizing carbon nitride films.

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Figure 1 The upper panel (a) shows the C *K* x-ray emission spectra of the ECR-deposited carbon nitride film and reference carbon compounds such as ion-beam-sputtered amorphous carbon film, graphite powder, and diamond powder. The excitation energy was tuned to 320 eV. The lower panel (b) shows the N *K* x-ray emission spectrum of the carbon nitride obtained with 430-eV excitation.

Figure 2 The lower panel shows the selectively-excited C *K* x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY absorption spectra are shown in the upper panel. The excitation energy was tuned from 318.6 to 281.6 eV, as shown by “a” through “m” in the figure.

Figure 3 The lower panel shows the selectively-excited N *K* x-ray emission spectra of the ECR-deposited carbon nitride film. TEY and FY-absorption spectra are shown in the upper panel. The excitation energy was tuned from 426.5 to 393.5 eV, as shown by “a” through “m” in the figure.

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SOFT X-RAY EMISSION STUDIES OF THIN Si/SiO₂ MULTILAYERS

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INTRODUCTION

The discovery of visible photoluminescence in ultra fine Si particles and Si/SiO₂ multilayers has lead to tremendous interest in their electronic and optical properties [1,2]. It is generally agreed that quantum confinement caused by the restricted size of the nanometer scale silicon particles is essential for the light-emitting properties. In this paper we have measured the change in the electronic structure of amorphous Si layers as a function of thickness in a set of Si/SiO₂ multilayers. The electronic structure of the Si nanostructures is investigated using total fluorescence yield x-ray absorption (XAS) and soft x-ray emission (SXE) spectroscopies. These methods have advantages over conventional electron spectroscopies since they are element specific bulk probes. Therefore we can selectively investigate the electronic structure of the buried Si layers in the Si/SiO₂ multilayer by tuning the excitation energy in the XAS or SXE measurement below the Si L-edge absorption threshold of SiO₂ [3]. Also since both these processes are photon-in photon-out it is possible to overcome charging problems that complicate electron spectroscopy measurement on insulating materials such as SiO₂. The SXE and XAS measurements were performed using synchrotron radiation from the undulator beamline at beamline 8.0 at the Advanced Light Sources. Multilayer film thickness was determined by grazing incidence x-ray diffraction.

EXPERIMENTAL

The Si/SiO₂ multilayers were grown onto Ge 111 substrates in an ion-beam sputtering (IBS) chamber described in details elsewhere.[4] The ion gun was a 3 cm Kauffman source with focusing optics. The Ar ions were incident on the sputter target at 1000 V at an angle of about 45°. The sputtering rate was approximately 0.6 Å/sec for Si and 0.1 Å/sec for SiO₂. The base pressure of the chamber was in the 10⁻⁵ Pa range, and the sputtering gas during deposition was Ar at 2.5 x 10⁻⁴ Pa. The substrates were rinsed in ethanol before loading into the vacuum chamber. The substrates were about 25 cm above the targets, and the nominal layer thickness was monitored by a quartz-crystal oscillator which was placed in close proximity to the substrates. The thickness of the individual SiO₂ layers was kept at 10 Å in all multilayers, and the nominal thickness of the Si layers in the samples was 14, 17, 24, and 64 Å. The bilayer period and the number of bilayer pairs in these samples were varied to obtain a total Si thickness of 640 Å for measurement comparison. A single amorphous Si film was also grown in the study to be used as a bulk standard. X-ray diffraction was performed using Cu K_α radiation generated from a rotating anode system outfitted with a graphite monochromator.

Changes in the conduction band were measured by total fluorescence yield X-ray absorption. With convention electron yield x-ray absorption it is only possible to probe to a depth of 50 Å but with fluorescence yield the electronic structure is sampled to a depth of 0.1 micron, therefore the Si from the entire multilayer is measured. Resolution of the absorption spectra at 100 eV the Si L-edge was approximately 0.07 eV. Changes in the electronic structure

of the VB were monitored by SXE spectroscopy. In the SXE process a valence electron fills the core vacancy previously generated by the absorption of a photon. The generated fluorescence photon was analyzed in a spherical grating Rowland spectrometer with resolution of approximately 0.2 eV. In all SXE spectra presented the excitation energy was 101 eV. Therefore, the fluorescence spectrum is generated by transitions from the valence band to the silicon 2p core hole. The SXE technique has an advantage over photoemission because it is insensitive to sample charging and is a bulk probe due to the large photon mean free path. By tuning the excitation energy to below the Si L-edge absorption threshold of SiO₂ we selectively investigate the electronic structure of the Si layer and not the SiO₂ layer.

RESULTS

Figure 1 shows the low angle x-ray diffraction scans of the samples. The grazing incidence data gives information about the quality of the film, the multilayer uniformity and interfaces. All the scans from the multilayers show strong high order Bragg's peaks indicating a reasonably strong compositional modulation along the growth direction. The bilayer thicknesses of the multilayers were determined using the equation:

$$n^2\lambda^2 = 4 \Lambda^2 \sin^2\Theta + 2\delta,$$

where λ is the x-ray wavelength (0.154 nm), $\Lambda = t_{\text{Si}} + t_{\text{Ge}}$ is the bilayer thickness, δ is the index of refraction at the x-ray wavelength, and Θ the angles of the Bragg's peaks in the measurements. To eliminate the unknown δ from the equation, we make use of the equation above from 2 peaks:

$$(n^2 - (n-1)^2) \lambda^2 = 4 \Lambda^2 (\sin^2\Theta_n - \sin^2\Theta_{n-1}),$$

and solve for Λ . From the deposition rate parameters, the nominal thicknesses of the Si layers deposited were estimated to be 14 and 24 Å. The actual thicknesses of the pure Si layers in the samples are less than these values due to some intermixing of the oxides and the Si during deposition to form a non-stoichiometric oxide layer at the interfaces.

Fig 1 Low angle x-ray diffraction profiles of the two Si/SiO₂ samples

In Fig.2 we show L_{2,3} edge x-ray absorption for bulk a-Si and the three Si/SiO₂ multilayer samples with different Si layer thickness measured in total fluorescence yield mode. The L-edge of the multilayer is shifted to higher energy relative to the bulk amorphous silicon in agreement with quantum confinement effect which raises the energy of the bottom of the conduction band as the Si layer thickness is decreased. Due to the spin orbit interaction the silicon 2p core level is split into two states separated by 0.61 eV[5]. Thus the L_{2,3} edge XAS spectrum is a

superposition of the absorption structure related to transitions from the Si $2p_{3/2}$ and Si $2p_{1/2}$ core levels. This spin orbit splitting is clearly seen in the bulk a-Si absorption edge but becomes less pronounced with increasing blue shift in the L-edge of the multilayers. We also note that the onset of the absorption edge of the Si in the multilayers is not as sharp as that in the bulk a-Si. We attribute these features to the variation of layer thickness at the Si-SiO₂ interface. As the Si layer thickness decreases the effects on the quantum confinement energy of a given fluctuation in the layer thickness increases. In other words a one monolayer fluctuation at the interface in a thin silicon layer broadens the absorption edge much more than a one monolayer fluctuation in a thicker layer. These broadening effects were not observed in recent electron yield measurement on Si/SiO₂ multilayers, perhaps due to the fact that the electron yield measurement is only sensitive to the top Si layer and don't see the other layers [2].

Fig. 2A. Fluorescence yield x-ray absorption spectra at the silicon L_{2,3} edges in bulk a-Si, and Si/SiO₂ multilayers with Si thickness of 14, 17 and 24 Å. Fig. 2B. The L emission spectrum of bulk a-Si and two Si/SiO₂ multilayers with Si thickness of 14 and 24 Å. The excitation energy is 101 eV for all spectra which is below the L-edge for SiO₂.

In Fig. 3 we show the SXE spectra for bulk a-Si and two of the multilayer samples shown in Fig. 2. The bulk a-Si SXE spectrum exhibits the two characteristic peaks: one at 92 eV associated with 3s states in the valence band, and a high DOS at 96 eV which is dominated by p-type states [6]. The splitting in the 3s states observed in the SXE spectra of crystalline Si is not observed in the a-Si spectra. No shift in the multilayer valence band spectra is observed when compared to that of bulk a-Si and the overall appearance of the multilayer spectra is identical than that of the bulk a-Si. This result is different than recent photoemission studies of Si/SiO₂ multilayers where small shifts on the order of 0.15 eV were observed in the valence band edge [2]. It is also different to results observed for thin films of silicon nanocrystals and porous silicon where the shift in the valence band is reported to be a factor of two larger than the shift in the conduction band [7,8]. At the present time it is not understood why no shift is measured in the valence band when shifts are clearly observed in the conduction band. It is interesting to note that a plot of the shift in the CB edge as a function of layer thickness in the Si/SiO₂ multilayers is the same as the shift in the CB edge as a function of particles size in silicon nanoclusters [7]. The

multilayer should have a smaller shift because the confinement is only in one dimension compared to three dimensions in the nanoclusters.

In conclusion, we were able to investigate the unoccupied and occupied electronic states of a-Si layers in a Si/SiO₂ multilayer combining total fluorescence yield x-ray absorption and selectively excited SXE spectroscopy. We observe shifts in the CB edge as a function of layer thickness but not in the VB. The onset of the absorption edge progressively broadens with increased blue shift due to interface roughness in the multilayers.

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Soft X-Ray Resonant Emission Spectra of Ti_2O_3 .

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INTRODUCTION

Recently, soft X-ray emission spectra (SXES) of TiO_2 were observed [1]. The TiO_2 have no Ti 3d electron nominally and has wide band gap of about 3 eV. It is known that the Ti 3d state in the TiO_2 is strongly mixed to the O 2p-state [2]. In the resonant SXES measurements of TiO_2 , a Raman peak corresponding to charge-transition excitation from O 2p-valence band to Ti 3d-conduction band was observed. The Raman peak is elucidated by the strong hybridization [1].

In this study, resonant SXES of Ti_2O_3 is observed. It is known that the Ti_2O_3 is typical Mott-Hubbard type semiconductor that has narrow band gap (< 0.1 eV)[3]. The Ti_2O_3 has one Ti 3d electron nominally and the Ti 3d band is located at about 1 eV. Recently, resonant photoemission (PES) spectra of Ti_2O_3 were observed [4]. The results suggest that the Ti 3d state in the Ti_2O_3 is strongly mixed to the O 2p state.

EXPERIMENTAL

The resonant SXES spectra were measured at the undulator beam line 8.0.1 of Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The spectra were observed using a spectrometer that has grazing-incidence monochromator and multichannel detector. A 1500 lines/mm spherical grating with 10-m radius was used. A Ti 3d $\rightarrow$ 2p-fluorescence peak of Ti metal was observed for energy calibration of the emission spectra. The overall energy resolution in the measurements was about 1.0 eV at excitation energy of 450 eV.

A single-crystal Ti_2O_3 was made by the floating-zone method in an Ar- H_2 gas atmosphere. The sample temperature is room temperature at which the Ti_2O_3 is semiconductor phase having narrow gap.

RESULTS AND DISCUSSIONS

Figure 1 shows Ti 2p XAS spectrum of Ti_2O_3 , which is observed by total fluorescence yield method. Ti 2p-resonant emission spectra are observed in the Ti 2p-absorption edge. The excitation energy used in SXES measurements are shown by vertical bars.

Figure 2 shows resonant SXES spectra of Ti_2O_3 observed at the Ti 2p-absorption edge. A strong fluorescence peak is observed at about 451 eV. This peak is assigned to Ti 3d state that is hybridized to O 2p-valence band. On the other hand, two fluorescence peaks are observed

Figure 1. Ti 2p XAS spectrum of Ti_2O_3 . Vertical bars denote excitation energy of resonant emission measurements.

weakly at 456 and 458 eV in the spectra excited by the energy between 465.6 and 468.6 eV. These peaks are assigned to localized Ti 3*d* state.

Figure 3 shows Raman spectra of Ti₂O₃. In the Fig. 3, the emission spectra in Fig. 2 are plotted against energy shift from excitation energy. Vertical broken line at 0 eV indicates an elastic scattering. An elastic scattering peak is observed in the spectrum excited by 457.6 eV. The other two broken lines indicate Raman scattering peaks. Two Raman peaks are observed at about 1.0 and 7.0 eV. The peak at 7.0 eV is assigned to an excitation from O 2*p*-valence band to Ti 3*d*-conduction band. This result is similar to that of TiO₂ [1]. On the other hand, the peak at 1.0 eV is assigned to an excitation from Ti 3*d* states in valence band to that in conduction band.

Recently, we observed Ti 2*p*-resonant PES of Ti₂O₃, which shows strong resonance of Ti 3*d* state [4]. The resonant PES spectra were elucidated by the cluster model calculation. That result suggests the strong hybridization of Ti 3*d* and O 2*p* states. The resonant SXES spectra in this study also suggest the strong hybridization.

CONCLUSION

Resonant SXES of Ti₂O₃ was observed in this study. Raman scattering peaks of both charge-transition excitation and *d-d* transition excitation were observed. The results suggest the strong hybridization of Ti 3*d* and O 2*p* states.

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Figure. 2 Ti 2*p*-resonant emission spectra of Ti₂O₃. Numbers beside the spectra indicate excitation energy. Vertical broken lines show Ti 3*d* → 2*p*-fluorescence energy.

Figure 3. Resonant Raman spectra of Ti₂O₃. Vertical broken line at 0 eV indicates elastic peak, while the other broken lines indicate Raman peak. Vertical solid lines indicate fluorescence peak.

Study of tribochemical processes on hard disks using Photoemission Electron Microscopy

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INTRODUCTION

With increasing storage density of magnetic media reaching 10 Gb/in² and increasingly smaller spacing between slider and hard disk surface approaching pseudo-contact, the interface between slider and disk becomes more and more important. Due to the small spacing there is a strong interaction between the hard carbon overcoat of the disk, the lubricant, and the surface of the slider, which often is also coated by amorphous hard carbon. Optimization of the tribological properties can only be obtained by considering the whole system and the interactions of the individual components. Tribochemistry plays a more important role for smaller spacings and thinner lubricants and protective overcoats.

We have applied Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and Photoemission Electron Microscopy (PEEM) to study the elemental and chemical structure and modification of disks exposed to various forms of wear.

WEAR TESTS OF DISKS

Three different sets of disks were tested under various conditions in vacuum and in air.

Set1:

95mm disks coated with 7.5 nm sputter deposited hydrogenated amorphous hard carbon CH_x with a low hydrogen content of 5% were exposed to a continuous drag test in ultra-high vacuum. The number of cycles until failure was monitored. Uncoated sliders (Al₂O₃/TiC) and sliders coated with sputter deposited CH_x were used at a speed of 0.2 m/s and a load of 40 mN. The disks were lubricated with 0.85nm of either a perfluoropolyether (Z-DOL), a cyclic phosphazene lubricant (X-1P), or a mixture of 94% Z-DOL and 6% X1P [1]. The tribological results are published in detail in [2]. The time between the tribotesting and the PEEM studies was several weeks.

Set2:

Supersmooth disks were coated with 5 nm hydrogen-free, amorphous hard carbon formed by cathodic arc deposition. The disks were lubricated with 0.85 nm Z-DOL. The disks were worn in a continuous drag test at a speed of 0.2 m/s and a load of 30 mN in UHV. Two kinds of sliders were used: uncoated sliders (Al₂O₃/TiC) and sliders coated with sputter deposited CH_x. The time between the wear test and the microscopy study was kept below 2h to prevent lubricant from flowing back into the wear tracks. Details of the wear test are described in [2, 3].

Set 3:

95mm disks coated with 15 nm sputter deposited CH_xN_y without lubricant were exposed to a continuous drag test under ambient conditions. Sliders coated with sputter deposited CH_x at a drag speed of 0.08 m/s and a load of 30mN were used for the test. The tests were run for durations from 30s to 2h, and the friction force was recorded during the wear. These disks were specifically worn for PEEM studies of disk and slider wear. Results on the wear of the sliders will be published in [4].

EXPERIMENTAL CONDITIONS FOR PEEM AND NEXAFS STUDIES OF WEAR TRACKS ON DISKS

PEEM microscopy was applied to study elemental composition and chemical state of samples using NEXAFS spectroscopy with high spatial resolution. A two-lens, electrostatic microscope operating at a nominal voltage of 10 kV was used for these studies. The microscope has a spatial resolution of 200 nm, and it is described in detail in [5]. We used the undulator beamline 8.0 equipped with a spherical grating monochromator having three different gratings to cover the energy range from 200-1500 eV with a resolving power of $E/\Delta E=10,000$.

In all cases it was checked that the X-ray radiation does not damage the samples by comparing successive NEXAFS scans.

RESULTS**Set 1:**

Local NEXAFS spectra were acquired outside and inside the wear tracks. The spectra outside the wear tracks showed the carbon π^* resonance at 285 eV and the broad σ shape resonance around 300 eV [6]. It was observed that a strong new peak is present in the spectrum of the wear track at 289.0 eV and a smaller peak at 290.9 eV. These peaks can be attributed to the formation of new carbon-oxygen bonds probably in carboxylic (289.0 eV) and carbonate form (290.9 eV) [6]. This demonstrates that the lubricant has been altered chemically and oxidation has occurred during or after the wear. The chemical modifications are the smallest for the mixed lubricant tested with a carbon coated slider. These findings agree with the results of the wear test which showed better tribological behavior for coated versus uncoated sliders and mixed lubricant versus the single components. Oxygen K edge spectra showed a considerable increase in oxygen concentration in the wear tracks for all cases, confirming the oxidation of the lubricant.

Set 2:

Figure 1c shows a PEEM image of a wear track produced by a coated slider. The scratch is caused by one of the rails of the slider. The image was taken at a photon energy of 280 eV which is below the carbon K edge, therefore the image contrast is mainly topological. Local NEXAFS spectra were taken in the undamaged area of the disk, in the wear track caused by the rail, and in the area between the rails. Figure 1a shows the carbon K edge spectra and Figure 1b the fluorine K edge spectra.

Figure 1: (a) Local carbon K edge NEXAFS spectra of indicated areas. (b) Local fluorine K edge NEXAFS spectra of indicated areas. (c) PEEM image of a wear track caused by a coated slider on a Z-DOL lubricated disk taken at a photon energy of 280 eV. The field of view is 75 μ m.

From the spectra we can see that the carbon overcoat/lubricant are identical in the undamaged area and between the rails. In the wear track caused by one of the rails the fluorine is almost completely removed. The removal of fluorine in the wear tracks was only observed when the time between the wear test and the PEEM studies was very short (below a few hours). In any other case when the time between the PEEM or NEXAFS study was many days the fluorine signal was identical inside and outside the wear tracks. This confirms that the lubricant is flowing back into the wear track and covers it after a while. The carbon spectrum shows a new peak around 289.0eV which can again be attributed to the formation of carboxylic bonds [6] and a small reduction of the total carbon signal. Whereas the modified carbon is still visible long after the wear test the fluorine reduction is only observed during a short period of several hours after the wear. It seems that the chemically modified carbon remains in the wear track and is later covered by unmodified lubricant flowing over the track from the side. Since the probing depth of NEXAFS and PEEM is about 10 nm for carbon materials, we see a superposition signal from the modified lubricant, the hard carbon overcoat, and unmodified lubricant if it had time to flow back into the track.

Set 3:

Local NEXAFS spectra at the carbon K edge were taken in the wear track and outside the wear track. Peaks were observed at 285 eV corresponding to the carbon π^* resonance, around 286.3 eV corresponding to C=N bonds, and a broad peak around 300 eV (σ shape resonance of carbon). It was found that the shape of the spectra is identical but the intensity in the wear track is reduced by about 40%. This indicates that the chemical state of the CH_xN_y has not been changed by the wear but some CH_xN_y has been removed.

SUMMARY

- (1) Lubricated disks exposed to wear tests show chemical modifications of the lubricant when the disks failed the wear test. These modifications consist of oxidation of carbon in the form of mainly carboxylic bonds, and a reduction of the fluorine and carbon content. The chemical modifications occur in tracks that are typically 10-50 μm wide.
- (2) Non-modified lubricant covers the tracks and the oxidized lubricant after a certain time period that is determined by the diffusion constant of the lubricant. The degraded, oxidized lubricant stays in the tracks over long periods of time (many weeks) and does not seem to move out of the tracks.
- (3) Unlubricated disks show no chemical modifications of the hard carbon overcoat in the wear tracks, just a reduction of the overcoat thickness.
- (4) The chemical modifications are correlated to the tribological behavior of the disks.

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The Effects of Boron Impurities on the Atomic Bonding and Electronic Structure of Ni₃Al

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INTRODUCTION

The intermetallic alloy nickel aluminide, Ni₃Al, exhibits several unique physical and mechanical properties which make it attractive for potential use in a wide variety of technological applications.¹ Among these are its low density, high melting temperature, resistance to oxidation, and unlike most conventional metallic alloys, an increase in yield stress when exposed to increasing temperatures. Single crystals of Ni₃Al are extremely ductile, a property not shared by polycrystalline forms of this alloy.² The brittleness observed in the disordered systems is believed to be due to intergranular fracture in the material. However, recent work involving the doping of boron impurity atoms has shown an increase in the ductility of this intermetallic system.³ Doping 250 parts per million (ppm) of boron atoms increases the elongation of polycrystalline Ni₃Al from a few percent to nearly fifty percent.⁴

To better understand the influence of boron doping on the mechanical properties of Ni₃Al, we performed a study of the electronic structure and atomic bonding of boron with the nickel and aluminum atoms in this alloy using x-ray emission spectroscopy (SXES). It is believed that the increased ductility observed in the boron doped systems is due to interplanar metallic bonding between the nickel and boron atoms, and the sensitivity of SXES to the local bonding environment of the emitting atoms makes it an ideal tool for studying these systems.^{5,6} This technique was used recently to obtain information about the structure of nickel compounds containing small amounts of sulfur.⁷

EXPERIMENTAL AND CALCULATIONAL DETAILS

Preliminary measurements were made at Louisiana State University's Center for Advanced Microstructures and Devices (CAMD) utilizing the Tulane University-National Institute for Standards and Technology-University of Tennessee (TNT) soft x-ray fluorescence spectrometer. A detailed description of this instrument can be found elsewhere.¹³ After these measurements were analyzed an in-depth set of measurements was obtained at Lawrence Berkeley National Laboratory's Advanced Light Source (ALS) at Beamline 8.0, employing the University of Tennessee at Knoxville's soft x-ray fluorescence (SXF) endstation. Photons with energies ranging from 180 to 220 eV, through the boron K absorption edge, were used to excite the samples.

All measurements reported here were made with a 100-micrometer entrance slit for the spectrometer. The spectra were obtained with a 1500 lines/mm, 10-meter radius grating. At the boron K edge the resolution of the spectrometer is approximately 0.8 eV. The energy resolution of the monochromator was set to 0.3 eV during most of these measurements. The boron K-valence emission spectra were calibrated with a reference sample of hexagonal boron nitride (h-BN).

The boron doped Ni₃Al samples (nickel doped with 24.8% aluminum and 500 ppm of boron) were supplied by C. T. Liu, a materials scientist at Oak Ridge National Laboratory. The

alloys were prepared by arc melting and drop casting techniques, followed by various thermomechanical treatments.⁸

Electronic structure calculations for nickel-boron and nickel-aluminum-boron bonding systems were performed by Dr. Jan van Ek using the linear muffin-tin orbital method within the atomic sphere approximation (LMTO-ASA).⁹ Exchange and correlation effects were treated within the local density approximation (LDA) of density functional theory.¹⁰ Self-consistent solutions to the Kohn-Sham equations were obtained for all the electrons in the system using the exchange-correlation potentials as parameterized by von Barth and Hedin.¹¹

RESULTS AND DISCUSSION

Soft x-ray emission from the K(valence) bands in boron corresponds to the filling of core level holes by electrons from the valence band in these materials. Emission occurs when a photon, with enough energy to remove an electron from the 1s core level, creates a hole in the core which is then filled by an electron from the valence band. The filling of the hole results in the production of a photon that has an energy equal to the difference between core and valence band energies. Therefore, this technique is used to gain information about the boron valence bands in these materials. Additionally, SXES is sensitive to the nature of the chemical bonds, displaying marked differences in the energy distribution and fine structure of emission from elemental boron systems, chemical compounds containing boron, and transition metal boride materials.¹²⁻¹⁵ Also, because the x-ray transitions are localized to the first coordination sphere of the emitting atom, XES is sensitive to short-range order (coordination number, bond lengths, etc.). All these factors make XES an invaluable tool for determining the surrounding environment and the local chemical bonding of boron impurity atoms in these intermetallic compounds.

The main difficulty in analyzing the boron K-valence XES in this boron doped system, $\text{Ni}_3\text{Al:B}$, is the absence of suitable reference samples whose boron spectra can be used as fingerprints for particular boron-nickel and boron-aluminum bonding. Therefore, we turned to the shape of the emission spectrum in order to understand the impurity bonding, and performed two electronic structure calculations for the $\text{Ni}_3\text{Al:B}$ system, as shown in Figures 1a and 1b. The first calculation examines the nickel-boron bonding for a system of boron atoms occupying

Figure 1. Total and partial density of states distributions for calculated boron $\text{Ni}_3\text{Al:B}$ systems. Boron-nickel type bonding for boron atoms surrounded by six nickel atoms (a) and boron-aluminum type bonding for boron atoms surrounded by four nickel and two aluminum atoms (b).

nickel-rich octahedral interstitial regions (boron atom surrounded by six nickel atoms) in the alloy's structure. The second considers the aluminum-boron bonding for a system with boron atoms occupying a different octahedral interstitial site (boron atom surrounded by four nickel atoms and two aluminum atoms). Figure 2 illustrates these two possible boron atom locations within the Ni_3Al lattice. The six-fold nickel atom configuration corresponds to the boron atoms occupying octahedral site B1. The four nickel-two aluminum atom configuration corresponds to the boron atoms occupying octahedral sites B2. The calculations show that for nickel-boron bonding there is hybridization between the boron 2p and nickel 3d states, and for aluminum-boron bonding the hybridization is between the boron 2p and aluminum 3s and 3p states. In order to determine which type of bonding is taking place in the $\text{Ni}_3\text{Al:B}$ system, thereby revealing the location of the boron atoms in the alloy, we compare an above threshold emission spectrum from the sample with the calculated boron 2p PDOS in Figure 3. The calculations have been broadened to account for the 0.5 eV experimental resolution of the spectrometer. The FWHM (5.1 eV) and shape of the emission from the sample is more consistent with the nickel-boron bonded system (4.5 eV), than with the aluminum-boron bonded system (6.8 eV). This comparison shows that the boron K(valence) emission measurements from the $\text{Ni}_3\text{Al:B}$ samples are more consistent with boron impurity atoms occupying the nickel-rich octahedral interstitial sites. This conclusion is in agreement with the results of other theoretical calculations which state that the formation energy for a boron atom placed at a nickel rich octahedral interstitial site in Ni_3Al is -4.4 eV per unit cell, as opposed to a nickel deficient octahedral interstitial site which is only -0.08 eV per unit cell.¹⁶ Analysis of the charge redistribution induced by the boron impurity atoms when placed at the nickel-rich interstitial sites shows that the boron atoms greatly enhance the observed interplanar ductility in $\text{Ni}_3\text{Al:B}$.¹⁶ This suggests that the boron 2p-nickel 3d hybridization between nearest neighbor atoms is the mechanism for this enhancement.

CONCLUSION

Measurements of boron K(valence) x-ray emission spectra of boron impurities in Ni_3Al (500 ppm boron) excited by tunable synchrotron radiation have been presented. These spectra are compared with electronic structure calculations of boron impurities in nickel-rich and nickel-deficient bonding systems. It appears that the boron impurity

Figure 2. Illustration of the Ni_3Al lattice showing possible sites for boron impurity atoms.

Figure 3. Boron 2p partial density of states distribution for the measured $\text{Ni}_3\text{Al:B}$ system compared with calculated values for boron-nickel and boron aluminum type bonding.

atoms preferentially bond with nickel atoms in Ni₃Al, and that boron 2p-nickel 3d hybridization takes place. It seems that the boron atoms prefer to occupy octahedral interstitial sites with six-fold nickel atom coordination. Together with electronic structure calculations, this suggests an enhancement of the interplanar metallic bonding between nickel atoms which results in an observed increase in ductility for boron doped Ni₃Al alloys.

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Transition Metal Carbide Compounds

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INTRODUCTION

Carbon forms compounds with all the transition metals except for the late elements of the second and third rows of the periodic table. There are considerable variations in the crystal structures of these compounds. The structures of compounds formed by transition metals from the left half of the periodic table tend to be rather simple, often resembling the structure of the pure metal. Compounds formed from the right half of the periodic table, involving more electropositive elements, tend to have rather complicated structures. The compounds studied here are mainly the group IVb and Vb monocarbides, but it should be mentioned that with an increase in the ratio of metal to carbon, the compounds tend to lose stability as evidenced by decreasing melting points. A maximum in the melting points of these carbides occurs for compounds containing group Vb transition metals.^{1,2} This corresponds to a filling of the bonding and anti-bonding parts of the metallic bands. The lack of stable late transition metal carbides can be explained by the filling of anti-bonding regions in the bands of these systems.²

EXPERIMENTAL AND CALCULATIONAL DETAILS

Due to the inherently low yield of the soft x-ray emission process, we made use of the high brightness available at Ernest Orlando Lawrence Berkeley National Laboratory's Advanced Light Source (ALS). The spectra were taken at Beamline 8.0, employing the University of Tennessee at Knoxville's soft x-ray fluorescence (SXF) endstation. At the carbon K absorption edge, the resolution of the spectrometer was approximately 0.8 eV. The energy resolution of the monochromator was set to 0.4 eV during most of these measurements. The carbon K(valence) emission spectra were calibrated with a reference sample of highly oriented pyrolytic graphite (HOPG).

In order to better understand our measurements, LMTO-ASA calculations of these carbide systems were performed. The transition metal monocarbides have face centered cubic structures, and are described by the Pearson symbol $cF8$, a member of the $Fm\bar{3}m (O_h^5)$ space group.³ In these calculations, the exchange and correlation effects were treated by the local density approximation of density functional theory. The exchange-correlation potential formulated by Hedin and Lundquist was used to obtain self-consistent solutions to the Kohn-Sham equations.⁴ The core electron states were obtained as solutions of the Dirac equations. Scalar relativistic terms were retained in the LMTO Hamiltonian for the electron band states.

The LMTO-ASA method provides rather good

Figure 1. Image of the $Fm\bar{3}m$ cubic crystal structure of the transition metal monocarbides. Carbon atoms are depicted as the light gray spheres, metals as the dark gray spheres.

results for TiC, VC, ZrC, and NbC, but was difficult to apply to the HfC and TaC systems. Calculations of these systems were performed by Dr. James M. MacLaren from the Department of Physics at Tulane University using full potential techniques. The full potential linear augmented Slater type orbital (FP-LASTO) method eliminates any approximation made with respect to the shape of the effective single-particle potential in the crystal. The interstitial region is treated with reciprocal space techniques. A basis consisting of two sets of s, p, and d functions and a single set of f functions per atom was used for hafnium and tantalum, and a basis set of two s, two p, and a single set of d functions per atom was used for carbon. Decay constants were obtained by optimizing the basis in an atomic calculation. Electrons in the core states were treated scalar relativistically.

RESULTS AND DISCUSSION

All of the transition metal monocarbides have similar soft x-ray emission spectra. The samples were excited through the carbon K (1s) absorption threshold using the undulator and monochromator at Beamline 8.0 of the ALS. The holes left by the electrons that were excited into the conduction bands of these samples were filled with electrons from the valence bands of these materials. This allows for a confirmation of the covalent bonding detailed in the calculations of these systems.

We were able to gain knowledge from these measurements regarding the electronic structure of these carbide compounds by examining features in the soft x-ray emission spectra (SXES) of these materials. The soft x-ray emission spectra of TiC are shown in Figure 2.

Soft x-ray emission spectroscopy (SXES) can be used to examine the occupied density of states of a material. The spectrum from the sample provides an intensity versus energy distribution of the photons that are emitted during excitation. This distribution represents the density of occupied states in the material over a particular range of energies. When the emissions from valence band electron transitions are measured, bonding properties can be deduced from these valence emission spectra as the spectra are proportional to the density of states of the material. In fact, SXES can provide specific information about the angular momentum density of states of the electrons in the material, because in the case of normal fluorescence, the radiative processes adhere to the dipole selection rule. Because of this selectibility, the soft x-ray emission spectra from different electron bands can be measured and directly compared to calculations of element projected and angular momentum projected densities of states in the material.

LMTO-ASA electronic structure calculations, as shown in Figures 3 and 4, show good agreement with the valence band emissions from the boron atoms of TiC. There have been three proposed models for describing the bonding in transition metal carbides: (1) The carbides are considered as intercalate phases. The metal-metal interaction is considered predominant with the

Figure 2. Soft x-ray emission spectrum of TiC. The sample is excited with photons with the energies listed to the right of the graph. The energies of the photons that are emitted from the interaction are plotted versus the number of emitted photons (intensity) that are detected by the instrument.

Figure 3. LMTO-ASA calculations of the electronic band structure of TiC. This material is strongly covalently bonded, with hybridization between all of the bands, especially between the titanium 3d and carbon 2p valence bands.

Figure 4. Comparison of above absorption threshold SXE spectra with LMTO-ASA calculations of the electronic band structure of TiC.

carbon atoms as electron donors.² (2) The carbon-carbon interactions are dominant since the carbides have bond lengths that are on the order of covalently bonded elemental carbon. Charge is transferred from the metal atoms to the carbon atoms.² (3) The covalent metal-carbon interaction is mainly responsible for the bonding of these compounds.² Our calculations show that the total density of states of TiC is comprised of roughly three peak structures. The lowest energy peak structure is centered around -10 eV and is composed mainly of electrons from the 2s bands of the carbon atoms and the 3p and 3d bands of titanium. The broad middle energy structure is centered around -3.5 eV and is primarily comprised of electrons from the 2p (valence) bands of the carbon atoms and electrons from the 3d (valence) and 3p bands of the titanium atoms. The sharp highest energy peak structure is centered around 3.5 eV and is primarily composed of electrons from the 3d bands of the titanium atoms, with a slight contribution from carbon 2p band electrons.

From our calculations, it appears that the bonding (broad middle energy structure) and anti-bonding (sharp highest energy peak structure) states are primarily composed of carbon 2p electron bands and titanium 3d and electron bands. This suggests that the bonding in this system is primarily between carbon and titanium atoms, corresponding to a combination of two of the suggested bonding schemes for the transition metal diborides (2, and 3). TiC, and in fact all of the transition metal monocarbides are hard because of the great degrees of covalency in these materials. The densities of states below the Fermi level are almost entirely composed of contributions from the metal 3d band and the carbon 2p band. Some degree of hybridization is observed between all the metal and carbon bands in TiC. Our results are in excellent agreement with calculations of this same system made by other researchers, as well as early experiments of this compound.^{5, 6-12}

CONCLUSION

From our measurements and calculations, it appears that the bonding (broad middle energy structure) and anti-bonding (sharp highest energy peak structure) states in these compounds are primarily composed of carbon 2p electron bands and metal d electron bands. This suggests that the bonding in this system is primarily between carbon and metal atoms, corresponding to a combination of two of the suggested bonding schemes for the transition metal diborides (2, and 3). All of the transition metal monocarbides are hard because of the great degrees of covalency in these materials. The density of states below the Fermi level are almost entirely composed of contributions from the metal d bands and the carbon 2p band, however, some degree of hybridization is observed between all the metal and carbon bands in these materials. Our results are in excellent agreement with calculations of these same systems made by other researchers, as well as early experiments of these compounds.

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Validity of the independent-particle approximation in x-ray photoemission: The exception, not the rule

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One fundamental assumption commonly applied to many-electron quantum systems is the one-electron or independent-particle approximation (IPA), in which effects of electron-electron interactions, i.e., electron correlation, are assumed to be negligible. Among the myriad of applications of the IPA is describing x-ray interactions with matter in all its forms; the IPA is readily used as a basis for theoretical calculations and tabulations of a variety of x-ray-interaction parameters such as total and partial cross sections, photon-scattering probabilities, and photoelectron angular distributions. With this central role in x-ray science, it is important to determine the limits of the IPA, or, equivalently, to identify the significance of electron-correlation effects to x-ray interactions. At present, it is a generally accepted axiom that the IPA is valid except in certain well-defined regimes where electron correlation is known to be important. Work at the ALS has proven this notion incorrect for x-ray photoemission; validity of the IPA is the exception, not the rule. Specifically at intermediate energies, far above outer-shell thresholds and away from inner-shell thresholds, interchannel-coupling effects are thought to be small and the IPA is reckoned to be reasonably good. A combined theoretical and experimental study of valence photoionization of argon demonstrates that this is not the case; IPA is invalid in a broad region of energy and subshell. This is of great interest owing to the upsurge in activity in the field of atomic photoionization, spurred by the development of third-generation synchrotron-radiation sources[1], along with the importance of atomic photoionization in various applications, e.g., radiation physics, astrophysical modeling[2].

It was recently shown for the valence shell of neon that, owing to interchannel coupling the independent particle model is inadequate to explain photoionization of nl ($l > 0$) electrons of atoms even at energies well above the ionization threshold [3]. New measurements of $3p$ photoionization of argon taken at ALS B.L. 8.0 confirm the earlier finding

Figure 1. Beta parameter for Ar 3p. Dots represent experimental points. Dotted line represents IPA values. Solid line represents RRPA calculations with full coupling. Dashed lines represent calculations with various levels of interchannel coupling.

regarding the physics at high energy. Electron time-of-flight measurements were taken following photoexcitation of argon in the photon energy range of 600-850 eV. The data were analyzed to determine the angular distribution asymmetry parameter β for argon 3p photoionization, and the ratio of the intensities of the 3p and 3s lines. Our findings emphasize the importance of coupling for photoionization channels under consideration with channels from energetically neighboring thresholds to accurately describe the high energy nl ($l > 0$) photoionization of atoms.

Photoemission cross sections and angular-distribution asymmetry parameters for valence 3p electrons of neutral argon have been calculated by the relativistic random-phase approximation (RRPA) methodology. [4-5]. Five levels of interchannel coupling scheme: all channels arising from (i) 3p, 3s, 2p, 2s and 1s (full RRPA); (ii) 3p and 3s; (iii) 3p and 2p; (iv) 3p and 2s; and (v) only 3p have been considered to describe channel interactions. Note that scheme (v) should yield virtually similar results to the IPA method as the contribution of intra-shell coupling is small at high enough energy.

The experiments were performed at the ALS on beamline 8.0 during two-bunch mode, using an experimental setup described previously [6]. Briefly, four time-of-flight (TOF) electron analyzers collect spectra simultaneously at different angles. A needle serves as an effusive source for the gas under study. All analyzers are differentially pumped to avoid pressure buildup near the MCPs. The cylindrically symmetrical analyzers view the same interaction region with the 2-mm entrance apertures at a distance of about 20 mm. The apertures and needle are grounded to maintain a field-free interaction regions. A straight electron flight path provides fundamental simplicity to the TOF technique.

Results for angular-distribution asymmetry parameter, β , are shown in Fig. 1, for 3p photoionization up to photon energies as high as 900 eV. The branching ratios, σ_{ns}/σ_{np} , also are presented in Fig. 2. Calculations tend to fall in two groups: (a) ones in which coupling with channels from the 3s subshell is included and (b) ones in which it is not. Importance of ns coupling in np processes is due to (i) strong overlap between continuum wave functions of channels arising from energetically neighboring thresholds (that is largely decided by the same n) and (ii) faster decay of 3p compared to 3s with increasing $h\nu$ at high enough energy [3]. The latter point is illustrated through the ratio of cross sections in Fig. 2. The experimental results for β_{3p} are in good agreement with all the calculations. For σ_{ns}/σ_{np} the situation is rather different; RRPA calculations are too large by $\sim 20\%$; whereas IPA is too large by almost a factor of 2, illustrating how important interchannel-coupling effects are, even far above threshold (Fig. 2).

In conclusion, we have shown in a combined experimental and theoretical study that interchannel coupling between 3s and 3p

Figure 2. Cross section ratio for Ar 3s/3p. Circles give experimental values. Dotted line gives values calculated using the IPA. Solid line gives values for RRPA with full coupling taken into account. Dashed lines indicate different levels of interchannel coupling.

photoionization channels in Ar dramatically alters the smaller 3s cross section from the predictions of the IPA, and other calculations which omit this coupling, by almost a factor of two in an energy region quite far from any thresholds. But there is nothing special about Ar, and therein lies the importance of these results. In *any* case where there are two (or more) degenerate photoionization channels emanating from subshells with similar binding energies and spatial extent, the smaller cross section(s) will be significantly affected through interchannel coupling with the stronger channel(s). Thus, calculations which omit interchannel coupling are reliable *only* for the dominant channel in such a situation; weaker channels will not be predicted reliably by Hartree-Fock or any other IPA calculation for virtually all energies. We are thus led to the inescapable conclusion that IPA is not valid for most subshells of most atoms at most energies. Finally, although the example presented was for an atom, these ideas should be equally valid for molecules, surfaces, and solids as well.

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X-ray Absorption Spectroscopy of Ge-Nanocluster Films

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INTRODUCTION

Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic properties. Germanium clusters are of particular interest, as recent publications suggest, since they display a strong blue luminescence. However, it is not clear, if this is due to surface species, oxide layers or quantum confinement. The presented experiment focuses on X-ray absorption of Ge-clusters, which have been synthesized in a narrow size distribution, to unambiguously identify quantum confinement effects in these nanostructures.

EXPERIMENT AND DISCUSSION

Clusters were formed by condensation of Ge-vapor in an Argon atmosphere *in situ* at beamline 8.0. The vapor was cooled by Argon gas and clusters condensed out of the oversaturated vapor and were deposited on a hydrogen passivated Si-substrate located one inch above the Ge-evaporator. The cluster size could be adjusted by two parameters, the crucible temperature and the Ar-pressure. Rising either of them forced larger clusters to form. The mass flow onto the substrate was controlled with a shutter which was opened only briefly. Typically the shutter was opened fifteen times for five seconds at Ar-pressures between 120 and 200mTorr.

The cluster sizes and geometries were characterized with an atomic force microscope (AFM). For that purpose, witness depositions of clusters on highly orientated pyrolytic graphite (HOPG) were made. The lateral resolution of an AFM is limited by the diameter of the AFM tip, which is large compared to the clusters. For this reason it was assumed that the clusters are spherical in shape and the cluster height over the baseline was taken as the cluster size. It is interesting to note, that the clusters on HOPG are very mobile and hence, they gather at defects and step edges and form snowflake-like structures (Fig. 1). The sizes of the clusters produced in this experiment range from 2nm to 4nm, scaling almost linearly with the pressure of the Ar-atmosphere. The conduction band of bulk Ge, Ge-clusters and GeO₂ powder was probed with total electron

Fig. 1: Atomic Force Microscope image of Ge clusters on HOPG. Clusters gather at defects and step edges and form snowflake like structures.

yield (TEY) X-ray absorption spectroscopy (XAS) at Beamline 8.0 at the Advanced Light Source. In this process a Ge 2p core electron was excited into the empty states of the conduction band. The spectra of bulk-Ge and GeO₂ show completely different features at the 2p edge (Fig. 2). Bulk-Ge has a very sharp absorption onset at around 1209eV and shows a weak excitonic feature right at the absorption edge (a) as well as some DOS features (b to d) [1,2]. The absorption onset of GeO₂ is shifted by about 5eV to higher energies and there is a strong excitonic feature below the edge.

For Ge-clusters a blueshift of the absorption edge compared to the bulk is observed (Fig. 3). The shift gets larger for lower aggrega-

tion pressures and smaller cluster sizes, respectively. The shift is measured at the intersection of the extrapolation of the edge to the background (Fig. 3) it ranges from 0.2eV for clusters of 3.5nm in size up to 0.4eV for clusters of 2.5nm in size. If it is measured at the inflection point of the edge it is even larger. The blueshift cannot be due to chemical shifts from oxidation as the characteristic absorption features of GeO_2 are missing i.e. the edge is similar in shape to the bulk absorption edge and the shift scales with the cluster size. However, the shift can be explained with quantum confinement effects in the cluster, which raise the bottom of the CB to higher energies depending on its size. In XAS the energy difference between the Ge 2p core level and the bottom of the conduction band is measured, hence a shift of the absorption edge implies, that the bottom of the conduction band is risen. As mentioned above, the cluster samples are made out of a size distribution of clusters and hence there will be a distribution of quantum shifts. Consequently, the absorption edges of the cluster samples are broadened compared to bulk-Ge.

SUMMARY

We were able to produce and deposit Ge clusters in the nm-range and for the first time a blue-shift in the X-ray absorption from these clusters has been measured. The shift of the conduction band scales with the particle size, in agreement with quantum confinement theory.

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Fig. 2: Absorption spectra of bulk-Ge and GeO_2 . In bulk-Ge an excitonic feature (a) as well as different DOS features can be seen (b-d) [1, 2]. The absorption onset of GeO_2 is moved to higher energies and there is a strong exciton below the edge.

Fig. 3: X-ray absorption of bulk-Ge (top) and Ge-clusters. With decreasing aggregation pressure and decreasing particle size, respectively the absorption edge moves to higher energies.

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X-ray Fluorescence Measurements of Irradiated Polymer Films and Organic Superconductors

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Fluorescent X-ray $C K\alpha$ and $O K\alpha$ emission spectra (XES) have been measured to study the electronic structure of polyimide films (PMDA-ODA) prepared by the spin-coating method and ionized cluster-beam deposition on the Si-substrate. We found that the spectral emission features are not changed when the time of exposure was increased from 600 to 1800 sec. This indicates that polyimide films are rather stable to the exposure of monochromatic synchrotron radiation and the experimental fluorescent $C K\alpha$ and $O K\alpha$ XES can be used for the analysis of the electronic structure of polyimide films. The occupied states of PMDA-ODA have also been investigated and compared with molecular orbital calculations of the model monomer containing 41 atoms using a semi-empirical Hydrogenic atoms in molecules version 3 (HAM/3) method. From the comparison of our calculations with the experimental results we identify the origin of the spectral features and find excellent agreement [1].

We have used fluorescent $C' K\alpha$ XES to characterize the bonding of carbon atoms in irradiated polyimide (PI) and polycarbosilane (PCS) films. The PI films have been irradiated with 40 keV N_2^+ or Ar^+ ions, at fluences ranging from 1×10^{14} to 1×10^{16} cm⁻². The PCS films have been irradiated with 5×10^{15} C⁺ ions cm⁻² of 500 keV and/or annealed at 1000⁰ C. We find that the fine structure of the carbon XES of the PI films changes with implanted ion fluence above 1×10^{14} cm⁻². This is attributed to the degradation of the PI into amorphous C:N:O. The bonding configuration of free carbon precipitates embedded in amorphous SiC, which are formed in PCS after irradiation with C⁺ ions or combined treatments, is close to either that one in diamond-like films or the one in silicidated graphite [2].

We have measured X-ray fluorescent $S L_{2,3}$, $C' K\alpha$ and $N K\alpha$ XES of superconducting inorganic polymer single crystals (SN)_x and (ET)₄Hg_{2.89}Br₈ and compared the results of the XPS and UPS measurements with our self-consistent *LMTO-TB* band structure calculations. The orbital composition of the energy bands of (SN)_x and (ET)₄Hg_{2.89}Br₈ is analyzed. The electronic states that dominate the density of states near the Fermi level are determined.

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X-ray Fluorescence Spectroscopy of $\text{GdBa}_2\text{Cu}_3\text{O}_x$ Thin Films.

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Oxygen content is a prominent factor controlling superconducting behavior of Cu oxide superconductors; in fact both the normal state electrical properties and superconductivity of $\text{MBa}_2\text{Cu}_3\text{O}_x$ ($6 \leq x \leq 7$) compounds ($M=\text{Y}$ or rare earths excluding Ce and Tb) depend strongly on oxygen content.

For bulk samples, there is a consistent body of literature linking the O deficiency in 123 compounds to some of the basic properties of high T_c superconductors. In particular the critical temperature T_c is known to depend strongly on the hole carrier density which can be varied by charge compensation or oxygen non-stoichiometry.

In thin films, however, some of these parameters become variable depending on the sample preparation technique and growth conditions. In particular, due to the variable copper valence, the equilibrium oxygen content can be varied continuously ($6 \leq x \leq 7$) in the thin films as a function of substrate temperature and oxygen partial pressure. This fact, together with the peculiar morphology of the films enables researchers to obtain important information on the structure and superconducting behavior of the material under examination.

However, effects of oxygen non-stoichiometry on electronic properties of thin films are not well known and comparisons with the same properties on bulk samples have not been reported.

This field has benefited greatly from spectroscopies such as photoemission and x-ray fluorescence spectroscopy (XES) [1,2,3,4]. The latter technique has the advantage of being less surface sensitive and so can be used to study bulk properties, and elaborate preparation is not necessary.

The samples available were $\text{GdBa}_2\text{Cu}_3\text{O}_x$ oxygen deficient films ($6.3 < x < 6.8$) deposited on (110) oriented NdGaO_3 . These have been prepared ex situ by controlled annealing under reduced oxygen pressure at 400°C. Films had thicknesses from 40 to 200 Angstroms and stacking fault densities about 0.5%, i.e. perfectly crystalline as far as this spectroscopy is concerned.[5,6]

To clarify the role and contribution to the superconducting behavior of inequivalent oxygen sites we have done XES and XAS measurements at beamline 8.0.1 and tried to have an identification of the absorption and emission lineshape in terms of different oxygen atoms and sites, the induced hole distributions and overall experimental and theoretical pDOS as a function of oxygen content of the samples.

We selectively excited the variable oxygen content films in the energy range needed to obtain absorption (total fluorescence yield mode) and emission spectra above, below and at the resonance for O K and Cu L edges and local partial density of states in the VB was experimentally obtained.

The valence band of high-Tc superconductors of perovskite type is known to be formed mostly by Cu-3d and O-2p states. X-ray emission Cu-L (3d to 2p transition) and O-K (2p to 1s transition) spectra arise from dipole allowed transitions from the valence band to inner shell vacancies. The experimental study of the electronic partial density of states is therefore facilitated in this case by the fact that the fluorescence spectra are well separated in energy.

Multiplet effects in emission and absorption measurements at the $L_{2,3}$ edge of 3d transition metals can significantly modify the edges from their single particle interpretation. The origins of these modifications are extremely important in correlated systems since they are a direct consequence of correlations between the 2p and 3d core holes and within the 3d band.

Absorption and emission measurements have therefore been done at the Cu $L_{2,3}$ edge in the hope to pinpoint significant differences and analogies with theoretical one electron type calculations.

A problem met in the investigation is that the obtained data are quite sensitive to the quality of the samples. In particular, there is an overlapping of the Cu L edge spectra with spurious signal coming from the substrate.

A high sensitivity to the quality of the samples was to be expected in the case of thin films and is also reported in literature.

In the O 1s absorption spectra a peak is present in the pre-edge region which is strictly related to the oxygen content of the sample and can be associated with the unoccupied O 2p states. The peak shifts in energy and changes in intensity in different samples according to O content. In O rich samples holes are formed upon p-type doping and the pre-edge peak shifts close to the Fermi edge with possible formation of states in the gap. [Fig.1]

In the O XES spectra, different O chemical environments will determine different emission energy values for transitions to core 1s states (2p-1s transitions). The chemical shift can be exploited to selectively excite different site O contributions. Experimental results show a shift both in the low energy shoulder and in the peak maximum energy value for different O content of the samples. [Fig2]

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Figure 1. O 1s X-ray absorption spectra taken in total fluorescence yield mode. 1) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.58}$ 2) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5+8}$ 3) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.8}$

Figure 2. O K α X-ray emission spectra taken at the prepeak maximum values of the absorption spectra for the respective samples. 1) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.58}$ 2) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5+8}$ 3) $\text{GdBa}_2\text{Cu}_3\text{O}_{6.8}$

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Beamline 9.0.2 Abstracts

193 nm Photodissociation of Thiophene Using Synchrotron Radiation

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INTRODUCTION

Thiophene is a five-membered heterocyclic compound with a sulfur atom. The photodissociation study of thiophene is important in fossil fuel combustion, molecular biology and material science.¹

Several gas phase photodissociation studies have been done on thiophene.²⁻⁶ Ng and co-workers examined the isomeric structures of photofragments formed in the 193 nm photodissociation of thiophene using photodissociation-photoionization and 2 + 1 REMPI experiments⁵ Only two dissociative channels, $C_2H_2S + C_2H_2$ and $C_4H_4 + S$, were identified by Ng and co-workers. They found that the S atoms were produced predominantly ($\geq 96\%$) in the 3P_J states. Using photofragment translational spectroscopy, Mayers et al. performed the first direct examination of primary photoproducts of thiophene at 193 nm. Six primary dissociative channels were identified.⁶

In this study, we have measured the time-of-flight spectroscopy and photoionization efficiency spectra (PIE) of photofragments from the photolysis of thiophene using photofragment translational spectroscopy and undulator synchrotron radiation from the Chemical Dynamics Beamline at the Advanced Light Source.

EXPERIMENTAL

The experiment was completed at beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.⁷ A pulsed molecular beam of 10% thiophene seeded in helium was skimmed twice and intersected at 90° with the photolysis laser (193.3 nm, Lambda Physik LPX 220I). Photofragments formed by 193 nm photodissociation entered the detector chamber region (2×10^{-10} Torr) and were photoionized using tunable synchrotron radiation. The tunability of the light source allows for selective ionization of products and very low background counts, permitting the measurement of the PIE spectra of photofragments. The photoionized products were mass selected by using a quadrupole mass filter and the ions were counted with a Daly ion counter. A multi channel scalar (MCS) was used to measure the time-of-flight (TOF). Thiophene (99%) was obtained from Aldrich and used without further purification.

Fig. 1 (a) The mass 58 (C_2H_2S) TOF spectrum at 20° . The data is presented by circles. The black line is the fit to the data using the $P(E)$ shown in Fig. 2(a); (b) The mass 26 (C_2H_2) TOF spectrum at 20° . The black line is the fit to the data using the $P(E)$ (dash line) from Fig. 2(a) and The $P(E)$ (dot-dash line) from Fig. 2(b).

RESULTS AND DISCUSSION

The TOF spectrum at m/e 58, 52, 51, 45, 44, 40, 39, 33, 32, and 26 have been done at different angles (20 - 50°). Five primary dissociative channels have been identified, including three closed shell channels and two radical channels, as summarized by processes 1-5.

Similar channels, (1) (4) and (5), were observed in the dissociation of furan at 193 nm.⁸ Two additional channels (2) and (3) were observed in this study because the C-S bond is weaker than C-O bond in furan. Fig. 1(a, b) shows the Time-of Flight (TOF) spectrum of $\text{C}_2\text{H}_2\text{S}$ and C_2H_2 at 20°. Some of the $\text{C}_2\text{H}_2\text{S}$ fragments were found to undergo secondary dissociation. Fig. 2(a) shows the translational energy distribution $P(E)$ of the $\text{C}_2\text{H}_2\text{S} + \text{C}_2\text{H}_2$ channel, which is used to fit Fig. 1(a) data. The C_2H_2 TOF spectrum, however, needs another contribution [shown in Fig. 2(b)] besides the $P(E)$ of Fig. 2(a). The $P(E)$ shown in Fig. 2(b) corresponds to secondary dissociation of $\text{C}_2\text{H}_2\text{S}$ to $\text{C}_2\text{H}_2 + \text{S}$. This secondary dissociation was not observed in Mayers' study.⁶ By measuring the PIE spectra of mass 58 and 22, the isomeric structures of the fragment $\text{C}_2\text{H}_2\text{S}$ and C_2H_2 were determined to be that of thioketene ($\text{CH}_2=\text{C}=\text{S}$) [the PIE spectroscopy of the mass 58 shown in Fig. 3] and acetylene, respectively. Our results are in good agreement with previous studies.⁵ The $P(E)$ shown in Fig. 2(a) indicates the presence of a barrier of at least

Fig. 3 Photoionization efficiency spectroscopy of the $\text{C}_2\text{H}_2\text{S}$ fragment.

16.5 kcal/mol for this process. Preliminary analysis indicates that the closed shell channels occur on the ground state

potential energy surface following internal conversion. Furthermore, it is believed that the dissociation of thiophene at 193 nm involves the formation of the biradical $\bullet\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{S}\bullet$ as the initial step. The rapid decomposition of this biradical may yield different channels.

Fig. 2 (a) The translational Energy Distribution $P(E)$ of $\text{C}_2\text{H}_2\text{S} + \text{C}_2\text{H}_2$; (b) The translational Energy Distribution $P(E)$ of $\text{C}_2\text{H}_2\text{S} \rightarrow \text{C}_2\text{H}_2 + \text{S}$.

The other fragments were identified as vinyl acetylene (C_4H_4 , $H_2C=CH-C\equiv CH$), 1-2-propadiene (C_3H_4 , $H_2C=C=CH_2$), and propargyl radical (C_3H_3 , $HC\equiv C-C^{\bullet}H_2$). Preliminary analysis indicates that sulfur is produced in both the 3P and 1D electronic states

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A characterization of vibrationally excited NO_2^+ by ZEKE high-resolution threshold photoionization spectroscopy

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INTRODUCTION

In addition to energetic reference points, statistical rate theory models for combustion systems require information to accurately calculate the state densities of reacting species. At chemically significant energies, anharmonicities play an important role in determining the distribution of vibrational levels, especially for weakly bound free-radical intermediates. Furthermore, free-radical reactions often encounter low-barriers, and in such cases, details in the anharmonic coupling of vibrational modes can affect dynamical outcomes, including the disposal of excess energy in products. Few experiments provide direct information, and model calculations must rely on theoretical potentials in order to estimate higher-order terms in vibrational force fields. Spectroscopic measurements provide an important means to test the validity of *ab initio* calculations.

Some time ago, we characterized the anharmonic terms in the vibrational potential of NO_2^+ that give rise to bend-stretch Fermi resonance [1]. Using ionization-detected two-photon absorption, we obtained the spectrum of a long progression of vibrationally excited levels in the $3p\sigma^2\Sigma_u^+$ Rydberg state of NO_2^+ . The linear NO_2^+ core of this Rydberg state possesses a vibrational potential that parallels the potential surface of the cation, so that the broad envelope of Franck-Condon factors for transitions from the bent neutral ground state provides a convenient means to observe cation vibrational structure over a wide energy range. Using a comprehensive fit to fifteen band positions through the (040)-(120)-(200) triad, we were able to estimate harmonic frequencies, diagonal anharmonicities and the cubic force constant, k_{122} . Three-color triple-resonant state-selected ionization experiments with ZEKE threshold photoelectron detection provided a direct measure of cation frequencies for comparison [2]. We found that the degree of vibrational coupling in the cation compares with the more extensively characterized $3p\sigma$ Rydberg state. The experimental results for the core cation agree well in both cases with CCSD(T)/[4s3p2d1f] *ab initio* calculations including Fermi resonance effects.

We have now begun work seeking to test this potential by extending ZEKE measurements of cation vibrational structure to higher energy levels, reached in direct VUV transitions from the neutral ground state. To obtain these spectra, we have used the multipurpose photoelectron-photoion apparatus on the Chemical Dynamics Beamline at the Advanced Light Source.

Like the Rydberg spectrum, the spectrum of photoionizing transitions from the bent ground-state neutral to the linear cation forms long vibronic progressions. This displaced Franck-Condon envelope makes the adiabatic threshold difficult to discern, but does provide a very effective means

to explore the higher vibrationally excited states of NO_2^+ . In this respect, NO_2 is representative of many free-radical neutrals that form higher-symmetry closed-shell cations. Weak vibrationless thresholds together with long multi-mode progressions have long been a feature of the conventional photoionization spectra of free radicals [3], and will be an issue in combustion free-radical photoionization experiments planned for the ALS.

HIGH-RESOLUTION PHOTOIONIZATION SPECTRUM OF NO_2

Our experiments have scanned the threshold photoionization spectrum of NO_2 from 9.5 to 20 eV (130 to 62 nm) with a resolution of 0.003 nm. We achieved ZEKE photoelectron discrimination by exploiting the time structure of the synchrotron radiation source, which consisted of alternating 544 ns periods of illumination followed by 112 ns dark gaps. During irradiation, the experiment maintained a nominally zero electrostatic field across the ionization region of an electron time-of-flight spectrometer. Accumulated ZEKE threshold photoelectrons were then extracted by a 1 V pulse which was applied to the repeller 20 ns after the beginning of each dark gap. The repetition rate of the experiment was thus 1.52 MHz. Figure 1 shows a complete scan over the region from 9.5 to 20 eV using a counting time of 30 seconds per point.

Figure 1. ZEKE threshold photoionization of NO_2 recorded at the Advanced Light Source.

ZEKE threshold photoelectron discrimination clearly resolves vibrational structure in these many electronically excited states of NO_2^+ . The inset gives an expanded view of the (030) band of the $a\ ^3\text{B}_1$ state, which shows that this approach can isolate electronically excited states of polyatomic cations with rotational resolution.

The ZEKE spectrum in the region of the cation ground state exhibits a broad envelope of transitions built on progressions in ν_2 arising from bent-to-linear photoionization. Figure 2 shows a detail from the adiabatic threshold to 11 eV (upper spectrum). Weak but evident are some of the same low-frequency bands that we observed in ZEKE spectra scanned in laser-induced transitions from the $3p\sigma^2\Sigma_u^+$ Rydberg state. With increasing energy, individually assignable bands give way to a complex system of irregular resonances that arise from bend-bend and bend-stretch interactions. The simulation presented in Figure 2 (lower, inverted spectrum) is constructed strictly from our force-field parameterization of the lower energy structure observed in higher-resolution laser experiments described above.

Figure 2. ZEKE threshold photoionization of NO_2 in the first threshold region. Simulation of cation vibrational structure using spectroscopic parameters derived from our earlier laser photoionization studies.

Further work will refine our higher-order characterization of the NO_2^+ vibrational potential by improving the experimental spectrum. The use of a supersonic jet in the ALS photoionization apparatus will provide a greater degree of cooling and increase sample density in the interaction region. This will sharpen the threshold photoionization spectrum and improve its signal to noise ratio. We will also complement our ALS data with higher-resolution VUV laser scans over key features using our laboratory ZEKE spectrometer. With better-resolved spectra, we will refine our force field to extend assignments for comparison with variational calculations of vibrational energy levels on ab initio potentials. An important issue will be the vibrational wavefunctions themselves and the detailed redistribution of Franck-Condon intensity that arises from bend-stretch mixing due to off-diagonal and higher-order anharmonicities.

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Dissociative Ionization by Ion Imaging with Undulator Radiation: Dissociation Dynamics of SF₆

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Interaction of molecules with VUV radiation dominates over all other regions, and dissociative ionization is the principle decay mechanism from excitation of molecules in the VUV. Dissociative ionization (D.I.) is thus arguably one of the most important photophysical processes. This is especially true for the stratosphere, in interstellar regions, plasmas, and any environment where VUV radiation is abundant. Despite this importance much that is known is based on experiments that are, in some ways, incomplete. For many of these processes, accurate angular distributions, for example, have not previously been obtained. Sophisticated approaches have been employed in recent years using coincidence methods[1,2], for example, to study dissociative ionization from energy selected ions. In general, these methods rely on analysis of the ion time-of-flight peak shape to characterize both the kinetic energy released as well as the angular distributions for the process. These approaches achieve a precise definition of the initial state of the ion, but because of possible couplings between the energy and angular distributions generally do not yield the complete kinetic energy or angular distributions for the process of interest. We have recently adapted the ion imaging technique [3,4] for use on the Chemical Dynamics Beamline, an undulator beamline at the Advanced Light Source [5]. The beamline provides intense (10^{16} photons/sec at 2% bandwidth, 5-30 eV), continuously tunable horizontally polarized VUV radiation for a range of studies of chemical reaction dynamics and photoionization processes. Ion imaging has the advantage that complete energy and angular distributions are recorded simultaneously, and the data analysis may be accomplished by direct inversion of the raw data. This approach is ideally suited for detailed characterization of dissociative ionization dynamics, in that the complete double differential cross sections (energy and angle) for the process are obtained directly.

Here we present a preliminary imaging-based study of the dissociative ionization dynamics of SF₆ in a pulsed molecular beam, excited at energies from 15 to 30 eV, with particular attention paid to the anisotropy in the angular distributions and the dynamics of the channels leading to SF₄⁺ and SF₃⁺. The experiments were performed in a recently commissioned ion imaging-based endstation on the Chemical Dynamics Beamline. Briefly, it features a molecular beam source pumped by a 2000 l/s magnetic bearing turbomolecular pump (Seiko-Seiki). The molecular beam is skimmed once before entering the ionization chamber, which has two 400 l/s magnetic bearing turbomolecular pumps. Dissociative ionization studies were performed using the tunable VUV undulator radiation, looking solely at the ionic products. Product ions are electrostatically accelerated into a 0.5 meter flight tube perpendicular to the plane of the beams. They then strike a position sensitive dual microchannel plate coupled to a phosphor screen viewed by an integrating fast-scan video camera system employing thresholding in conjunction with a linear video look-up table. Typical accumulation times were 10 minutes for each image.

The Photoion efficiency (PIE) curves were obtained by collecting the integrated ion signal for each of the fragments in 0.5 eV intervals from 15 to 30 eV. Mass-selected images were obtained by gating the microchannel plate with 300 nanosecond duration "on" pulse. The detector is viewed by an integrating fast-scan video camera system (Data Design AC101/I) employing

thresholding in conjunction with a linear video look-up table. Images of SF_5^+ , SF_4^+ and SF_3^+ were recorded (when observed) at photon energies from 15.0 to 30 eV. To isolate contributions from particular electronic states, difference images were created during analysis. These difference images show the ion contribution from newly accessed electronic states. Analysis of the images was performed using the conventional inverse Abel transform to reconstruct the product-flux contour maps from the images, which are 2-dimensional projections of the 3-dimensional fragment distributions [4]. These were then integrated radially and about the polar angle to yield the velocity and angular distributions, respectively.

The PIE curves we see are consistent with the literature. The onset of SF_5^+ formation is ~ 15.5 eV, with SF_4^+ and SF_3^+ being seen at ~ 19 eV and 20 eV respectively (Figure 1). A dominant feature in the PIE curves of SF_5^+ and SF_4^+ is the large peak at ~ 25 eV. This is ascribed to a shape resonance in the SF_6 parent potential surface[6]. Because this is not an energy selected experiment for the electron, difference images were generated to isolate the contributions from newly accessed excited. On the rising edge of a feature in the PIE curve, two images were taken, and then subtracted. The resulting images contains only the contribution of the higher energy. The arrows on Fig. 1 indicate where these images were taken.

Immediately apparent from the SF_5^+ images (Figure 2) is that any analysis method which can not quantitatively determine the anisotropy and use it as a parameter for TOF kinetic energy fits will necessarily be missing information to accurately determine translational energy release. Using the familiar equation $I(\Theta) = 1 + \beta P_2(\cos(\Theta))$ to obtain the β parameters [7] we find β 's of about 1 for the $SF_6 \rightarrow SF_5^+ + F + e$ process. This is indicative of a transition moment relatively parallel to both the recoil axis of the (non-electron) fragments and the polarization of the VUV light. Such behavior in a molecule of such high symmetry means that

Fig 1 Photoion Efficiency curve of the Dissociative Ionization of SF_6 . Arrows indicate energies where images were collected. Curves are labeled as to their fragment channel.

Fig 2 SF_5^+ Images (clockwise from top left) SF_5^+ at 16 eV, SF_5^+ at 17-16 eV, SF_5^+ at 24-22 eV, and SF_5^+ at 18-17 eV. The images show marked anisotropy in the dissociative ionization event. VUV polarization is indicated by arrow. The β parameters for these processes are ~ 1 indicating a parallel transition.

the transition moment is localized on a particular bond axis; in fact, the first 3 electronic states of SF_6^+ arise from the removal of an electron from a lone pair on one of the fluorine atoms[8].

Examining the translational energy release (Figure 3), there is not much change despite a large increase in excitation energy. This excess energy can be realized as internal energy in the SF_5^+ fragment. From photoion efficiency data taken on this endstation, we see the SF_4^+ fragment formed precisely when the excess energy available to the SF_5^+ is equal to the thermodynamic threshold for the decomposition of SF_5^+ to $SF_4^+ + F$. The actual translational energy releases are likely to be governed by the barrier arising from the extensive electronic and nuclear rearrangement that SF_5^+ must undergo after initial formation from SF_6^+ . (The newly formed SF_5^+ is square pyramidal, while the ground state structure is trigonal bipyramidal [9]).

Also interesting to note is the large increase in SF_5^+ production in the region of the shaped resonance. Excitation of SF_6 with a 24 eV photon produces an excited bound state of SF_6 with over 8 eV excess energy as compared to the $SF_5^+ + F + e$ process. This is well above the threshold for subsequent fragmentation to $SF_4^+ + F + F + e$, yet the SF_4^+ production does not increase. There must be efficient conversion from this excited state of SF_6 to the lower lying states of SF_6^+ . As this would not be a zero energy electron process, PEPICO studies are blind to this interesting phenomenon. Further work on this endstation is underway; imaging the photo-electrons from this process. The photoelectron spectra of this process pinpoint the final states and energies of the resulting SF_5^+ fragment.

The SF_4^+ and SF_5^+ fragments have a nearly isotropic angular distribution (Figure 4). This is consistent with SF_4^+ being formed via statistical decomposition of SF_5^+ with large levels of internal excitation. The lack of anisotropy is likely due to a combination of long lived SF_5^+ parent relative to its rotational period, and statistical symmetry of different F atoms in the SF_5^+ ion. SF_3^+ displays

SF_5^+ Total Translational Energy

Fig 3 SF_5^+ Total translational energy distributions for the process $SF_6 + h\nu \rightarrow SF_5^+ + F + e$. The translational energy release is essentially constant with an 8 eV increase in photon energy implying that the SF_5^+ fragment must contain significant amounts of internal energy after high energy excitation.

Fig 4 SF_n^+ Images (clockwise from top left) SF_3^+ at 24-22 eV, SF_5^+ at 24 eV, SF_4^+ at 22 eV, and SF_3^+ at 22 eV. The images are nearly isotropic indicating a long lived parent ion and a statistical dissociation.

similar behavior in its angular distribution, consistent with a stepwise decay of SF_5^+ into daughter fragments, which then decompose yielding SF_4^+ .

Conclusion

We have adapted the technique of photofragment imaging, widely used in the study of neutral photochemistry, to use on a VUV undulator beamline at the Advanced Light Source. The technique allows direct inversion of the raw data to yield the full angular and translational energy distributions for the product ions. The method was applied to study the dissociative ionization of SF_6 at photon energies from 16 to 24 eV. The experiment allows for detailed characterization of the angular and translational energy distributions of the fragments, yielding clear insight into the decay mechanisms of these excited ionic states even in the absence of energy selection of the initial ion.

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High resolution pulsed field ionization photoelectron spectroscopy using multi-bunch synchrotron radiation: time-of-flight selection scheme

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INTRODUCTION

We have developed an efficient electron time-of-flight (TOF) selection scheme for high resolution pulsed field ionization (PFI) photoelectron (PFI-PE) measurements using monochromatized multi-bunch undulator synchrotron radiation at the Advanced Light Source. By employing a simple electron time-of-flight (TOF) spectrometer, we show that PFI-PEs produced by the PFI in the dark gap of a synchrotron ring period can be cleanly separated from prompt background photoelectrons. The rotational-resolved PFI-PE band for H_2^+ ($X^2\Sigma_g^+$, $v^+=0$) measured using this electron TOF selection scheme is nearly free from residues of nearby autoionizing features, which were observed in the previous measurement by employing an electron spectrometer equipped with a hemispherical energy analyzer. In addition to attaining a high PFI-PE transmission, a major advantage of the electron TOF scheme is that it allows the use of a smaller pulsed electric field and thus results in a higher instrumental PFI-PE resolution. We have demonstrated instrumental resolutions of 1.0 cm^{-1} (FWHM) and 1.9 cm^{-1} (FWHM) in the PFI-PE bands for $\text{Xe}^+(^2P_{3/2})$ and $\text{Ar}^+(^2P_{3/2})$ at 12.123 eV and 15.760 eV, respectively.

EXPERIMENT

The electron TOF spectrometer used in this study has been modified from the one used in our previous experiments. The main difference was that the hemispherical analyzer has been removed. A schematic diagram showing the present lens arrangement for the electron and ion TOF detection can be seen in Fig. 1. The distance between lenses I1 and E1 was 1.0 cm. The midpoint between lenses I1 and E1 defined the PI/PEX region. The apertures in lenses E1 and E4 used here were 10 mm and 2 mm in diameter, respectively. Micro-spherical plates (MSP) were used for the electron detection.

Figure 1 Schematic diagram showing the electrostatic lens arrangement, the ion and electron TOF spectrometer. The electron and ion detectors are micro-spherical plates (MSP).

Figure 2(a) shows the emitting pattern of the ALS light pulses in multi-bunch mode. Following a delay of some 20-60 ns with respect to the beginning of the 112-ns dark gap, an electric field pulse in the range of 0.3-1.5 V/cm was applied to lens E1 [see Fig. 2(b)]. The frequency of the electric field pulse for the PFI was 1.53 MHz, consistent with the ring period.

When the photon energy was set to coincide with the $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ PFI-PE peak at 15.7596 eV, the observed TOF spectrum (solid circles) for PFI-PEs was found to exhibit a single peak with a full width of ≈ 40 ns as shown in Fig. 2(c). We note that the time zero of the TOF spectra shown in Fig. 2(c) corresponds to the triggering bunch-marking pulse provided by the ALS, the position of which is arbitrary. As the photon energy was slightly increased above the IE for the formation of $\text{Ar}^+(\text{}^2\text{P}_{3/2})$, the single TOF peak for PFI-PEs disappears and an electron TOF spectrum for prompt electrons resembling the synchrotron orbit pattern was observed as these electrons are extracted continuously by the small dc field. The electron TOF spectrum (open circles) observed using a 1.5 V/cm Stark pulse with the photon energy set at 15.7655 eV corresponding to the position of the $\text{Ar}(11\text{s}')$ autoionizing Rydberg state is also shown in Fig. 2(c). In this spectrum, a small electron signal due to prompt electrons was observed uniformly in time except in a window of ≈ 110 ns corresponding to the width of the dark gap, where essentially no electrons were formed.

The location of the TOF peak for PFI-PEs in the TOF spectrum depends on the

Figure 2 The timing structures for (a) the pattern of VUV light bunches emitted in the ALS multi-bunch mode; (b) the electric field pulses applied to lens E1 (see Fig. 1); and (c) the electron TOF spectra of PFI-PEs (●) as observed at the $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ PFI-PE peak and hot or prompt electrons (○) as observed at the $\text{Ar}(11\text{s}')$ autoionizing state.

height of the Stark pulse and the delay with respect to the beginning of the dark gap. These parameters were adjusted such that the TOF peak for the PFI-PEs fell in the middle of the 110-ns TOF window where no hot electrons were observed and thus achieved a clear separation of prompt electrons from PFI-PEs. As a result, PFI-PEs can be easily detected free from background prompt electrons by setting a gate with a width corresponding to the width of the TOF peak for PFI-PEs as shown in Fig. 2(c).

RESULTS

In order to illustrate the superior performance of the TOF PFI-PE scheme as compared to the previous synchrotron based PFI-PE method in terms of the achievable resolution and prompt electron background suppression, we show below the PFI-PE spectra for $\text{Xe}^+(^2\text{P}_{3/2})$, and $\text{H}_2^+(\text{X } ^2\Sigma_g^+, v^+ = 0, \text{N}^+)$ obtained using the TOF PFI-PE method.

A. PFI-PE bands for $\text{Xe}^+(^2\text{P}_{3/2})$

As pointed out before, the previous PFI-PE detection scheme using a hemispherical energy analyzer requires a sufficiently high Stark pulse for attaining a high electron transmission. The relatively high Stark pulse required also limits the attainable PFI-PE resolution. The transmission of PFI-PEs in this TOF selection scheme does not have a strong dependence on the applied pulsed electric field. Figure 4(a) shows the PFI-PE bands of $\text{Xe}^+(^2\text{P}_{3/2})$ in the regions of 12.128–12.131 eV, measured using the TOF PFI-PE detection method. The pulsed field used in these measurements was ≈ 0.3 V/cm. The Gaussian fit to these PFI-PE spectra reveals a resolution of 1.0 cm^{-1} (FWHM) for the $\text{Xe}^+(^2\text{P}_{3/2})$ bands. This resolution is more than a factor of two better than the best resolutions recorded for these PFI-PE bands in previous ALS experiments and is close to the best resolution (0.8 cm^{-1} , FWHM) reported using VUV laser PFI-PE techniques at ≈ 18 eV.

B. PFI-PE band for $\text{H}_2^+(\text{X } ^2\Sigma_g^+, v^+ = 0)$

The PFI-PE spectrum for $\text{H}_2^+(\text{X } ^2\Sigma_g^+, v^+ = 0)$ in the energy range of 15.34–15.47 eV obtained using the TOF PFI-PE scheme with a 0 V/cm dc field at the PI/PEX region and 1.5 V/cm Stark pulsed field is depicted in Fig. 4(a). Using the 2400 lines/mm grating and monochromator entrance/exit slits sizes

Figure 3 (a) PFI-PE band for $\text{Xe}^+(^2\text{P}_{3/2})$ (open circles) obtained using a pulsed field of 0.3 V/cm. A Gaussian fit obtained using a least squares fit is also shown (line), revealing a FWHM maximum of $1.0 \pm 0.2 \text{ cm}^{-1}$.

Figure 4 PFI-PE spectrum for $\text{H}_2^+(\text{X } ^2\Sigma_g^+, v^+ = 0)$ recorded (a) using electron TOF analysis with a 0 V/cm dc field, and a 1.5 V/cm pulsed field across the interaction region. The 4800 lines grating was used. The monochromator entrance/exit slits are set at 10/10 μm corresponding to a nominal resolution of $0.0064 \text{ \AA}$ (FWHM), (b) using a hemispherical and steradiancy analyzer in tandem and a 0.67 V cm^{-1} pulsed field at a nominal wavelength resolution of $0.048 \text{ \AA}$ (FWHM).

of 10/10 μm , the nominal wavelength resolution used was 0.0064 $\text{\AA}$ (FWHM). Figure 4(b) shows the H_2^+ ($X^2\Sigma_g^+$, $v^+ = 0$) spectrum in the same energy range recorded previously using a tandem steradiancy-hemispherical spectrometer at a nominal optical resolution of 0.048 $\text{\AA}$ [see Fig. 4(b)].

In the previous experiment, we had examined the achievable resolution by using a higher wavelength resolution and found that the observed PFI-PE resolution could not be significantly improved because of contamination by strong nearby autoionizing resonances as shown in Fig. 4(b). In view of this previous exercise, we may conclude that the higher resolution observed in Fig. 4(a) is due partly to a better suppression of prompt electrons.

Since the spectrum of Fig. 4(a) is essentially free from contamination of autoionizing resonances, it provides a more reliable measure for the relative photoionization cross sections of the marked rotational transitions. Based on the FWHM of the (0, 0) transition, we estimate that the PFI-PE resolution for the spectrum of Fig. 4(a) is 2.5 cm^{-1} (FWHM), significantly higher than $\approx 7\text{ cm}^{-1}$ (FWHM) attained in the spectrum of Fig. 4(b).

SUMMARY

The spectra presented in Figs. 4(a) and 4(b) have demonstrated that the TOF PFI-PE detection method described here is superior compared to the previous synchrotron based PFI-PE measurement schemes in both resolution and background electron suppression. The basic difference between this and the previous arrangement is that the hemispherical energy analyzer is eliminated in the present setup. Consequently, the electron transmission through the analyzer should be higher. Since the TOF axis is perpendicular to the VUV light beam, the TOF resolution is determined only by the height of the VUV beam along the TOF axis. It should be possible to significantly increase the PFI-PE signal by enlarging the entrance and exit apertures of the TOF spectrometer without affecting the TOF resolution.

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Photodissociation of phenylacetylene at 193 nm: Observation of two primary channels using photofragment translational spectroscopy

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INTRODUCTION

Phenylacetylene (PA) is an aromatic molecule with an unsaturated side group and is commonly used as a precursor for the synthesis of the polymer polyphenylacetylene $[(-RCCH)_n]$, where $R = \text{phenyl}$. The polymer is stable in air, soluble in most organic solvents, and has many interesting properties such as non-linear optical properties¹ and its potential use in semiconductor, electrophotographic photoreceptor, and chemical sensor devices.²⁻⁴

Poly-PA is commonly synthesized using a variety of catalytic methods with PA as the starting material. The catalysts used in these syntheses include Ziegler-Natta-type catalysts, transition metal halides and carbonyls, ionic catalysts, and free radicals.⁵⁻⁹ Recently, photo-induced catalysis of poly-PA has been investigated as an alternative approach to the traditional methods mentioned above.¹⁰⁻¹⁶ For molecules such as PA which absorb strongly in the ultraviolet, the photochemical initiation of polymerization is an efficient process. Surprisingly little is known about the photochemistry of PA. Knowledge of the primary photochemical processes is critical in the control and design of polymerization processes involving PA.

Several vibronic bands of PA have been observed in the UV and are attributed to excitation of the ring electrons with vibrational coupling to the C-C stretch of the acetylenic moiety.¹⁷⁻¹⁸ We have carried out an investigation of the photodissociation of PA at 193 nm to gain more insight into the primary processes involved. At 193 nm, the vibronic transitions have been assigned to the excitation of the $A^1A_1 \rightarrow D^1A_1$ or $A^1A_1 \rightarrow E^1A_1$ systems.¹⁷ Two primary photochemical pathways have been identified:

Serendipitously, the UV photochemistry of PA is simple. Reaction (1) produces the free radicals – ethynyl and phenyl, while reaction (2) gives way to two closed shell molecules – benzyne and acetylene. The amount of energy released in reaction (2) is sufficient to induce a secondary reaction:

Only the internally excited benzyne molecules undergo dissociation. From the energetic threshold for reaction (3), we derived an enthalpy of formation of $669 \pm 14 \text{ kJ mol}^{-1}$ for 1,3,5-hexatri-yne.

EXPERIMENTAL SECTION

All experiments were conducted at beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam machine which has been described in detail elsewhere.¹¹ Helium was bubbled through a furan sample held at -21°C . At this temperature and a total pressure of 800 Torr, a 10% molecular beam of furan/He was generated. This mixture was fed through pulsed valve (General Valve) and expanded from a nozzle heated to $\sim 100^{\circ}\text{C}$ in a differentially pumped source region and into the main chamber.

The photolysis laser was an ArF excimer (193.3 nm, Lambda Physik LPX 220i), focused to a spot of size 2x4 mm and aligned perpendicular to the plane containing the molecular beam and detector axis, on the axis of rotation of the molecular beam source. Photofragments entering the triply differentially pumped detector region (9×10^{-11} Torr) were photoionized 15.2 cm from the interaction region using tunable synchrotron radiation. The characteristics of the light source are discussed in detail elsewhere, but include an intensity of 10^{16} photons/sec (quasi-continuous), an energy bandwidth of 2.2%, and a cross section in the probe region of 0.2×0.1 mm. The tunability of the light source allows for selective ionization of products and very low background counts. The photoionized products were mass selected by using a quadrupole mass filter and the ions were

counted with a Daly ion counter.¹²

Time-of-flight of the products were measured with a multichannel scalar (EG&G Ortec

Turbo MCS). The bin width for the MCS was fixed at 0.75 or 1 μsec for the measurements reported here. Timing sequences for the laser, pulsed valve, and the MCS were maintained by a digital delay generator (Stanford Research Systems, Inc. Model 535). Furan (99%) was obtained from Aldrich and used without further purification.

RESULTS

Signal was observed for m/e 25, 26, 24, 76, and 77. Due to lack of space, however, we will show data for only reactions (2) and (3). Photo-ion efficiency measurements for m/e 76 and 74 allowed us to identify these fragments as benzyne and 1,3,5-hexyne, respectively.

The measured time-of-flight (TOF) spectra for reaction (2) is shown in the Figs. 1 and 2. These figures also show the fit to the data using the forward convolution technique. The

Figure 2. TOF spectra for m/e 76 (C_6H_4) at 15° and 20° laboratory angles.

Figure 1. TOF spectra for m/e 26 (C_2H_2) at 15° and 30° laboratory angles.

resulting center-of-mass translational energy distributions $[P(E)]$ are shown in Fig. 3. For reaction (2), the fit for m/e 26 gave a $P(E)$ with an average translational energy, $\langle E_T \rangle$, of 12.09 kcal/mol. Using this distribution, we were unable to fit the slow part of the m/e 76 TOF. The slow fragments in turn have more internal energy. The data suggests that these fragments (i.e benzyne molecules with internal excitation) were undergoing secondary dissociation [i.e. reaction (3)]. In fact, from the difference between the m/e 26 and m/e 76 center of mass translational energy distributions, one can derive the ΔH_{rxn} for reaction (3). Figure 3 shows the difference for these distributions. Note the sharp cutoff in the resulting $P(E)$. This cutoff is the energetic threshold for the secondary dissociation of benzyne and from which we have derived $\Delta H_f = 669 \pm 14 \text{ kJ mol}^{-1}$ for 1,3,5-hexatriyne.

Figure 3. Center of mass translational energy distributions for reactions (2) and (3). Refer to text for further explanation.

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Photoelectron spectroscopy on a liquid water jet: an exploratory experiment

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INTRODUCTION

Surfaces of volatile liquid solutions can be studied in a high vacuum environment, only, when the surface area is sufficiently small in relation to the molecular mean free path in the vapor phase near the liquid surface. For neat liquid water at room temperature the vapor pressure corresponds to a mean free path in the order of ten micrometer. Exploiting this, we could recently demonstrate the feasibility of photo-electron spectroscopy experiments on a fast flowing jet of liquid water with only 6.3 micrometer diameter [1]. A high flow speed of approximately 120 m s^{-1} prevents excessive cooling of the liquid filament by the free molecular evaporation. It also prevents efficiently the buildup of photoelectric charges on the non-conducting liquid samples. Near the nozzle exit such jets have an unperturbed cylindrical section of two to three millimeter length which is used for the surface photoelectron studies. For the first experiments the 21.2 eV radiation of a HeI light source was employed and photoelectron spectra were recorded using a 10cm radius hemispherical electron energy analyzer. These initial studies show a gas-to-liquid energy shift of the electron binding energies by one to several Electron Volts reflecting the ion solvation enthalpy in chemical solutions. In ongoing PhD work these experiments could be extended to salt solutions and show the solvation energies of halogen anions in water and in further simple dielectric solvents. In a next step it appears desirable to study cations as well in order to clarify the role the orientation of the water solvent molecules in the hydration process. However, the above experiments with He I radiation are restricted to negative electrolyte ions with particularly low ionization energies. The He I studies suffer also from low photoelectron intensities due to the small liquid jet surface. For overcoming these major present restrictions the new third generation synchrotron source with tunable light and with intensities exceeding the focussed He lamp limit of $10^{12} \text{ photons mm}^{-2}$ appears to be ideally suited for proceeding with experiments on liquid water solutions.

WATER JET PHOTOELECTRON TEST MEASUREMENTS AT AN ALS BEAMLINE

For a first functional test of the liquid water jet operation at a synchrotron beam end station the beam line 9.02 appeared most suitable. [2] It is designed as a molecular beam machine and can handle the large amounts of gas evaporating from the volatile liquid jet. In addition, this vacuum apparatus contains a threshold photoelectron spectrometer and employs tunable VUV and XUV radiation, including the familiar He I energy region of our previous studies at liquid jets. For the test a $10 \text{ }\mu\text{m}$ liquid jet nozzle assembly [1] was installed near the detection center of the threshold photoelectron spectrometer [2]. The available pumping capacity of turbomolecular pumps and of two cryotraps in the liquid jet beam dump had to be extended by a third refrigerator cryopump in the photoionization region in order to reduce the pressure in the experimental chamber to safe limits for the XUV photon beamline vacuum. Eventually, in the

last phase of the test the gas load originating from the 6 μm water jet at 2 centigrade nozzle temperature was still very high at the XUV exit mirror chamber and was only removed temporarily by external liquid nitrogen cooling of the walls of this chamber. The liquid water jet did then run for several hours exposed to the synchrotron photon beam. A Threshold PhotoElectron spectrum for water was measured repeatedly during the last day of this one-week feasibility test. Due to high signal levels, data acquisition was rapid. The spectrum shown in Figure 1 between 11.5 and 21 eV with a step-size of 10 meV was recorded with only 1 second/point acquisition time.

PRESENT RESULTS AND CONCLUSIONS

Unfortunately, the evaluation of two spectra at slightly different photon beam positions showed later that we could not obtain significant difference spectra of the liquid surface and of the water vapor phase contributions in the measured overall spectrum in Fig.1. A further flaw in our here conducted experiment is a poor knowledge of the actual extent of spontaneously occurring electrokinetic charging on our pure water jet. Intentionally, we had not added here a small fraction of salt (10^{-3}m) which usually stabilizes the electrical potential of the liquid jet. This was omitted here in order to avoid salt contaminations in this beamline which are difficult to clean up afterwards. For an accurate energy calibration and for an estimate for the contribution of the

Figure 1. Threshold Photoelectron Spectrum (TPE) obtained on a thin fast flowing jet of liquid water with 6.3 μm diameter. The TPE signal for electrons within 7meV bandwidth is recorded as a function of the undulator radiation for photon energies from 11 eV to 21 eV. The comparison with available literature gas phase measurements of the photoionization spectrum (PI) for H₂O [3] and of a photoelectron energy spectrum (PES) obtained at the He I photon energy of 21.2 eV,[4] allow an assignment of the main spectrum structure to the vapor phase surrounding the liquid jet. In addition, the shoulder in the here measured TPE spectrum, visible at 12 eV to 12.6 eV, can be attributed to the liquid water photoelectron spectrum which is characterized by a 1.2 to 1.4 eV lower ionization threshold. [1]

water vapor phase we use, therefore, the literature photoionization spectrum of water (PI) [3] and a He I photoelectron spectrum (PES) [4], shown in the lower part of Fig. 1. Noteworthy, we could not find a wide range TPE spectrum for gaseous water, although elaborate high resolution TPE and PFI spectra for individual ion vibration states are available in narrow ranges near the ionization threshold (cf [5]).

The three principal peak structures of the PES spectrum at electron binding energies of 12.6 eV, at 14.7 eV and at 18.5 eV, similarly, appear in the photoion spectrum as steps in the ion intensity signal. By comparison of these gas peak signatures with the clearly visible peak structures in the present TPE spectrum we can deduce a (flow induced, electrokinetic) liquid jet charging to approximately 1 volt in the present experiment. The additional shoulder in the TPE spectrum of the liquid water jet, appearing in the range between 12 eV and 12.6 eV, thus, is to be interpreted as a photoelectron signal originating from the liquid water surface. In further detail, however, the different electric field distortions for the gas phase spectrum versus the photoelectron spectrum of the liquid jet surface here prevent a more substantial quantitative interpretation of the liquid spectrum contribution in this preliminary experiment.

In the basic technical and experimental goals of this first brief test for synchrotron radiation photoelectron spectroscopy at a volatile liquid water surface we feel we were fully successful: critical vacuum interface regions between the free liquid surface of the water jet and the ultrahigh vacuum regions of the synchrotron radiation light source have been located and can be optimized in subsequent experiments; in addition, this experiment confirmed that the intensity of 10^{11} photons s^{-1} of high resolution monochromator selected X-UV radiation with 0.1 mm focus spot size allows rapid photoelectron spectrum measurements on volatile micron size liquid jets. The poor liquid-to-gas signal ratio will be improved in future experiments by an appropriate matching of the viewing area of the photoelectron entrance slits to the narrow liquid jet surface width.

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Pulsed field ionization photoelectron photoion coincidence spectroscopy using two-bunch and 'dark-gap' multi-bunch synchrotron radiation at the Advanced Light Source

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INTRODUCTION

Recently we have developed a scheme for measuring pulsed field ionization (PFI) photoelectron spectra (PFI-PE) of various molecules using two-bunch and multi-bunch synchrotron radiation at the Chemical Dynamics Beamline at the Advanced Light Source. Such detection schemes for PEs are far superior to conventional threshold photo-electron (TPE) measurements in terms of achievable resolution. Using our electron time-of-flight spectrometer, resolutions down to about 1.0 cm^{-1} have been achieved which is roughly 8-10 times better than that achieved in similar TPE measurements.¹ A natural progression from PE measurements is PEPICO spectroscopy where parent and fragment ions of ionized species are collected in coincidence with energy selected electrons, producing mass analyzed spectra. The internal energy of the ions can thus be selected and fragmentation patterns can be determined state selectively. Plots of fractional abundance of all the product channels, called breakdown diagrams, can often be used to determine very precise onsets for ionic dissociations from which accurate heats of formation of fragment species can be derived. The accuracy of such diagrams is limited by the resolution in the PE measurement. The prospect of performing PFI-PEPICO measurements with resolutions far greater than TPE techniques is therefore an attractive one. Another advantage of examining the mass of fragments formed in PFI-PE spectroscopy is that contaminants present in samples can effectively be eliminated from the scans. One good example of an experiment where contaminants would be problematic is the study of radicals following photodissociation. Here PFI-photoelectrons from the parent species may complicate spectra and mass analysis would therefore alleviate these complications. PFI-PEPICO may also prove to be a useful technique for studying ion molecule chemistry at a rotational level. By performing PFI-PEPICO with two samples present in the reaction region at one time and determining the masses of the observed ions, the relative rates of reaction as a function of energy corresponding to the different excited levels of the photoexcited cation can be evaluated.

Here we present results on the PFI-PEPICO of O_2 performed using two-bunch and multi-bunch synchrotron radiation around its dissociation threshold and demonstrate resolutions of the order of 1 meV.

EXPERIMENT

Electrons and ions were extracted in opposite directions from the interaction region and electron discrimination was obtained by timing. Coincidence spectra were recorded using a multi-channel scalar with the electrons providing the start and the ions the stop. In the two-bunch experiments performed here, a DC field of between 0 and 2 V cm⁻¹ was maintained across the two plates that straddle the interaction region with a 6.95 V cm⁻¹ field pulse applied for 160 ns approximately 100 ns after each light pulse reached the interaction region. Since this high field PFI pulse was on for a good length of time (roughly half the total time in this case), it caused very efficient ion extraction. Collection efficiencies measured for the Ar⁺ 2P_{3/2} were 7.3% for the electron and 19.3% for the ions measured with zero volts DC across the interaction region. We performed PFI-PEPICO using multi-bunch synchrotron radiation by applying a 200 ns, 6.95 V cm⁻¹ PFI/extraction pulse across the interaction region ~ 10 ns after the last light pulse prior to a 144 ns dark gap. A DC field of 0.20 V cm⁻¹ was applied across the interaction region to clear the hot electrons prior to the PFI-pulse. This small field is necessary to sweep the hot electrons away and to ensure that the PFI-PE spectra are clean of autoionizing and direct ionization structures. Pulses of length greater than the dark gap are possible since the overlap is far removed (~130ns) from the PFI region and electrons from the first light bunches will therefore not interfere with our signal. Of course by overlapping the light, we will field ionize and lose any Rydberg states formed in the first set of bunches in the multi-bunch, but an overlap of around ~50 ns was found to have little effect on the PFI-PE signal levels. This indicates that the lifetime of the Rydberg states in this first region are too short to be detected in the present experimental arrangement. Therefore an overlapping pulse of 200 ns duration was used to aid ion extraction.

RESULTS

PFI-PEPICO was performed on O₂ using both 2-bunch and multi-bunch synchrotron radiation. In the two-bunch mode we performed PFI-PEPICO scans on the O₂⁺ b state from v⁺ = 5 to 7 using a photon energy corresponding to the maximum intensity of the peaks observed in the PFI-PE spectra. The PFI-PEPICO TOF spectra recorded with a bin-width of 5 ns can be seen in Figure 1.

Figure 1. PFI-PEPICO TOF spectra for O₂⁺ at energies corresponding to the b state v⁺ = 5 to 7.

The dissociation limit is believed to occur at $v^+ = 4$, $N^+ = 9$.³ The width of the peaks seen in Figure 1 reflect the kinetic energy released in dissociation which increases as the photon energy is increased. In our molecular beam sample we estimate that our rotational temperature is $\sim 10\text{K}$ from a Buckingham-Orr-Sichel² (BOS) model of the $v^+ = 4$ branch performed on O_2 during multi-bunch. This temperature is too cold to allow population of the $N^+ = 9$ level, so the only way that we can observe O^+ at this vibration is from the effusive part of the beam.

Determination of the breakdown diagram over the $v^+ = 4$ band was therefore performed using an effusive sample and the data were taken in multi-bunch mode. PFI-PEPICO TOF spectra were taken in the energy region 18.713 to 18.726 eV and the areas under the O_2^+ and O^+ peaks were determined following background subtraction. The resulting breakdown diagram can be seen in Figure 2 where the filled circular symbols represent O^+ and the filled squares O_2^+ . To obtain an accurate measure of the AE of O^+ ,

Figure 2. Branching ratio of O_2^+/O^+ (squares/circles) from O_2 at varying photon energies. Simulated (adjusted BOS model, see text) and experimental PFI-PE spectra are also shown. From the simulation breakdown diagrams are calculated assuming the dissociation limit occurs at $N^+ > 5, 7$ and 9 and data are compared. (solid lines O^+ , dashed O_2^+)

the PFI-PE spectrum was recorded under the same experimental conditions with $30\ \mu\text{m}$ slits resulting in a resolution of $\sim 1\text{meV}$ and a BOS simulation was performed on this spectrum. $B_{v^+} = 1.175\text{ cm}^{-1}$ and $\text{IE}_{v^+} = 15.7224\text{ eV}$ were used in the simulation and BOS coefficients C_0 and C_2 were set at 0.3 and 0.7 , respectively. The fit was relatively poor in the region 18.717 to 18.722 eV and it was necessary to independently adjust the bands resulting in $N^+ = 7, 9, 11, 13$ and 15 multiplying each by $0.34, 1.50, 1.36, 1.21$ and 1.41 respectively. When this was performed, an excellent fit to the experimental data was obtained.

The reason for the poor fit using the BOS model we believe is caused by a lifetime effect that we have also observed in other molecules such as CH_4 and C_2H_2 . Basically, the lifetime of O^+ is greater than O_2^+ at the dissociation limit as it is less prone to autoionization. An increase in the PFI-PE intensity is therefore observed as the

dissociation threshold is passed. A relative increase in the $N^+ > 7$ levels can therefore be explained. However for the best fit, the levels resulting in $N^+ = 7$ had to be decreased. This may indicate that the lifetime of the O_2^+ is decreased for some reason at this level or that some type of low- n Rydberg interaction is occurring. Once a good fit was obtained, then the three separate breakdown diagrams were calculated assuming that $N^+ > 5$, $N^+ > 7$ and $N^+ > 9$ rotational levels led to dissociation. Each of these simulated breakdown diagrams are shown in Figure 2 along with a duplicated set of experimental data. The dashed line represents O_2^+ and the solid line O^+ . As can be seen, the $N^+ > 9$ simulation gives a poor fit in the region 18.718 to 18.721 eV, $N^+ > 5$ gives a poor fit in the region 18.712 to 18.716 eV with the $N^+ > 7$ simulation giving the best overall fit. This therefore agrees very well with previous findings on the dissociation limit³ and demonstrates that PFI-PEPICO can now be performed with resolutions down to about 1 meV.

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Rotationally Resolved Pulsed Field Ionization Photoelectron Spectroscopy

Study of $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$ and $\text{O}_2^+(\text{X}^2\Pi_g, v^+=0-38)$

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INTRODUCTION

Using third generation multi-bunch undulator synchrotron radiation at the Chemical Dynamics Beamline of ALS, we have obtained rotationally resolved pulsed field ionization photoelectron (PFI-PE) spectra of $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$ and $\text{O}_2^+(\text{X}^2\Pi_g, v^+=0-38)$ in the vacuum ultraviolet region. For the first time, higher energy levels [$\text{NO}^+(\text{X}^1\Sigma^+, v^+>6)$, $\text{CO}^+(\text{X}^1\Sigma^+, v^+>1)$, and $\text{O}_2^+(\text{X}^2\Pi_g, v^+>24)$] were rotationally resolved. This allowed the accurate determination of high-order spectroscopic constants for these molecular states. Such PFI-PE experiments make possible the detailed investigation of molecular photoionization dynamics and chemical reaction mechanisms near the dissociation limit.

EXPERIMENT

The Chemical Dynamics Beamline consists of a 10 cm period undulator, a gas harmonic filter, a 6.65 m off-plane Eagle monochromator, and a photoion-photoelectron apparatus, all of which has been discussed in detail previously.^{1,2} In the present experiment, Ar, Ne, and He were used in the harmonic gas filter to suppress higher undulator harmonics with photon energies greater than 15.76, 21.56 and 24.59 eV, respectively. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by either a 2400 lines/mm (dispersion = 0.64 Å/mm) or a 4800 lines/mm grating (dispersion = 0.32 Å/mm) before entering the experimental apparatus.

The ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns. Each electron bucket emits a light pulse of 50 ps with a time separation of 2 ns between successive bunches. In each storage ring periods, a dark gap (16-80 ns) consisting of 8-40 consecutive unfilled buckets exists for the ejection of cations from the orbit.

Figure 1. PFI-PE spectra for $\text{NO}^+(\text{X}^1\Sigma^+, v^+ = 16-32)$. The branch heads for rotational branches $\Delta J = \pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2$, and $\pm 9/2$ of the $\text{NO}^+(\text{X}^2\Sigma^+, v^+=0-32)$ PFI-PE bands are linked by dotted lines.

The NO and CO samples were introduced as effusive beams through a metal orifice at room temperature, while a continuous molecular beam of pure O₂ was produced by supersonic expansion through a stainless steel nozzle at a stagnation pressure of 760 Torr and a nozzle temperature of 298 K. The molecular beam was skimmed by a conical skimmer before intersecting the monochromatized VUV light beam. The rotational temperatures used in the simulations of the PFI-PE spectra were 298 K (NO and CO), 220 K (O₂), and 20 K (O₂). The procedures for performing PFI-PE measurements using the photoion-photoelectron apparatus have been described in detail previously.²

Figure 2. Comparison of the experimental (●) and simulated (○) PFI-PE spectra for CO⁺(X²Σ⁺, v⁺=9). Positions for individual rotational transitions are marked in the figure according to the level of origin (N'') for each observed rotational band (N, O, P, Q, R, S, & T).

The absolute photon energy scale was calibrated using the Xe⁺(²P_{3/2}), Kr⁺(²P_{3/2}), Ar⁺(²P_{3/2}), and Ne⁺(²P_{3/2}) PFI-PE bands recorded under the same experimental conditions before and after each scan. This calibration procedure assumes that the Stark shift for ionization thresholds of target gases and the rare gases are identical. On the basis of previous experiments, the accuracy of the energy calibration is ± 0.5 meV.

RESULTS

A. NO⁺(X¹Σ⁺, v⁺=0-32)

The main point of note for the NO⁺ spectra was that the maximum ΔJ values and intensities for high ΔJ rotational branches are found to generally increase as v⁺ increases (see Figure 1).³ This observation is attributed to an increase in the inelastic cross-section for collisions between the outgoing photoelectron and the non-spherical molecular ion core as bond distance for NO⁺ is increased. This provides strong support for the electron-molecular-ion-core scattering model for angular momentum and energy exchanges in the threshold photoionization of NO.

B. CO⁺(X²Σ⁺, v⁺=0-42)

We have obtained rotationally resolved pulsed field ionization photoelectron (PFI-PE) spectra of CO in the energy range of 13.98-21.92 eV, covering the ionization transitions CO⁺(X²Σ⁺, v⁺ = 0-42, N') ← CO(X¹Σ⁺, v'' = 0, N'').⁴ The PFI-PE bands for CO⁺(X²Σ⁺, v⁺ = 8-42) obtained here represent the first rotationally resolved spectroscopic data for these states. The high-resolution features observed in the PFI-PE spectra allow the identification of vibrational bands for the CO⁺(X²Σ⁺, v⁺=10, 13, 14, 15, 18, 21, 25, and 30) states, which were not observed previously due to overlap with prominent vibrational bands of the CO⁺(A²Π_{3/2,1/2}, B²Σ⁺) states. The PFI-PE bands for CO⁺(X²Σ⁺, v⁺ = 0-42) were simulated using the Buckingham-Orr-Sichel (BOS) model⁵ derived for prediction of rotational line strengths in the single-photon ionization of diatomic molecules. Generally good agreement is observed between the experimental and simulated spectra, indicating that the one-electron BOS model adequately describes the single-photon

threshold ionization of CO. This simulation provides accurate molecular constants for $\text{CO}^+(\text{X}^2\Sigma^+, v^+ = 0-42)$, including ionization energies, vibrational constants ($\omega_e^+ = 2218.8 \pm 3.5 \text{ cm}^{-1}$, $\omega_e^+\chi_e^+ = 16.20 \pm 0.32 \text{ cm}^{-1}$, $\omega_e^+\gamma_e^+ = 0.074 \pm 0.011 \text{ cm}^{-1}$, and $\omega_e^+z_e^+ = -0.00183 \pm 0.00013 \text{ cm}^{-1}$), and rotational constants ($B_e^+ = 1.9755 \pm 0.056 \text{ cm}^{-1}$, $\alpha_e^+ = 0.0184 \pm 0.0011 \text{ cm}^{-1}$, $\gamma_e^+ = -7.6 \times 10^{-6} \pm 61 \times 10^{-6} \text{ cm}^{-1}$, $z_e^+ = -2.8 \times 10^{-6} \pm 0.9 \times 10^{-6} \text{ cm}^{-1}$). Enhancement of $\Delta N < 0$ branches was observed for each vibrational level where rotational structure was clearly resolved. The $\Delta N < 0$ enhancements were attributed to field-induced rotational autoionization. Significant local enhancements due to near-resonance autoionization were observed for $\text{CO}^+(\text{X}^2\Sigma^+, v^+ = 5-9)$, the region of which has a high density of autoionizing interloper Rydberg states (see Figure 2). The observation of a long vibrational progression in the Franck-Condon gap region where no strong autoionization states are present suggests that high- n Rydberg states converging to these highly excited vibrational levels are populated via excitation to a dissociative state. The relatively constant PFI-PE intensities found for these highly vibrationally excited levels are also consistent with the direct excitation model.

C. $\text{O}_2^+(\text{X}^2\Pi_g, v^+ = 0-38)$

It is well known that extensive overlaps exist between vibrational bands for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g})$ and $\text{O}_2^+(\text{a}^4\Pi_u, v^+)$ [and/or $\text{O}_2^+(\text{A}^2\Pi_u)$] at energies above 16.4 eV. However, we were able to make unambiguous identifications of individual vibrational bands for these states by spectral simulations of the PFI-PE bands obtained at 20 and 220 K.⁶ Figure 3 shows the cold PFI-PE spectrum (20K) for O_2^+ in the region of 17.01~17.06 eV where the most serious overlap involving vibrational bands of the $\text{O}_2^+(\text{X}^2\Pi_g, \text{a}^4\Pi_u, \text{and A}^2\Pi_u)$ states occurs. An excellent simulation was obtained [middle curve of Fig. 2(b)] which also constitutes a very minor contribution from $\text{O}_2^+(\text{A}^2\Pi_u, v^+ = 0)$.

As was observed in previous studies, we found that C_1 and C_2 were the dominant BOS coefficients for most vibrational bands, indicating that the p - and d -partial waves of the ground electron wave function are the major contributors in the ionizing transitions. Based on the simulations, we were able to obtain accurate vibrational, rotational, and spin-orbit coupling constants. Accurate ionization energies for states up to $v^+ = 38$ were also determined. This covers 90% of the potential well depth.

Figure 3. Deconvoluted (or simulated) PFI-PE band for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+ = 28)$. The rotational transitions for the $\text{O}_2^+(\text{X}^2\Pi_{1/2g})$ and $\text{O}_2^+(\text{a}^4\Pi_{3/2g})$ are marked using downward pointing and upward pointing sticks, respectively. (b) The upper spectrum is the experimental PFI-PE spectrum for O_2 in the region of 17.01-17.06 eV obtained using an O_2 sample with a rotational temperature of 20 K; The deconvoluted (or simulated) PFI-PE band for $\text{O}_2^+(\text{a}^4\Pi_u, v^+ = 8)$ is shown as the bottom spectra; and the middle spectrum represents the sum of the deconvoluted (simulated) bands for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+ = 28)$ and $\text{O}_2^+(\text{a}^4\Pi_u, v^+ = 8)$.

To interpret local enhancements observed in the PFI-PE spectra for $v^+ < 14$, we concluded that these rotational lines are perturbed by nearby autoionizing Rydberg states. For the $v^+ \geq 14$ bands, we believe that direct excitation to a neutral dissociative state and subsequent coupling to high- n Rydberg states which were then pulsed field ionized would be a possible model for the photoionization mechanism.

SUMMARY

Using the broadly tunable high-resolution undulator synchrotron source at the Chemical Dynamics Beamline of the Advanced Light Source, we have obtained rotationally resolved photoelectron bands for $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$, and $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+=0-38)$. Highly accurate spectroscopic constants for these molecular states were obtained from the simulation of the experimental data using the BOS model. Possible photoionization mechanisms were discussed in detail. With the improvements made to our current instrumentation, obtaining high-quality PFI-PE spectra has become a routine yet exciting process.

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**The Dynamics of Hydrogen Abstraction Reactions:
Crossed-beam reaction $\text{Cl} + n\text{-C}_5\text{H}_{12} \rightarrow \text{C}_5\text{H}_{11} + \text{HCl}$**

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Metathesis reactions, in which a single atom is transferred from a stable molecule to an atom or radical, are the only truly bimolecular (i.e. bimolecular in both directions) gas phase reactions¹. Those involving hydrogen atom transfer arguably represent the most important subclass of this vast body of reactions, particularly for combustion dynamics. Free radical abstraction of hydrogen atoms in saturated hydrocarbons, for example, are reactions of great importance in combustion, and the differing propensities for reaction of primary, secondary, or tertiary H atoms, as well as the different dynamics underlying these pathways, are important to a detailed understanding of combustion chemistry. These processes have come under increasing scrutiny in recent years as experimental innovations have allowed more direct probing of the dynamics.

We have used reaction of Cl atoms with saturated hydrocarbons as a step toward a detailed investigation of these metathesis reactions. Our initial studies focused on the slightly exoergic reactions of Cl with propane (C_3H_8), with probe of the C_3H_7 product using synchrotron radiation². The use of tunable undulator radiation, offering a unique combination of universality and selectivity in product detection, enables us to probe the doubly differential cross sections for the hydrocarbon radical fragment. The propane studies suggested different dynamics for the forward and backward scattered products. The former were ascribed to facile abstraction of the secondary H atoms, while the latter were believed to result from more strongly coupled collisions involving the terminal H atoms. Here we extend these studies to reaction of Cl with n-pentane³, in an effort to examine the underlying trends in the reaction dynamics, in particular allowing us to probe the role of the extended carbon skeleton in these reactions.

These experiments were performed using a rotatable source molecular beam apparatus, Endstation 1, on the Chemical Dynamics Beamline⁴ at the Advanced Light Source at Lawrence Berkeley National Laboratory. The apparatus has been described in detail elsewhere⁵. Briefly, a molecular beam of the hydrocarbon reagent, n-pentane, crosses a chlorine atom beam and the reactive scattering products are detected by a quadrupole mass spectrometer. The two molecular beam sources are fixed at 90° and the whole source chamber is rotatable to allow data collection at angles of -20° to 110° between the pentane beam and detector. The significant feature in the experimental setup is the use of the VUV undulator radiation for photoionization probe of the neutral scattering products, in place of the conventional electron impact ionizer. Detection of the scattered C_5H_{11} reaction products was accomplished using 9.5 eV photoionization radiation with a MgF_2 filter that has transmission cutoff at about 11 eV, thus removing any residual radiation above that energy. The ionization potential (IP) of n-pentane is 10.35 eV, while for the pentyl radical it is 7.7 eV. By using a photoionization energy of 9.5 eV there is almost no background from dissociative ionization of the C_5H_{12} reactant. A multichannel scaler triggered by the chopping wheel was used to record TOF at various laboratory scattering angles, defined with respect to the pentane beam. The center-of-mass translational energy and angular distributions were obtained by the forward convolution technique.

The reaction of chlorine atoms with n-pentane proceeds via either primary or secondary H atom abstraction:

Reactions 2 and 3 will be considered together since they both represent secondary H atom abstraction and are energetically indistinguishable.

Figure 1. Lab angular distribution (top) and Newton diagram for the title reaction.

The Newton diagram for the reaction is shown in Fig. 1, along with the measured laboratory angular distribution. The maximum available energy for the 2-pentyl radical product from this slightly exothermic reaction gives the recoil limit circle indicated. Also shown in conjunction with the measured angular distribution is the simulated distribution resulting from the best fit to all of the data. The inherently coupled nature of the angular and energy distributions can be inferred directly from inspection of the angular distribution: the forward scattering extends beyond the beam in the forward direction, nearly to the recoil limit. The backscattered distribution, in contrast, drops sharply at a lab angle of 60° , well before the translational energy limit. This is confirmed by the time-of-flight distributions (not shown). These distributions serve to constrain the simulations from which the translational energy and angular distributions are obtained.

Although it was impossible to obtain a satisfactory fit to the data with a single uncoupled translational energy $P(E)$ and angular distribution $T(\Theta)$, excellent fits were obtained simply by decomposing the center-of-mass distributions into two components, one forward and the other backward-scattered. The average energy release obtained for channel 1 (forward scattered) is $\langle E \rangle_1 = 20.4$ kcal/mol, which is 92% of the available energy (E_{avail}), while for channel 2 (back-scattered) it is $\langle E \rangle_2 = 7.7$ kcal/mol, which is 35% of E_{avail} . The branching fractions are 58% for channel 1 and 32% for channel 2. As in any forward convolution simulation of crossed-molecular beam results, the fit obtained is not unique. Nevertheless, the velocity-flux contour map we obtain, shown in Fig. 2, does faithfully reproduce the measured distributions. However, for the forward-scattered products in particular the decomposition into two components is somewhat arbitrary, and driven by the fit to the backscattered distribution.

The dynamics for the forward-scattered channel obtained from the fit are largely consistent with previous studies of Cl-hydrocarbon reaction dynamics. The $P(E)$ peaks at the maximum energy available for formation of the isoenergetic 2-pentyl (butyl-1-methyl) or 3-pentyl (propyl-1-ethyl) radicals, with an average of only 1.8 kcal/mole remaining in rotation and vibration of the products. The bulk of the forward scattered distribution appears at translational energies exceeding the limit for formation of the 1-pentyl radical (the inner circle in Fig. 2). Abstraction of primary H atoms is thus ruled out for channel 1; however, there is little here to suggest any different propensities for abstraction of the hydrogen atoms from the 2- or 3- carbons.

The results for this channel are reminiscent of those reported for the Cl-cyclohexane reaction, and identified by others in propane and even for vibrationally excited methane. That is, the products are formed with very little internal energy. This has been attributed this to a collinear transition state; yet the correlation between forward scattering and a collinear transition state is problematic. Zare and coworkers⁶ considered several possible mechanisms that could reconcile these, but finally suggested an alternative interpretation of the dynamics. They argued that if the reaction is not in the impulsive limit, then a cold product rotational distribution need not imply a collinear transition state. Accordingly, we suggest the coincident observation of a cold rotational distribution with forward scattering argues for a fairly loose transition state.

The dynamics for channel 2, the backscattered distribution, diverge dramatically from previous work on H abstraction dynamics in hydrocarbons, even differing significantly from our own studies of the analogous Cl-propane reaction. The $P(E)$ for channel 2 peaks at 6.8 kcal/mol, with an average release of 7.7 kcal/mol, a fractional energy release of only 35%. This may be compared to results for Cl-propane, for which the fractional energy release for the backscattered component ranged from 52% at 11.5 kcal/mol collision energy to 48% at the highest 31 kcal/mol collision energy. This means that an average of 15 kcal/mol remains in internal degrees of freedom of the products. State-resolved studies for propane have shown only a small yield of vibrationally excited HCl product, so it is unlikely that this accounts for much of the energy. Furthermore, we anticipate little difference between the HCl energy content from propane or pentane, since the energetics are virtually the same for both reactants. The likely repository of the bulk of this energy is thus in the hydrocarbon fragment; the question is whether it is in rotation or vibration. Plausible reasons for greater vibrational excitation in the case of pentane vs. propane are readily apparent. There are many more vibrational modes for n-pentane (45 vs. 27), and perhaps more significantly, many more involving the low-frequency C-C-C bends. For these modes, with vibrational frequencies on the order of 800 cm^{-1} , the half-period is roughly 20 fs. We can compare this to the collision time under the conditions of the experiment: for an effective interaction region of 0.5 X at 2400 m/s we estimate a collision time of 21 fs, a remarkable match to the vibrational period. The combination of the higher density of states and the excellent match between the collision time and the bending mode vibrational period greatly favors coupling between the collision energy and the internal modes of the hydrocarbon. This suggests that in pentane we are seeing the direct participation of the extended carbon backbone in the reaction.

A final question concerns the nature of the two different channels. In our previous work on the propane reaction, we argued for the association of the forward-scattered distribution with the abstraction of secondary H atoms, while the backscattered product was associated with primary H atoms. It is even clearer in the pentane case, since the bulk of the forward scattered products are formed at translational energies well exceeding that possible for production of the 1-pentyl radicals, that the forward scattered products are indeed the result of secondary H atom abstraction. The question remains for the backscattered products: Are they preferentially associated with primary H abstraction? Although attempts were made to discriminate between these two radical isomers based upon their ionization potentials, we found no significant differences in the angular distributions as a function of probe photon energy. However, the vastly different internal energy distributions for the forward and backward scattered products may account for the absence of any significant differences, and would make interpretation of such an effect problematic in any case.

Although there is no direct evidence indicating a connection between the predominantly backscattered 'channel 2' and the primary abstraction channel, several lines of evidence point this direction. Firstly, the maximum energy release apparent in the contour map in Fig. 3, extends well below the limit of the available energy for production of the higher energy isomer. This distribution came directly from the best fit to the laboratory data and was in no way enforced. Secondly, there is the total branching between forward and backward scattered products. For the propane reaction, the fraction scattered forward of 90° was very close to 50% of the total. Assuming simply a limiting case association of forward scattering with secondary H abstraction we find, effectively, three times higher reactivity of the secondary vs. primary H atoms. For pentane, then, we expect the fraction forward scattered to increase from $1/2$ to $3/4$, since there are three times the number of secondary

Figure 2. Contour map for pentyl radical derived from experiment. Forward scattering is to the left of the figure.

H atoms, if this limiting assumption is a good one. Indeed, if we look only at the fraction of the total scattered in the forward direction, in the same way we considered the propane case, we find a value of 74%, a remarkable agreement. If we compare the fraction of the total scattered into 'channel 1', then the value is 64%. If we make the association between channel 1 and secondary H abstraction, and channel 2 and primary H abstraction, this implies roughly a 1.8-fold higher reactivity of the secondary H atoms. However, we cannot directly compare this to the propane results since the distributions were decomposed differently.

These translational energy distributions argue for a bit of caution on the part of those employing state-resolved laser methods relying on measurements of one of the fragments to extract the speed and angular distributions for the reaction. These studies are generally blind to internal energy in the undetected fragment. Moreover, the reconstruction of the product distributions require some assumptions about the unmeasured fragment. If these assumptions are in error, then the derived distributions are inaccurate. Usually the assumption is made that the undetected fragment is internally cold, although in at least one case this issue was considered explicitly. As we have seen, for the forward-scattered products in the pentane and propane case, this is a fairly accurate assumption. For the backscattered distributions, however, this is grossly incorrect. The implications of this for the inferred distributions are not clear, but these issues should be considered for any quantitative analysis of the photoloc-type experiments.

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UV Photodissociation Of Furan Probed by Tunable Synchrotron Radiation

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INTRODUCTION

Unimolecular dissociation pathways of cyclic molecules play an important role in the combustion of organic matter.¹ It is believed that chemical pathways leading to the destruction and formation of cyclic molecules determine the fate of combustion by-products such as polycyclic aromatic hydrocarbons (PAHs) and in soot formation.^{1,2} Unimolecular dissociation (or thermal decomposition) of molecules in combustion processes occurs as a result of the elevated temperatures, and dissociation proceeds mostly on the ground state potential energy surface (PES). Pyrolytic studies of cyclic compounds has yielded useful information on the thermal decomposition of many cyclic molecules.³⁻⁷ These studies are, however, complicated by the presence of multiple secondary reactions and rigorous computer modeling must be done to determine the primary processes.³ Photochemical studies in molecular beams, on the other hand, can provide unambiguous information on the primary processes following unimolecular dissociation.

In this abstract, we will present results for the ultraviolet photodissociation of furan obtained on the Chemical Dynamics Beamline at the Advanced Light Source. The unique combination of photofragment translational spectroscopy with intense, tunable undulator radiation available on the Beamline allows for detailed investigation of complex polyatomic dissociation dynamics, as has been shown for a number of systems⁸.

Ultraviolet excitation of polyatomic molecules is often rapidly followed by internal conversion to the ground state potential surface. When the corresponding dynamics are clearly distinct from those involving excited electronic states, one may study ground state dissociation dynamics under collision free conditions and at well-defined energies. Furthermore, excited state dissociation dynamics can also be studied to yield information about the nature of the excited state PES's.

Figure 1. A schematic representation of the photodissociation of furan and the observed primary dissociation pathways.

SUMMARY OF RESULTS

The radical channel

The strongest signal was found for the radical channel. Figure 2 shows the measured time-of-flight (TOF) spectra for HCO and C_3H_3 fragments. Although this channel was not observed in the pyrolytic studies of furan, it was proposed as a key reaction for producing free radicals. Our results clearly show the presence of this primary process. Furthermore, this channel appears to be the major one since the signal is the strongest.

In these measurements we utilized one of the advantages of tunable VUV radiation to photo-ionize the products. Photo-ion

Figure 3. PIE spectra for m/e 29 and 39. These fragments have been identified as HCO and propargyl radical, respectively. The arrows indicate the known ionization onsets for these free radicals.

Measured TOF spectra for these two masses at 20° and 50° are shown in Fig. 4. Figure 5 shows the PIE spectrum for m/e 40. The identity of m/e 40 product is more challenging to establish since the two likely isomers of C_3H_4 – propyne and allene – have similar ionization potentials, 10.36 eV and 9.69 eV, respectively. There appear to be two ionization onsets in the photoion yield

Figure 2. TOF spectra for m/e 29 (HCO) and m/e 39 (C_3H_3) fragments

efficiency (PIE) spectra were measured for m/e 29 and 39. From the PIE spectra, we have established the identity of m/e 39 as the propargyl radical. Figure 3 shows the PIE spectra for m/e 29 and m/e 39.

The angular distribution of the products of this channel was measured and was found to be anisotropic with a β parameter of -0.2. A negative β indicates that the transition dipole moment has a component perpendicular to the dissociation coordinate. Also, a nonzero β indicates that dissociation occurs on a rapid time scale relative to the rotational period.

The molecular channels: $CO + C_3H_4$

For m/e 28, CO, the momentum-matched partner is m/e 40, C_3H_4 . Both of these fragments show large contributions from the dominant radical channel shown above.

spectrum in Fig. 5, one at 8.75 eV and another at 10.25 eV. The ionization onset at 8.75 eV is identical to that shown above for m/e 39, the propargyl radical. The signal for m/e 39 is about 100 times larger than that for m/e 40, so that a small contribution resulting from mass leakage in the quadrupole from m/e 39 to the m/e 40 signal is responsible for the observation of two onsets. By scaling the m/e 39 contribution at the obvious break that appears in both spectra, we can subtract this contribution to obtain the PIE spectrum for the m/e 40 contribution alone, shown by the dashed line in Fig. 5.

Figure 5. PIE spectra for m/e 40. A large contribution from m/e 39 was observed for this mass and after subtraction, a distinct ionization onset is realized. The m/e 40 fragment has been identified at propyne.

Figure 4. TOF spectra for m/e 28 (CO) and 40 (C_3H_4) at laboratory angles of 20° and 50° .

The corrected signal for m/e 40 shows an onset of 9.5 eV. This is near the threshold for allene; however, as these are largely vibrationally excited products, we anticipate a significant red-shift in the ionization onset. As a result, it is most likely due to propyne, consistent with the findings of Liu, *et al.* whose calculations indicated that ground state unimolecular dissociation of furan to CO + propyne followed a path 23 kcal/mol lower in energy than the path leading to CO + allene.¹⁰ The angular measurements for this fragment yielded an isotropic distribution, thereby indicating that the process occurs on a *slow* time scale relative to the period of molecular rotation. The experimental evidence suggests that this reaction occurs on the ground state potential energy surface following internal conversion.

C_2H_2 + ketene

The TOF spectra for the momentum-matched fragments m/e 26 (acetylene, C_2H_2) and m/e 42 (ketene, H_2CCO) were recorded as for the two channels mentioned above. Due to lack of space, the data for this channel is not shown here. A potential energy barrier of 25 kcal/mol was found for this channel and is in reasonable agreement with the calculated value of 35 kcal/mol¹⁰ and the experimentally derived value of 33 kcal/mol⁷ for the ground state unimolecular dissociation of furan to acetylene and ketene. This channel is believed to occur on the ground state PES following internal conversion and a larger fraction of the available energy is released into the translational degrees of freedom of the products.

CONCLUSIONS

We have studied the dissociation dynamics of furan at 193 nm using photofragment translational spectroscopy with tunable VUV probe provided by intense synchrotron radiation. Three product channels are observed. Two of these result in closed shell molecular products and occur on the

ground electronic surface following internal conversion. The results for these channels are consistent with recent theoretical studies and shock-tube results. The third channel gives rise to radical products and is shown to occur as a direct process on an electronically excited potential energy surface.

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Beamline 9.3.1 Abstracts

An End Station for Intermediate X-Ray Absorption Spectroscopy of Biological Samples in a Controlled Environment

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X-ray absorption spectroscopy (XAS) is an element-specific technique with widespread applications in structural biology. Most notably, it has been used in the hard x-ray region (> 6 keV) to probe metal centers in metalloproteins. In contrast, investigations of low-Z atoms (e.g., S, Cl, Ca) within proteins and other biological samples have been scarce. Such experiments require the use of a cryostat with vacuum insulation since low temperatures are required for protein samples to minimize radiation damage and for data collection in the EXAFS region. Existing instrumentation does not allow substantial transmittance of intermediate x-rays through the windows to reach the sample which inhibits adequate flux of fluorescent x-rays to reach the detector.

A new end station on Beamline 9.3.1 at the ALS has been designed and built for such XAS experiments in the 2-6 keV region for solid, liquid or solution samples under selectable temperature and pressure. The sample chamber contains provisions for a liquid helium cryostat such that samples may be cooled to any temperature down to 10 K and maintained at 1 atm pressure. The sample and exchange gas are housed within an inner sample chamber with minimally attenuating windows that are able to withstand a 1 atm pressure differential (0.25 mil Mylar/Kapton or 38 mm Be). The sample surface is positioned at a selectable angle (e.g., 45°) to the incident beam, and the fluorescent signal is collected by a Si photodiode housed within the inner sample chamber. The internal detector is situated 1 cm away from the sample which allows collection of a large solid angle of fluorescent x-rays. There are also provisions for an externally mounted Ge energy-resolving detector. A retractable Si

Figure 1. Beamline 9.3.1 end station.

photodiode downstream from the internal sample chamber may be used for transmittance experiments or sample positioning.

Upstream from the sample chamber is a smaller chamber which houses a grid for monitoring incident beam intensity and standard samples for energy calibration. An ion chamber enclosed by 2000 Å parylene-N windows may also be used for incident flux/energy calibration.

The new instrumentation is ready for beam immediately and will provide a general purpose XAS end station for samples in a controlled environment. Initially it will be suited for protein samples, but modifications are being planned for applications in material science.

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Multi-Ion Coincidence Measurements of Methyl Chloride Following Photofragmentation Near the Chlorine *K*-Edge

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INTRODUCTION

Multi-ion coincidence techniques, often referred to as charge-separation mass spectroscopy (CSMS)[1], provide a powerful experimental tool for the determination of the dissociation dynamics of photoexcited molecules. Detection of several positively charged fragments from a single dissociation event allows differentiation among specific processes when a multitude of decay paths are possible, simplifying characterization of the photofragmentation mechanism. Synchrotron radiation (SR) is an excellent excitation source for these types of measurements because it is readily made both tunable and monochromatic. Using x-ray SR, it is possible to excite a core electron localized around a specific atom in a molecule, providing a chemical-site specific probe. By localizing the initially excited state, it is possible to determine if site-selective-fragmentation effects, where the fragmentation pathways change as a result of excitation of electrons from chemically different sites, are present [2]. Both extremes for site selectivity exist, where either the decay pathway is dependent on the location of the initial excitation [3-4], or where the system has no memory of the initially excited state [5-6].

Relaxation dynamics of CH_3Cl following core-shell photoexcitation in the neighborhood of the chlorine *K* edge (≈ 2.8 keV) was studied via multi-ion coincidence measurements using a time-of-flight

Figure 1. Projection of the coincident triplet (H^+ , C^+ , Cl^+) onto the (a) C^+ - Cl^+ plane, (b) the C^+ TOF axis, (c) the Cl^+ TOF axis.

mass spectrometer. The data provide evidence for sequential fragmentation moderated by Coulombic interactions among the fragments. The sequential nature of the fragmentation indicates that chemical forces, especially between the carbon and chlorine atoms, are dominant in determining the kinematics of the fragmentation. This is especially true on resonance where fast dissociation is observed following electron excitations to the $8a_1$ antibonding orbital.

EXPERIMENT

The experiments were performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS)[7-9]. This beamline provides a flux of 10^{11} photons s^{-1} in a bandpass ≤ 0.5 eV. An ion-time-of-flight (TOF) mass spectrometer [10] oriented with its axis parallel to the polarization vector of the incident SR, was used to detect ions created following x-ray absorption. The gas under study is supplied effusively by a grounded needle centered between two stainless-steel plates held at equal but opposite voltages. The ions created via x-ray absorption traverse a series of regions with different electric-field strengths until they are detected by a pair of microchannel plates.

For CH_3Cl , spectra were collected at photon energies in the vicinity of the K -shell ionization threshold with three levels of complexity. "Singles" spectra were collected using an electronic setup described previously [10]. A time-to-amplitude converter (TAC) measures the time difference between the detection of a single ion and the subsequent ring-timing pulse, thus flight times are inverted relative to the mass-to-charge ratio. Only one ion is detected for each fragmentation event and the data are recorded as the number of counts versus flight time. For "doubles" and "triples" spectra, a PC-based, multi-stop, time-to-digital converter (TDC) acts as a nanosecond stopwatch to record ion flight times. The ring timing signal is used to start the TDC, and detection of an ion is used to stop it. However, because the frequency of the ring-timing signal (≈ 3 MHz) is much greater than the ion count rate, it is necessary to use a logic circuit to reduce the amount of dead time from TDC starts with no corresponding stops. For doubles and triples spectra, two or three ions are detected following a single fragmentation event; doubles data record flight times for two ions (t_1, t_2 , counts), while triples data record flight times for three ions (t_1, t_2, t_3 , counts). Figure 1 shows data collected for the coincidence triplet (H^+, C^+, Cl^+). In the figure, the three dimensional coincidence volume is projected

Figure 2. Slopes of contour plots produced by projection of coincidence volumes onto planes defined by the ion time of flight axes.

onto a plane [Fig. 1(a)] and the axes [Fig. 1(b)-(c)] defined by the flight times of the second and third ions respectively. Because of the information it contains on the momentum released in the fragmentation process, the most important parameter in determining fragmentation mechanisms from multi-ion coincidence measurements is the slope of the coincidence peak [1]. This is determined from contour plots such as Fig. 1(a) created when a coincidence volume is projected onto one of the three different planes defined by the ion flight times. For a molecule such as CH_3Cl , the slopes of the coincidence peaks will allow differentiation between deferred charge separation (DCS) mechanisms, where a neutral fragment is ejected in the first step of dissociation; secondary decay (SD), where a neutral is ejected in the second step of dissociation; and concerted dissociation (CD) processes where all fragments separate simultaneously.

Figure 2(a) shows that for singly charged ions (C^+ , Cl^+) measured in coincidence with H^+ there appears to be little or no change in slope, and thus dissociation mechanism, as a function of energy. The slopes also appear to agree well with calculated values. However the situation is different for more highly charged ions [Fig 2(b)]. The slopes of the $\text{H}^+ - \text{Cl}^{4+}$ clearly change in the first few eV above resonance, and show better agreement with the calculated values on resonance. Looking at the widths of the chlorine peaks as a function of energy (Fig. 3) indicates that for all charge states, there is a greater amount of energy released in fragmentation on resonance than at energies above resonance. A likely explanation is, on resonance, the excitation of the core electron into the $8a_1$ antibonding orbital initiates the C-Cl bond rupture, consequently, the electrostatic repulsion introduced by population of an antibonding orbital causes a more energetic ejection of the chlorine ion in a manner analogous to the fast dissociation observed for resonant excitation of HCl [11]. Because of this, the chlorine ion has less Coulombic interaction with the other ions, the fragmentation is more sequential, and the slopes of coincidence peaks show better agreement with the values calculated using the sequential model. In addition, for all ionic triplets, the FWHM for the H^+ ions (not shown) are consistently narrower on resonance, as would be expected in the case of a reduced Coulombic interaction. In contrast, upon excitation to Rydberg orbitals (3.4 eV above resonance) or to the continuum (5 eV above resonance), rupture of the C-Cl bond results solely from electronic depletion following Auger decay. In addition, with the higher ionic charge states inherent to above-threshold energies comes greater mutual repulsion between the ions, making fragmentation a more concerted process and changing the slope. These results suggest that by using multi-ion-coincidence techniques it is in principle possible to determine an upper bound for the energy of electrostatic repulsion arising from excitations to the $8a_1$ antibonding orbital, and to use this information to map out the potential curves for different fragmentation

Figure 3. FWHM of chlorine ion peaks versus photon energy. Squares (■) represent the FWHM of CL^{4+} measured in coincidence with H^+ and C^{2+} . Circles (●) FWHM of CL^{3+} measured in coincidence with H^+ and C^{2+} . Up triangles (▲) FWHM of CL^{4+} measured in coincidence with H^+ and C^+ . Diamonds (◆) FWHM of CL^+ measured in coincidence with H^+ and C^+ . Down triangles (▼) FWHM of Cl^+ measured in coincidence with H^+ and C^+ .

pathways. However, because a large extraction voltage was used in these experiments, the resolution for the kinetic energy of the fragments is poor, and it is difficult to derive any quantitative results.

In conclusion, the fragmentation dynamics of CH_3Cl were studied using triple-coincidence CSMS methods. By measuring the slopes of different coincidence maps, and looking at the FWHM of the different ions, it is found that a sequential decay mechanism, initiated by the rupture of the C-Cl bond, describes the dissociation process well for all ionic charge states, and that the process is moderated by Coulombic interaction among the particles. In addition, an increase in the FWHM on resonance, combined with better agreement of the slopes of the more highly charged chlorine ions with the calculated values was attributed to fast dissociation caused by the electrostatic repulsion following excitation of a core electron to the $8a_1$ antibonding orbital. The sequential dissociation as well as the additional electrostatic repulsion following resonant excitation provide strong evidence that chemical forces are the dominant factor governing the kinematics of the fragmentation, and that Coulombic repulsion plays a subordinate role in the dissociation.

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Performance Upgrades to Bending-Magnet Beamline 9.3.1 for Atomic, Molecular, and Materials Science

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Beamline 9.3.1 is a bending-magnet beamline which provides high-resolution x-ray beams between 2.2 and 6 keV, allowing electron, ion, and x-ray spectroscopy measurements for atomic, molecular, and materials sciences. Because recently proposed experiments require taking the beamline beyond its original design parameters, including beam stability and the photon-energy range, an effort was begun in August 1999 to improve the performance of beamline 9.3.1.

The heart of the beamline is a double-crystal monochromator. The two crystals forming the monochromator ride on a very precise boomerang-type mechanical linkage which keeps the two crystals parallel in both χ and θ directions, where χ can be defined either as a pitch of the crystal holder or a roll about the photon beam axis and θ either as a roll about the crystal holder or a vertical pitch relative to the photon beam-axis. Three sources of unwanted beam motion were due to the monochromator itself. The first source requires a simple χ adjustment of the second crystal, making the crystal faces parallel in a plane perpendicular to the photon-beam axis. Uncorrected this error causes the photon beam to walk horizontally when the photon energy is changed. While making this correction it was observed that adjustments in χ also changed θ slightly in a previously unobserved coupling of the two axes of motion. A change in θ affects the 2d spacing (Bragg's law) of the crystal resulting in destructive interference or loss of photon flux. To remove this cross-talk between the χ and θ adjustments, new crystal holders have been designed that place the χ adjustment on the first crystal and leaving the θ adjustment on the second crystal, effectively separating the two piezo-electric motors. The new crystal holders will be installed during the June 1999 shutdown. The second source of beam motion was found to be a flaw in the precision boomerang supporting the two crystals. This source caused the observed photon beam to walk erratically (χ and θ) in a few specific photon-energy ranges. The correction of this source was completed in January 1999 and required replacement of the precision

boomerang. The final source of unwanted beam motion occurs just after a storage ring refill, is time dependent, and is defined by the photon beam walking horizontally and walking a minor amount vertically for the first few minutes after the refill. This is due to the heating of the monochromator crystals causing them to be misaligned until reaching their final operating temperature. Misalignment also causes the 2d spacing between the crystals to change, resulting in incorrect spacing between the crystals when a photon energy scan is performed, leading to a rise and drop in photon flux as the crystals move in and out of the optimal crystal spacing, effectively causing a shortening of the range in a particular photon energy scan at low energies. The solution to this is passive cooling of the first crystal, and required the purchase of thin Si (111) crystals to allow for rapid heat transfer. The new crystals and cooling mechanism are to be placed in the new crystal holders and will be installed during the June 1999 shutdown.

Finally, a second set of crystal holders was constructed for a pair of recently purchased Ge (111) crystals. The new crystals will triple the flux provided by the Si (111) crystals and lower the minimum photon energy to nearly 2.0 keV. However, they will also reduce the photon resolution by a factor of three.

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X-Rays Emitted by Implanted Argon Atoms

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INTRODUCTION

Experiments have been performed on argon atoms in a gas and implanted in solids to determine whether the crystal structure modifies the energy levels of the implanted argon atoms.

EXPERIMENTS

Argon atoms were implanted in various solid targets (metals, semiconductors, and insulators) at depths of the order of 1000 angstroms and ionized in the K shell with photons at an energy slightly greater than the Ar K-shell binding energy. Typical samples studied were metals such as W, Be, C, and Ni, and insulators, such as BeO and SiO₂. Concentration of the implantation was in the range 10¹⁵ to 10¹⁶ cm⁻².

This experiment was conducted on beamline 9.3.1 at the Advanced Light Source in Berkeley; this beamline uses a double-crystal monochromator to cover an energy range from 2 to 6 keV. Typical photon flux is of the order of 10¹⁰ photons/mm².

The fluorescence from the implanted Ar atoms following K-shell ionization was detected with a very high-resolution Si(Li) detector. These fluorescence spectra have been compared with those emitted by Ar atoms in a gas cell following excitation. The K_α lines of implanted Ar atoms were found to be shifted downward in energy by about 2 eV for most targets relative to Ar gas atoms, while the relative intensity of the K_β and K_α lines is similar in gas and solid targets.

PLANS

Plans for upcoming beamtime are to do similar measurements with much higher spectral resolution of the fluorescence radiation by replacing the Si(Li) detector with a crystal spectrometer.

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Beamline 9.3.2 Abstracts

Atomic Structures of Anomalous Carbon Dimers on the 3C-SiC(001)c(2x2) Surface

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INTRODUCTION

SiC has attracted much recent interests due to its potential for novel device applications as well as due to its unique surface structures/properties provided by the partly ionic character of Si-C bonding [1, 2]. Among the numerous polytypes, most of the current discussion on surface structures has been devoted to cubic 3C-SiC(001) [1] and hexagonal 6H(4H)-SiC(111) [2] surfaces. It has been known that the 3C-SiC(001) surface exhibits three major surface phases [1]: the carbon-terminated c(2x2) surface, the Si-terminated 2x1 (or c(4x2)) surface and the Si-rich 3x2 surface [3-6]. Although interesting and peculiar surface properties have been reported on these surfaces, further detailed discussion is mainly prohibited by the lack of consensus on the atomic structures of the surface reconstructions. As for the C-terminated c(2x2) surface, the possibility of a very unusual bridge-bonded dimer (BD) structure has been discussed (Fig. 1a) [7], which is unprecedented among the known semiconductor surface reconstructions, against a more conventional dimer structure (Fig. 1b) [8]. This structure seems to violate the most important rule of semiconductor surface reconstructions - minimization of the number of unsaturated dangling bonds. Extensive theoretical efforts have been devoted to find the ground state structure of the c(2x2) surface but to fail to get an unambiguous answer [9, 10]. Experimentally, a recent NEXAFS study provided an indirect evidence for the BD structure [11], which is, however, far from being conclusive.

In the present work, we unambiguously determined the quantitative details of the atomic structure of the 3C-SiC(001)c(2x2) surface by scanning-tunneling-microscopy (STM) and by photoelectron diffraction (PED) of the C 1s surface core level [12].

EXPERIMENTS

STM studies were done at Electrotechnical Laboratory (Tsukuba, Japan) and surface-core-level-resolved C 1s PED experiments on the beam line BL 9.3.2 of Advanced Light Source. Well-ordered single-domain 3C-SiC(001)c(2x2) surfaces were prepared by annealing 3C-SiC(001) films at ~ 1450 K (Si sublimation) *in situ* for the PED experiments [2, 4, 6]. In the STM study, the methods of Si sublimation and C₂H₂ or C₂H₄ exposure [2, 11] were extensively compared.

RESULTS AND DISCUSSION

Figures 1c and 1d show high-resolution filled-state STM topography of the c(2x2) surface. These images clearly show one oval-shaped protrusions in each c(2x2) unit cell for the first time, which is slightly elongated along the [110] azimuth (the C dimer bond axis of the BD model). These protrusions and their characteristic bias dependence appear uniformly over the whole surface. Extensive STM imagings of the surfaces prepared by C₂H₂ (C₂H₄) exposure and by Si

sublimation showed no essential difference. This result apparently denies any substantial coexistence of different $c(2 \times 2)$ or 2×1 surface reconstructions suggested by theories [9, 10]. However, due to the dramatic bias dependence of the STM images and its mismatch with the presently available calculations [9], the STM image alone can not point out the correct $c(2 \times 2)$ structure.

Fig 1. The two structure models of $3C\text{-SiC}(001)c(2 \times 2)$: (a) the bridge-dimer (BD) and (b) the staggered-dimer model (SD). Filled-state STM images of the $3C\text{-SiC}(001)c(2 \times 2)$ surface: (c) a wide scan ($195 \times 195 \text{ \AA}$) at a sample bias of -2.95 V and (d) a close-up ($40 \times 40 \text{ \AA}$) scan at -3.05 V . A $c(2 \times 2)$ unit cell is depicted by hatched diamonds.

Further structural information can be achieved by resolving out the C 1s photoemission from the surface C atoms. Yeom et al.'s previous high-resolution C 1s study (done at Max-Lab BL-22) [6] have shown that the C 1s level is composed of two main components originating from the bulk C and the topmost C layers (**B** and **S**, respectively, in Fig. 2). The energy shift between **B** and **S** is as large as 1.1 eV indicating a large deviation of the electronic and structural environments of surface C atoms from those of bulk. However the fact that both SD and BD models have only single surface C sites prevents to distinguish them through the C 1s spectra. In order to obtain quantitative information on the surface structure, the PED from the surface C 1s component (**S**) was investigated [13, 14]. As shown in Figs. 2a and 2b, **S** shows a large intensity modulation when its kinetic energy ($h\mathbf{k}^2/4\pi m_e$) is varied. This modulation, due mainly to the scattering of photoelectrons by the near-surface atoms, is measured in detail by scanning the photon energy and is, then theoretically simulated including the multiple scattering of photoelectrons fully with more-than-200-atom clusters of the two structure models. The optimized results of simulations through R-factor analyses [14] are compared to the experimental results in Fig. 2c. As evident in this

comparison, the SD model can be ruled out due to the apparent disagreement with the experiment. In sharp contrast, the BD model gives an excellent agreement between the experiment and simulation with a convincingly low R-factor of 0.11. The optimized structural parameters for the BD model are $1.22 \pm 0.05 \text{ \AA}$ for the C-C dimer length (d_1), $1.84 \pm 0.02 \text{ \AA}$ for the C-Si bond length between the top and the 2nd layers (d_2) and $2.70 \pm 0.1 \text{ \AA}$ for the Si-Si bond length (d_3). This C-C bond length corresponds well to that of the triple-bonded C_2H_2 molecule and agrees very well with the theoretical calculations [9, 10]. This suggests the unique *triple bonding* of C dimers [9-11], which was further confirmed by Yeom et al.'s angle-resolved valence band photoemission study identifying two characteristic π -bond surface state bands as predicted by theory [12].

Fig. 2. (a) C 1s spectra of 3C-SiC(001)c(2x2) with decompositions taken along the [110] azimuth at an emission angle (θ_e) of 45° for the two different kinetic energies ($hk_e/4\pi m_e$ where $k = 4.0$ and $4.5 \text{ \AA}^{-1}$). S and B denote the surface and bulk components, respectively [6]. (b) Intensity modulation of the S component as function of photoelectron wave vector (k). This is given in the c function: $c = (I - I_0)/I_0$, where I is the photoelectron intensity and I_0 is its smooth background. The dots with a thin solid line represent the experimental data and the thick solid (dashed) line is the optimized result of theoretical simulations for the BD (SD) model.

CONCLUSIONS

The atomic structure of the c(2x2) reconstruction of the C-terminated 3C-SiC(001) surface was unambiguously determined by scanning tunneling microscopy and surface-core-level-resolved

photoelectron diffraction studies. This surface is found to uniformly consist of bridge-bonded C dimers with a C-C bond length of 1.22 Å. This indicates that the surface carbon atoms form unprecedented *triple-bonded* dimers, which is further corroborated by detailed angle-resolved valence-band photoemission study identifying two occupied π -state bands due to the surface-normal and -parallel π orbitals of the triple-bonded C dimers [12].

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Depth-Resolved MCD Studies of Magnetism at Buried Interfaces Using X-Ray Standing Waves

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INTRODUCTION

Interfaces between two phases and/or elements are of great interest because macroscopic properties of materials are often controlled by the microscopic details of how the transition in chemical, electronic and geometric arrangement of atoms is made across them [1-10]. Understanding how this transition is made across buried interfaces between condensed phases is both very important and tremendously difficult. The difficulty lies in depth-resolving properties of interest at buried interfaces, since most techniques involving electron or photon detection have depth sensitivity determined by exponential penetration or escape depths that provide only limited capabilities to resolve changes in depth over sub-nanometer length scales [11-13]. We are extending optical standing wave techniques [14] familiar at longer and shorter wavelengths into the 500 – 1000 eV range for the first time to study depth-resolved magnetic properties using magnetic circular dichroism (MCD) at $L_{2,3}$ edges for 3d transition metals and other x-ray magneto-optical techniques.

Magnetic properties of ultrathin films can be drastically altered by their interfaces. The broken symmetry and other aspects of disorder at surfaces or interfaces are thought to be responsible for these changed magnetic properties, through changes in local electronic structure that affect the local of magnetic moments and their orientations at the interface [1-10]. X-ray magnetic circular dichroism (MCD) has become an established tool to separate orbital (M_l) and spin (M_s) magnetic moments [4-8,11-13,15,16] through sum rules [17,18]. To understand surface and/or interface magnetism, there have been many measurements of M_l as a function of the thickness of magnetic layers [5,6]. However it is often overlooked in such measurements that the measured values of M_l are averaged over the entire thickness so that the signals from the interface region can be suppressed by those from the interior of the entire thickness as the Co layer becomes thick.

Our goal is to combine standard standing wave (SW) techniques with soft x-ray magneto-optical techniques to more directly probe magnetism at buried interfaces. This initial experiment combines standing waves with MCD to discriminate the magnetic response at interface region from the interior of the 20 Å thick Co layer in a designed structure of Pd(10 Å)/Co(20 Å)/Pd(20 Å) sandwich film having the in-plane magnetization.

EXPERIMENTS

A spatially varying optical SW is generated by a multilayer interference structure of $[B_4C(21.4 \text{ Å})/W(17.5 \text{ Å})]_{40}$ and extends into the region above the multilayer substrate. The magnetic trilayer system of interest is grown directly onto the multilayer standing wave generator (SWG), and the entire structure is designed so that the periodicity of the standing wave produced by the multilayer matches the dimensions of interest to probe in the Co film. Figure 1(A) shows the x-ray reflectivity of the SWG and trilayer/SWG structure, and reveals that the diffraction properties of the SWG are not destroyed by the trilayer. Figure 1(B) shows the calculated electric field

intensity $E^2(z)$ in the trilayer using measured Co magneto-optical properties for opposite helicity. By varying incident angle around the first order Bragg peak of the SWG at a given photon energy, $h\nu$, the phase of SW is shifted by π with respect to the period. The structure is designed so that the strongest standing wave, occurring at the interference maximum of the SWG, has peak $E^2(z)$ near the bottom Co/Pd interface. This corresponds to scattering vector $q = 0.17$ for the present sandwich structure, where $q = 4\pi \sin \theta / \lambda_{vac}$, with grazing incidence angle θ .

To investigate the SW enhanced MCD signals, we measured absorption through commonly used total electron yield (TEY) technique [5-7]. Measurements were made by scanning θ ranging from 10° to 15° (the Bragg peak remains within this range for all $h\nu$) at fixed $h\nu$, ranging from 764 to 814 eV using left circularly polarized x-rays with the degree of circular polarization of 0.76 as measured with our polarimeter. Reference absorption spectra were collected as a function of $h\nu$ at $\theta=10^\circ$ to correct for experimental asymmetries in the θ -scans in the presence of magnetic field. The absorption spectra measured at $\theta=10^\circ$ corresponding to an average over the entire thickness of Co layer are not sensitive to the layer position other than through standard escape depth considerations. Spectra were all recorded at an external magnetic field of about 1 kOe, which is greater than the in-plane coercivity of the sample, whose remenant magnetization almost equals the saturation value. This applied field was essentially parallel to the x-ray propagation direction, and was reversed to obtain MCD absorption data with fixed photon helicity. Data were collected on bending magnet beamline 9.3.2.

RESULTS

Figure 2 shows all θ -scans as a function of $h\nu$ for $\pm$ helicity, renormalized by reference absorption spectra of the corresponding helicity measured at $\theta=10^\circ$. These data are plotted as a $q-h\nu$ surface because the standing wave position occurs at fixed q for all $h\nu$. Since photoelectron yield is much larger than fluorescence signal in soft x-ray ranges, TEY is used in this study even though this mode cannot exclude the contribution from the top and bottom Pd layers, and SWG itself. According to the typical effective electron escape depth of λ_{eff} [5,12,13], the absorption of the SWG does not contribute to the measured signal. The SW resonance at both pre- and post-edges shown in Figure 2 are thus due to the photoelectron contribution from the top and bottom Pd layers.

Figure 1. (A): x-ray reflectivities measured at x-ray tube Cu K_{α} . (B): Calculated intensity of SW from the over-structure of the sandwich film on the top of the interference multilayer structure based on the thickness parameters in text. $\pm$ helicity dependent optical constants of Co L_1 edge measured from the present sample were used. Scattering vector, q is shown only ranging from 0.16 (circle) to 0.20 (square).

Data analysis requires careful normalization of the surfaces in Figure 2 to a per Co atom scale to remove the Pd background contribution to obtain the standing wave enhanced absorption of only the Co. This analysis requires detailed consideration of $E^2(z, h\nu, q)$, i.e., how the electric field intensity varies not only in depth but also as functions of photon energy and incidence angle. First an appropriately normalized Pd contribution is subtracted, and then the resulting Co signal is normalized. Calculations of this full $E^2(z, h\nu, q)$ are required in this process, in turn requiring reliable values for the optical properties of both the SWG and trilayer components. We find that generally the $h\nu$ dependence of normalization corrections is much less than the q dependence, because the SWG contains no Co and the 20 Å Co layer is a relatively small optical perturbation to the standing wave field. With care reliable depth sensitive absorption coefficients $\bar{\mu}_{+/-}^{Co}$ weighted by $E^2(z)$ at each q can be obtained, from which polarization averaged and difference (MCD) spectra can be obtained.

The magnetic moments are related to the spin and orbital moments by $M_L = -\mu_B L$ and $M_S = -2\mu_B S$, where L and S are the expectation values of orbital and spin moments along the magnetization direction. μ_B is the Bohr magneton. The sum rules [17,18] relate these L and S moments with the integrated area at the corresponding edges in the difference and the sum of +/- absorption spectra. Accordingly, this standing wave technique allows the spatial variation of these properties as a function of position at buried interfaces which was reported for the first time [19]. Further details of the analysis, results including depth-resolved changes in the number of d holes, orbital and effective spin moments, and interpretation will be presented elsewhere [20].

The standing wave technique demonstrated here will be useful to study various other problems and systems where depth-resolved information at buried interfaces is crucial.

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Figure 2. All angle scans as function of $h\nu$ renormalized to the corresponding absorption spectra measured at $\theta=10^\circ$, converted into q - $h\nu$ surface.

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Determination of Adsorbed CO Molecular Orbital Positions by Photoelectron Diffraction

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The molecular orbitals of intact molecules adsorbed on metal surfaces display spectra akin to those of the free molecule, but typically with shifts in properties such as relative binding energies and vibrational frequencies. The stability of such systems is usually attributed to electron redistribution between the substrate and the molecular orbitals of the adsorbate: this redistribution characterizes the surface chemical bond. For example, in the Blyholder model [1] of CO adsorbed on a transition metal surface atom, in the linear geometry M-C-O, the CO 5σ orbital is polarized toward the transition-metal atom M, accompanied by the “back donation” of this atom's d-orbital electron density into the unoccupied CO $2\pi^*$ orbital, while the CO 4σ orbital remains concentrated in the C-O bond. This model accounts for the observed spectral properties, but more direct experimental evidence for the spatial distribution of the CO orbitals would be valuable. We present such evidence below.

Adsorbate structural studies by photoelectron diffraction have involved measuring the positions of substrate scattering atoms relative to the effective centroid of a photoelectron “source” orbital, an atomic core orbital in an adsorbate atom or molecule. The centroid of such a core orbital is located, of course, at the atomic nucleus: hence analysis of the photoelectron diffraction data establishes the position of this nucleus, and with it the atomic structure of the adsorbate-surface system.

The present work was performed on the system $c(4\times 2)2\text{CO}/\text{Pt}(111)$. Three source orbitals were used, in three separate measurements: the C 1s core orbital, as described above, to establish the position of the carbon atom, which is used as a fiducial reference point, and two molecular orbital peaks, which also show large-amplitude photoelectron diffraction oscillations. These oscillations reflect the effective centroids of the 4σ and 5σ orbitals, respectively, along the Pt-C-O axis, with the 4σ centroid falling between C and O, and the 5σ centroid between Pt and C.

While photoelectron diffraction is commonly associated with core electrons, this effect was apparently first observed with valence electrons, both in the scanned-angle mode [2] and in the scanned-energy mode [3], where it was observed in the present system and interpreted as photoelectron diffraction. Diffraction has been reported in photoelectrons from both localized and itinerant valence bands, in nickel [4] and aluminum [5], respectively. However, the present work is the first to interpret molecular-orbital based photoelectron diffraction to determine the location of adsorbate molecular orbitals.

The experiment was performed in an ultra-high vacuum chamber equipped for angle-resolved photoemission on beamline 9.3.2 at the Advanced Light Source in Lawrence Berkeley National Laboratory. The platinum crystal was repeatedly cleaned during the experiment by sputtering and annealing cycles. Surface cleanliness and order were periodically checked with synchrotron XPS and LEED. The CO gas was introduced into the chamber through a leak valve. The desired $c(4\times 2)$ LEED pattern was consistently reproduced by backfilling the chamber at room

temperature with CO at 1×10^{-6} torr for 10 seconds, as described in the literature [6]. The sample surface temperature was kept at 110K throughout the data collection. The photon polarization vector was oriented 30° from the sample surface normal direction, along which photoelectrons were collected.

The energy-dependent intensity of the C 1s core-level peak, and those of the CO 4σ and $(5\sigma + 1\pi)$ peaks, were measured as functions of the photoelectron momentum wave vector, $I(k)$. To facilitate Fourier-transform analysis, data were collected at small and equal k intervals over wide energy ranges in each case. The molecular-orbital data confirmed the earlier [3] measurements, which were relatively sparse and over a smaller photon energy range. After careful peak-fitting and data reduction by standard procedures, a $\chi(k)$ curve,

$$\chi(k) = \frac{I(k) - I_0(k)}{I_0(k)}$$

was generated for each (peak) data set. These are depicted in Fig. 1.

Large intensity oscillations in $I(k)$ were observed with normal-emission photoelectrons from

Fig. 1. The three χ curves. The unit of the horizontal axis is $\text{\AA}^{-1}$.

all three peaks. Visual inspection of the three $\chi(k)$ curves reveals a single strongest frequency in each case, albeit with different values from one curve to the next. *This appears to indicate that the effective centroids of the photoelectron initial-state orbitals lie at different points along the Pt-C-O axis.*

The C 1s data confirm the local adsorbate site geometry of the accepted $c(4 \times 2)$ surface structure. To date, the only published results on the distances between the carbon atoms and the platinum surface at those two different adsorption sites were obtained in a low energy electron diffraction (LEED) experiment by Ogletree, Van Hove and Somorjai [11], which gave C-Pt interplanar distances of 1.85 $\text{\AA}$ and 1.55 $\text{\AA}$ at the top and bridge site respectively.

In this analysis, we modeled the angle-resolved photoemission extended fine structure (ARPEFS) [12] $\chi(k)$ curve with a cluster-model multiple-scattering code using the Rehr-Albers separable propagator [13]. The Pt lattice constant

was fixed at 3.923 $\text{\AA}$. The C-O bond length was fixed at 1.130 $\text{\AA}$, as it should not be affected much by the platinum surface. The C 1s photoelectron scattering effects are quite insensitive to the position of the oxygen atoms in this geometry and in the fixed-angle-scanned-energy mode [14]. As noted above, all symmetry-allowed adsorption sites were considered in the simulation and indeed the accepted model gives the smallest R-factor. Upon minimization of the R-factor, the C-Pt interplanar distances were found to be $1.452 \pm 0.002 \text{\AA}$ at the bridge site and $1.828 \pm 0.001 \text{\AA}$ at the top site (statistical errors only!), corresponding to a Pt-C bond length of 2.008 $\text{\AA}$, in excellent agreement with the LEED result of Ogletree, Van Hove and Somorjai. systematic errors, common to all electron-scattering methods, limit the ultimate accuracy at this time to no better than $\pm 0.01 - 0.02 \text{\AA}$.

Before turning to a discussion of the molecular orbitals, we note that the C 1s Fourier transform spectrum is dominated by a single peak at 4Å. This arises from the atop site, in which the C-O axis is collinear with the strongly-backscattering Pt atom in the configuration Pt-C-O. A similar dominance is also expected to hold for the 4σ and 5σ molecular orbitals, and the 1π orbital is expected to contribute little signal along the normal direction. We shall therefore interpret the molecular orbital spectra below in terms of the position of the 4σ and 5σ orbitals along the atop-site Pt-C-O axis.

Having determined the positions of the atop-site C atoms in the c(4×2)2CO/Pt(111) system, we can now use them as fiducial markers for the molecular orbitals, in the approximation that most of their normal photoemission intensity variations arise from backscattering off the Pt atoms in the atop sites. We interpret these data by the same methods used for structural studies by ARPEFS with core levels. By thus determining the effective mean positions of the molecular orbital electron distributions along the Pt-C-O axis relative to the Pt scatterer, we can test the putative polarization of the 5σ orbital toward the surface, as required to form the surface chemical bond accordingly to the Blyholder model.

The wavefunctions for an atop adsorbate system were depicted, e.g., by Rhodin and Gadzuk [15]. However, we do not have quantitative adsorbate wave functions to compare with.

As noted above, our normal emission data in the form of an intensity ratio compare favorably with similar, but much more limited, measurements done much earlier [3]. Both of the molecular orbital χ curves oscillate by nearly 100%, much more than the C1s core-level χ curve. The Fourier transform of the 4σ χ curve shows one dominant peak at 4.8Å, a larger path-length difference (PLD) than the main peak of C1s FT at 4.0Å, while the 5σ+1π FT shows one dominant peak at 3.3Å, a smaller PLD than C1s FT. This confirms our inferences from visual inspection of the three χ curves in Fig. 1. We therefore infer that the centroids of the three orbitals along the Pt-C-O axis fall in the order 4σ > C1s > 5σ relative to the Pt atom, with the 4σ in the C-O bond and the 5σ centroid between Pt and C, as predicted in the Blyholder model.

To model the molecular-orbital photoelectron diffraction in this system in an approximate way, we used a linear combination of atomic orbitals (LCAO) model to simulate the CO molecular orbitals and a Pt 5dz² orbital on the Pt atom for the top sites only. This atomic approach should provide a qualitatively correct, albeit an oversimplified, model. We calculated separately the final state wavefunctions of diffracted photoelectrons from Pt 6s, Pt 6p, Pt 5d, C 2s, C 2p, O 2s and O 2p atomic orbitals, and linearly combined these wavefunctions to simulate the observed final state that would originate from the molecular orbitals.

As the LCAO/MO coefficients are not known, especially for this adsorbate system, we elected to use the same data reduction process as for core-level photoemission to produce χ_E and χ_T, and varied the atomic orbital coefficients to minimize the R-factor. This kind of coefficient determination is independent of any conventional theoretical calculation of the LCAO coefficients based on cluster models: thus it could in principle provide a test of such *ab initio* models. The prospect of using photoelectron diffraction from molecular orbitals to study chemical bonds in this way poses a challenge for theoretical advances in seriously modeling the surface chemical bond, as well as photoemission from that bond. As we have no *ab initio* results to compare with, at this time we can only assess whether the coefficients from our minimization procedure appear to be reasonable. Apparently they do: 4σ = 1.000 C2s + 5.763 C2p - 5.521 O2p; 5σ = 7.365 C2s + 3.380 C2p + 4.720 Pt6s + 3.500 Pt6p + 1.510 Pt 5d. The Fourier transforms of the χ curves show credible, if mediocre, fits. In particular, the very large amplitude modulations in χ are modeled, as are the single dominant low-PLD peaks.

We have observed and interpreted photoelectron diffraction from molecular orbitals. The C-Pt interplanar distances of $c(4\times 2)2\text{CO}/\text{Pt}(111)$ are determined as 1.83 Å at the top site and 1.45 Å (2.01 Å Pt-C bond length) at the bridge site, with systematic uncertainties of ca. 0.01-0.02 Å. The 4σ orbital has an effective electron-density centroid between the C and O atoms, while for the 5σ orbital this centroid lies between the C and the Pt atoms. This experiment demonstrates the capability of photoelectron diffraction for studying the surface chemical bond.

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HIGH-RESOLUTION OXYGEN K-EDGE STUDY OF $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$

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INTRODUCTION

Metallic substitution studies have enhanced our understanding of the superconducting and normal state properties of high- T_c superconductors. Substitution of metals in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) usually depresses T_c and has other negative effects on the superconducting properties. The superconducting properties of YBCO depend not only on the oxygen stoichiometry but also on the oxygen ordering. Substitution of Cu can provide a selective tool to investigate the specific effects because depending on the dopant characteristics, the substituted compounds may exhibit modified microstructures without any substantial change in the overall oxygen content. Much work has been done in this direction. Trivalent metal ions like Fe, Co, or Al replace Cu in Cu1 site on the Cu-O chain and depress T_c more slowly than divalent Zn and Ni which replace Cu in Cu2 site in the CuO_2 plane [1]. Substitution of Cu by Fe may lead to (i) reduction of T_c , (ii) structural transformation with increasing impurity concentration, (iii) increase in oxygen content accompanied by a rearrangement of oxygen, and (iv) local magnetic ordering. When Cu is replaced by Fe, the oxygen atoms might rearrange themselves in order to provide the most stable Fe site. This modifies the local electronic densities of states. Little is known about the variation of electronic structure due to the substitution. Yang et al. [2] have studied the variation of electronic structure of YBCO upon Fe doping, at the Fe site using x-ray absorption spectroscopy (XAS). In this study we compliment their work by investigating O site using XAS.

EXPERIMENTAL

Polycrystals of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ (YBCFO) with starting x values of 0.01, 0.05 and 0.15 were prepared by standard solid state reaction method. The critical temperatures of these samples were determined by standard four-probe technique, using a constant current source and a Keithly-181 nano voltmeter. X-ray diffraction patterns of the samples were obtained using a Phillips PW1700 automated diffractometer. The analysis is computer assisted so that the interplanar spacing values can be corrected for the instrument error function by analyzing a silicon standard and subsequent phase identification.

X-ray absorption near edge structure (XANES) measurements were performed using Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2 [3]. High-resolution XANES spectra were taken in the Ba M and O K absorption edge regions, while the monochromator was set at a resolving power ($E/\Delta E$) of > 7000 . The YBCFO poly crystal samples were cooled to about 90 K before scraping them in a vacuum of about 1×10^{-10} Torr, in order to minimize oxygen loss from the fresh surface [4]. Since the size of the synchrotron radiation photon beam at the sample was ~ 1 mm, it was not difficult to align the system to make sure that only the sample was illuminated by the photon beam. XANES measurements were performed using a partial electron yield detector consisting of 40 mm channel plates in the pulse counting mode. I_0 signal from a freshly evaporated gold grid was used for normalization of spectra.

RESULTS AND DISCUSSION

The zero-resistance transition temperatures of the samples were 93, 92 and 71 K for $x = 0.01, 0.05$ and 0.15 respectively. The XRD patterns confirmed that all three samples have single phase with orthorhombic symmetry. This is consistent with the resistivity measurements that revealed all three samples were superconducting.

Fig.1: O K edge of $\text{YBa}_2\text{Cu}_{1-x}\text{Fe}_x\text{O}_{7+x}$ poly crystals at 90 K as a function of x .

Fig.1 shows the O K edge of YBCFO poly crystals at 90 K as a function of x. Energy scale was corrected by comparing Ba M edge of the samples with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ single crystal [5], with the assumption that the Fe substitution does not affect Ba site. A straight line fitted to the region before the peaks (below 523 eV) has been subtracted as background. The spectra shown in the figures have not been smoothed or filtered in any way. Two small peaks at 524.5 and 526.5 eV (labeled A and B respectively) and a prominent peak at 530 eV (labeled C) precede the main edge which starts at about 531 eV. Multiple scattering calculations assign peak A and B to holes in O sites in the CuO_2 plane (O_2 and O_3) and Cu-O chain (O_1) respectively [5]. Intensity of peaks A and B decreases with increasing Fe content, indicating hole filling in both CuO_2 plane and Cu-O chain. This is in agreement with the recent results from Mossbauer Spectroscopy and neutron diffraction [6,7]. Furthermore, this seems to support that T_c degradation with increasing iron substitution is due to hole filling. In other words, Fe enters the structure primarily in the formally trivalent oxidation state. We interpret the peak C as the signature of the O holes being removed and localized around the Fe sites in the compound. Note that the intensity of this peak increases with increasing Fe content. Our interpretation is further supported by the general observation that many of the insulating transition metal oxides exhibit such sharp peaks between 529 and 530 eV in the O K edge spectra [8].

CONCLUSION

In summary, our high-resolution XANES spectra at O K edge in $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-y}$ for $x = 0.01, 0.05$ and 0.15 show hole filling with increasing Fe content in both CuO_2 plane and Cu-O chain. This means that Fe enters the structure primarily in the formally trivalent oxidation state. A detailed study of this work including Cu L_3 and Fe $L_{2,3}$ edge regions will be published in the near future.

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Multi-Atom Resonant Photoemission: Theory and Systematics

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The recently discovered inter-atomic multi-atom resonant photoemission (MARPE) effect [1] has been the subject of theoretical investigation that has permitted to establish the relevant elements involved in this phenomenon [2], where core photoelectron intensities are enhanced when the photon energy is tuned to a core-level absorption edge of non-identical neighboring atoms, thus enabling a direct determination of near-neighbor atomic identities. Both the multi-atom character of MARPE and relativistic retardation effects in the photon and electron interactions in the resonant channel have been shown to be crucial. In particular, they lead to constructive interference of resonant and direct emission in the MnO example under study, resulting in experimentally-observed peak-intensity enhancements of the order of 40-65% and spectral shapes similar to the corresponding x-ray absorption profiles.

In a first discussion of the theory of MARPE [1] the conventional model used to describe the well-known intra-atomic single-atom resonant photoemission (SARPE) [3-6] has been generalized to apply to this new phenomenon. Specifically, photoemission is assumed to occur via absorption of a single photon and two different channels that leave the crystal in exactly the same final quantum state, and thus have to be added coherently: the direct emission channel in which an O1s electron absorbs a photon and the resonant emission channel that is assisted by the Mn2p→Mn3d resonance. In the resonant channel, the photon promotes a Mn2p electron to a Mn3d state, from which it decays instantaneously to refill the Mn2p hole, while exciting the O1s electron to the continuum. This decay can also be termed an inter-atomic auto-ionization process (AI), and it is thus closely related to the much weaker inter-atomic Auger processes. Notice that several Mn neighbors of the emitter must be summed coherently. A first estimate from such a theoretical treatment gives an energy-integrated effect of 2.5%, or about 4 times less than experiment [1]. However, the model used previously did not permit treating the precise many-electron states and energies involved, and so could not predict the form of the spectral enhancements as a function of energy. We have shown that this model was too simplified as to the electromagnetic interactions involved. The present work thus introduces a significantly more quantitative first-principles approach to the theory of MARPE that yields very good agreement with experiment in most respects and permits further assessing the systematics of this new phenomenon. In particular, many-electron configuration interaction states are used to describe the Mn2p→Mn3d excitation and relativistic effects in photon excitation and auto-ionization are included.

Use of the Kramers-Heisenberg formula has been made to calculate photoelectron intensities, where the intermediate states are obtained within a configuration interaction scheme for an octahedral cluster formed by a Mn²⁺ ion surrounded by six O²⁻ ions. Both the interaction with the external photon and the inter-atomic interaction incorporate

retardation effects, which are important due to the combination of relatively large inter-atomic distances and photon energies; actually, the change in the phase of a photon that travels across the nearest-neighbor distance in MnO is 42° when the photon energy matches the Mn2p resonance. The interaction between dipole currents induced during the two-electron transition dominates over the charge-charge term. Further details on the theory are given elsewhere [2].

The absorption and re-emission of a photon by Mn in MnO is described in terms of the Mn polarizability, which enters the Kramers-Heisenberg formula. The imaginary part of this quantity is roughly proportional to the absorption coefficient, as can be seen in Fig. 1(a), where experimental data are compared with this theory.

The results of our calculations of the MARPE effect for two different measurement geometries are shown in Figs. 1(b)-(c). Plotted is the quantity I/I_0 , where I is the actual O1s intensity and I_0 is the non-resonant background under it. Curves are shown for both a full sum over all Mn atoms, and a sum limited to a distance of $10d$ from the emitter, where d is the nearest-neighbor distance. The predicted enhancements follow quite closely the shape of the x-ray absorption profile, showing little evidence of the constructive/destructive interference patterns that are often seen in so-called Fano profiles [3], in agreement with experiment [1]. In general, the more limited sum agrees better with experiment as to both peak positions and intensities, suggesting an effectively more rapid convergence with distance in experiment. In magnitude, there is also excellent agreement for the geometry in Fig. 2(b) for an x-ray incidence angle of 20° , but in Fig. 2(c) the principal Mn2p_{3/2} peak is predicted to be too weak by a factor of 2 for an incidence angle of 40° . The possible reasons for this discrepancy are inaccuracies in our treatment of nearest-neighbor effects and the O1s hole state, multiple scattering and resultant phase averaging of the radiation (much enhanced at the resonance), and neglect of atomic vibrational motion.

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Figure 1. (a) Real (dashed curve) and imaginary (solid curve) parts of the average polarizability of Mn^{2+} in MnO, calculated using a configuration interaction scheme [6], as compared with the experimental absorption coefficient [7] and its Kronig-Kramers transformation (dotted curves). (b) Enhancement in the O1s photoelectron intensity emitted along the normal of a MnO(001) surface illuminated with linearly polarized light incident at an angle of 20° with respect to the surface. The polarization vector lies in the plane containing [100] and [001]. The experimental result [1] (dotted curve) is compared with theoretical curves for a full sum over all Mn atoms in each plane (solid curve, $\eta=\infty$) and for a sum only out to 10 nearest-neighbor distances (dashed curve, $\eta=10$). (c) The same as (b) for an incidence angle of 40° .

Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding

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INTRODUCTION

Recent experiments have provided evidence of a previously unconsidered resonant process between interatomic electronic levels [1]. The process is conceptually similar to the well-known resonant phenomena between electronic levels within a single atom. However, the multiple atom nature of the new phenomenon is expected to make the process useful as a tool for studying near-neighbor bonding information.

The mechanism involved in multiple atom resonant photoemission (MARPE) is best introduced by comparison with the familiar single atom case (SARPE). In the SARPE case, it is known that as the photon energy is tuned across a given level in an atom, the photoemission from another less deeply bound level may be significantly enhanced [2, 3, 5, 6]. As an example, consider the case of atomic Mn shown in Fig. 1. In this case, the Mn3d photoemission is enhanced as the photon energy crosses the deeper Mn3p level. The Mn3p level is excited into Mn3d but decays, producing an electron of the same energy as if the Mn3d had been directly excited by the photon. This process is then providing a second coherent channel for the Mn3d to photoelectron process. The figure presents experimental [3] and theoretical [5] results for this particular process.

In the case of MARPE, we find that the two levels involved in the resonance do not need to be associated with the same atom. In Fig. 2A, the process is diagramed for the case of O1s resonating with Mn2p_{3/2,1/2}. As depicted in the figure, the photon energy must be sufficient to excite the Mn2p_{3/2} and 2p_{1/2} electrons into a Mn3d level. The process couples to the O1s when the Mn3d decays back to Mn2p, simultaneously producing an electron from the O1s level with the same energy as if the photon had directly excited an O1s electron.

As the absorption edge of Mn2p_{3/2} is crossed, we experimentally find the O1s intensity to be enhanced by a factor of about 11% when integrated over the entire range of the Mn2p_{3/2} contribution. For comparison, the SARPE case shown in Fig. 1B indicates an overall enhancement of the Mn3d intensity of about 63% when similarly integrated across the extent of the effect.

EXPERIMENT

All experimental data was recorded at the Advanced Photoelectron Spectrometer/Diffractometer on beamline 9.3.2 of the Advanced Light Source in Berkeley [8,9]. The beamline allows photon energy to be selected between 30 to 900 eV. For these experiments, linearly polarized light was chosen. This instrument allows significant degrees of freedom in the experimental geometry. A sample manipulator permits an arbitrary sample angle relative to the spectrometer acceptance (or photon incidence). Furthermore, a rotatable Scienta ES200 analyzer allowed the analyzer acceptance and photon incidence to be adjusted independent of the manipulator degrees of freedom.

Samples used in this study were single crystal MnO(001), single crystal Fe₂O₃(001), and La_{0.7}Sr_{0.3}MnO₃(001). Photoelectron diffraction measurements confirmed each sample to have a highly ordered surface and allowed precise orientation of the sample geometry during subsequent measurements [8].

For clarity, we will discuss the experimental method in the specific case of an MnO sample where the O1s level (binding energy ~530eV) is in resonance with the Mn2p_{3/2} and 2p_{1/2} levels (binding energies ~639 and 650eV). The details may be trivially modified to apply to subsequent examples. We are interested in the variation of the O1s peak intensity as the photon energy is scanned through the Mn2p edge. We recorded an O1s spectrum for incremental photon energies across the Mn 2p range: 634 to 657eV. For each peak, the

Figure 1:

- A. Single Atom resonant photoemission (SARPE) for the case of Mn3d emission from atomic Mn with the resonance occurring via the mn3p level. The direct excitation is indicated by the solid arrow from the Mn3d to the continuum while the resonant process is shown by the solid arrow between the Mn3p and 3d levels and the dashed arrows representing the autoionization decay.
- B. The measured variation of the Mn3d emission with photon energy (solid points) shown with Hartree-Fock (HF) and many-body perturbation theory (MBPT) theoretical models. By defining the nonresonant contribution by a smoothly varying background through photon energy range of about 30 to 87eV, we find the integrated resonant contribution to be 63% above the nonresonant contribution.

Figure 2:

- A. Multi-atom resonant photoemission for the case of O1s emission from MnO, with the resonance occurring via the Mn2p_{3/2} level (or at a slightly higher photon energy, also the Mn2p_{1/2} level). The solid arrow from the O1s level to the continuum indicates the direct excitation. The resonant process is indicated by the other arrows, showing a Mn2p to Mn3d excitation along with the decay and coupling back to O1s to continuum excitation.
- B. Our measured variation of the O1s intensity over the Mn2p_{3/2} and Mn2p_{1/2} edges. The nonresonant intensity is given by the smoothly varying background (dashed line) through this region. In this case, the resonant contribution is 11% above the nonresonant background.

inelastic background was then subtracted and the curve fit in order to obtain the peak intensity (area). Fig. 3A shows examples of such fit curves for the particular cases of on-resonance and off-resonance. This intensity as a function of excitation energy is plotted in Fig. 2B, showing the MARPE enhancement as a deviation from a smooth non-resonant background. From this curve, we remove the contribution of the non-resonant background by subtraction of a smooth polynomial and setting of the new baseline to unity as shown in Fig. 3C. Note in Fig. 3A that the O1s peak lies on an inelastic background whose magnitude varies across the Mn2p edge. The variation of this background is a measure of the X-ray absorption of the Mn2p levels as illustrated by Fig. 3B where the background level as a function of photon energy is compared to previous measurement of the X-ray absorption by Butorin, et al [7].

RESULTS

The three samples used in this investigation allowed us to observe interatomic resonance between a variety of levels. In the MnO sample, we measured the previously discussed O1s resonance with the Mn2p_{3/2} and 2p_{1/2} levels. As indicated in Fig. 3B and discussed above, our extracted X-ray absorption coefficient exhibits excellent agreement with previous work. Referring to Fig. 3C, the resonance contributes up to 43% to the O1s photoelectron intensity with an overall enhancement of 11% across the entire Mn2p_{3/2} level.

In the Fe₂O₃ sample, we observe the O1s resonance with the Fe2p_{3/2} and 2p_{1/2}. Again, our X-ray absorption coefficient matches previous work, in this case by Kuiper et al [10]. The resonance enhancement of the O1s intensity is here as large as 62% and integrates to 24% across the Fe2p_{3/2} portion of the effect.

Figure 3

- A. O1s photoelectron spectra taken on (hollow points) and off (solid points) resonance, $h\nu = 640.2$ eV and 637.6 eV respectively. Note the increased inelastic background on resonance (dashed curves).
- B. X-ray absorption coefficient for MnO, as measured in this study from the energy dependence of the inelastic background under the O1s spectra (solid curve) and from ref.7 (dashed curve).
- C. O1s intensities above inelastic background for normal emission as a function of $h\nu$, with the smoothly varying nonresonant intensity at each energy (see Fig2B) subtracted and set to unity. Note the similar results for two different incident photon angles (solid and dashed curves).
- D. X-ray absorption coefficient for Fe_2O_3 over the $\text{Fe}2p_{3/2}$ and $2p_{1/2}$ levels as measured in this work (solid curve) and from ref. 10 (dashed curve).
- E. O1s intensity in resonance with $\text{Fe}2p_{3/2}$ and $2p_{1/2}$ in Fe_2O_3 after normalization of the nonresonant contribution. Note the difference between the solid and dashed curves, obtained at varied electron entrance angle and fixed photon-electron angle.

The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample provided another example of O1s resonating with the Mn2p levels. In this case, the effect was as large as 33% and integrated to 17% over the Mn2p_{3/2}. Resonance between the O1s and the $\text{La}3d_{5/2,3/2}$ levels exhibited O1s enhancements of up to ~100% and an integrated effect of 29% over the $\text{La}3d_{5/2}$ edge. Finally, resonance between the Mn2p and the $\text{La}3d_{5/2,3/2}$ levels show a maximum and integrated enhancement of 60% and 20%, respectively. In each case, we were able to demonstrate agreement of our own extracted X-ray absorption coefficient with previous results [11, 12, 13].

DISCUSSION

For each case considered above, the resonance enhancement or MAPRE signal is seen to be a significant contribution to the non-resonant intensity. Through monitoring of the inelastic background intensity upon which the photoelectron peak lies, the X-ray absorption coefficient of the level may be reliably extracted. Note also the similarity between the x-ray absorption profile and the MARPE profile. The MARPE signal closely if not exactly follows the x-ray absorption in each case studied.

In Fig. 3C, note that the resonance profile has been measured for two cases differing only in the incident photon angle. Within the statistics of the experiment, the curves are indistinguishable. This is important evidence that the effect is in fact due to MARPE and not to any X-ray attenuation length changes as the edge of the deeper level is crossed.

In Fig. 3E, we demonstrate evidence for angular dependence in the resonance effect. For two different photoelectron emission angles, the resonance curves have similar, but obvious differences. Furthermore, the energy integrated magnitude of the effect differs: over the $\text{Fe}2p_{3/2}$ portion of the curve, the normal emission case ($\theta = 90^\circ$) shows an enhancement of 24% compared to 17% for the 45° off-normal emission case.

CONCLUSIONS

Future study of this effect promises to be quite rewarding. The very existence of the MARPE effect, especially at the magnitudes so far observed, is inherently interesting. Further investigations of the effect are therefore justifiable simply to further understand the basic process.

Even more interesting is the potential of this effect to be used as a quantitative tool in determining near-neighbor bond information. Initial theoretical calculations have indicated that the resonance will be primarily between near-neighbor atoms and the magnitude of that effect will be very sensitive to the atomic separations.

In both cases, it will also be interesting to observe the effect in new systems and with different methods. Besides the photoelectron spectroscopy used to record the presented data, one could observe the secondary Auger electrons emitted in process. Similarly, the secondary fluorescent photons could also be monitored, with the experiment then becoming much more bulk sensitive.

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Photo Double Ionization of Neon

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Double ionization of an atom by a single photon has been the topic of many investigations in the recent years. Most efforts have focused so far on helium [1,2] resulting in the complete determination of the final state (apart from the electron spins) at 1 eV and 20 eV above the threshold. Recent convergent close-coupling calculations by Kheifets and Bray [3] show a good agreement in shape and absolute scale of the fully differential cross sections with our experimental data. Besides helium also other noble gases have attracted some interest (see i.e. [4]) as they allow the study of the initial state's influence on the photo double ionization process.

We have tried to extend our highly successful technique of cold target recoil ion momentum spectroscopy [2] to measure the fully differential cross sections for photo double ionization of neon. This technique relies on the measurement of the momentum of both the electron and the doubly charged recoil ion. The second electron can then be calculated via momentum conservation. However, the error in the measurement of the ion's momentum scales linear with the ion's mass. It thus turns out, that the momentum resolution for the Ne^{2+} ion is not sufficient to achieve reasonably accurate cross sections.

Based on previous experiences with multi-hit detection techniques for molecular fragmentation [5] we have modified our experimental setup to detect both electrons up to 15 eV energy with a geometrical solid angle of 4π on the electron detector in addition to the recoil ion. This geometrical solid angle however is reduced by the pulse pair resolution of our detection system. Only signals which are more than 15 ns apart in time can be clearly resolved. This means that certain regions of the emission angles will be lost. With this setup, in contrast to our earlier experiment, the recoil ion is used only for background suppression, while the cross sections are obtained directly from the two electrons.

First experiments were performed at the bending magnet beam line 9.3.2 of the ALS with linearly polarized light. The Stokes parameter S_1 has been determined experimentally to $S_1 = 0.94 \pm 0.03$. Fig. 1 shows the energy sum of both electrons at a photon energy of 72.8 eV. The ^3P ground state and the ^1D first excited state of the Ne^{2+} recoil ion are clearly resolved. The ^1S second excited state is very weak and can be seen as a shoulder at 3.3 eV. The single electron energy distribution is shown in fig. 2. For the ^1D final state this distribution is basically flat as in the case of helium. For the ^3P ground state however the distribution has two peaks, one at the low energy end and the other at the high energy end. These are the result of single ionization and excitation to the $1s^2 2s 2p^5 3s \ ^4\text{P}$ state of Ne^+ with the ejection of a photo electron with 2.6 eV energy. The excited state then decays via autoionization by emitting an electron of 7.6 eV energy. This process is energetically possible only for the ^3P final state of Ne^{2+} .

Further analysis is still in progress and while fully differential cross sections have been obtained their interpretation is complicated as the regions of the final phase space which are lost due to the pulse pair resolution have to be taken into account. Based on these experiences we are currently

Figure 1: Energy sum of both electrons at 72.8 eV photon energy. The two lines result from photo double ionization events with the remaining Ne^{2+} ion in the ^3P ground state (line at 10 eV) and in the ^1D first excited state (line at 7 eV). The ^1S excited state is visible as a shoulder at 3.3 eV.

testing a detection system with improved pulse pair resolution. In addition future experiments are planned at other energies where the autoionizing state of Ne^+ will not be populated and where the ^1S state can be clearly seen above the background. Especially the ^1S state is of interest as it resembles the helium case most closely, although the electrons final state is an overlap of ϵsep and ϵped states whereas in helium only ϵsep is allowed.

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Figure 2: Single electron energy distribution at 72.8 eV photon energy: solid line 3P final ionic state, dashed line 1D final ionic state.

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Beamline 10.0.1 Abstracts

Angular Distribution Measurements of the Xenon $N_{4,5}O_{2,3}O_{2,3}$ Auger electrons

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INTRODUCTION

We measured the angular distribution of the Xe $N_{4,5}O_{2,3}O_{2,3}$ Auger lines, after ionization of free Xe atoms by monochromatized synchrotron radiation of 140-210eV photon energy. In the framework of the two-step model of Auger decay the alignment of the primary hole states $4d^{-1} {}^2D_{3/2}$ and $4d^{-1} {}^2D_{5/2}$ could be derived. This quantity yields important information about the behavior of the dipole matrix elements around the Cooper minimum of the $4d$ photoionization cross section. Angular distribution and spin polarization measurements of Auger electrons give valuable insight into the primary photoionization process which is governed by the dipole interaction and the successive radiationless decay process which is governed by the Coulomb interaction.

The transition from the single-hole to the double-hole state is described by the Coulomb operator, which is a scalar operator. This means, that Auger electrons from an isotropic initial state can have only an isotropic angular distribution and no spin polarization. The photoionization process usually leaves the singly charged photoion in a polarized state, i.e. with an anisotropic charge distribution. Thus, decay of a polarized photoion may lead to an anisotropic angular distribution and also to spin polarization of Auger electrons [1, 2].

Up to now a thorough investigation of the angular distribution of the Auger decay process which follows the $4d$ photoionization was done only up to 142eV photon energy [3]. Between 150 and 190eV four data points with large uncertainties exist [4]. The major difficulty in performing these measurements above 150eV photon energy is the relatively low $4d$ photoionization cross section (<1 Mb) which results in very weak Auger lines. An additional problem is posed by the $4p$ photo-lines ($E_{\text{bind}} \approx 146\text{eV}$) which overlap with the $N_{4,5}O_{2,3}O_{2,3}$ Auger group in the 175-188eV photon energy range.

EXPERIMENT

The experiment was carried out at the AMO undulator beamline 10.0.1 of the Advanced Light Source. Gratings with groove density of 925 lines/mm and 2100 lines/mm were used for operating at photon energies below and above 160 eV, respectively. High photon energy resolution was not required for the present measurements; photon bandwidths in the range of 40-150 meV were obtained using the 925 lines/mm grating in combination with entrance and exit slit widths of 100 and 100 μm . The 2100 lines/mm grating with entrance/exit slit settings of 100 and 800 μm provided photon bandwidth between 380 and 600 meV at the photon energies from 160 to 210 eV.

The electron spectra were measured using an endstation designed for gas-phase angle-resolved studies and based on the Scienta SES-200 hemispherical analyzer [5]. The analyzer is rotatable in a plane perpendicular to the propagation direction of the beam of linearly polarized photons (the degree of linear polarization is estimated to be higher than 99%), allowing studies of the angular distribution of electrons. The analyzer was operated at the constant pass energy of 40 eV with the electron energy resolution of 25-30 meV. The spectra were not corrected for the transmission of the analyzer, which was assumed to be independent of the measurement angle. The target gas was introduced into a differentially pumped gas cell, achieving about 10^{-3} mbar pressure in the interaction region.

Figure 1. Xe N_{4,5}O_{2,3}O_{2,3} Auger group after excitation by 160.4 eV photons taken at three different angles, after subtracting a linear background. The resolution of the electron spectrometer was approx. 30 meV. The solid lines represent the sum of fitted Voigt-profiles. All three spectra are normalized to the same scale. Notations in *italic* refer to N₅ lines.

THEORETICAL BACKGROUND

In the two-step model of Auger decay, i.e. the photoionization and Auger decay processes are assumed to proceed subsequently and independently of each other, the angular anisotropy parameter can be factorized into a parameter describing the anisotropy of the primary hole state and into an ‘intrinsic’ parameter α_2 describing the Auger decay itself [1]:

$$\beta = \alpha_2 A_{20}. \quad (1)$$

A_{20} is the alignment parameter of the primary hole state and is proportional to its electric quadrupole moment. A_{20} is given here with respect to the direction of the electric field vector $\mathbf{E}$. Whereas the Auger anisotropy parameter α_2 depends on the Coulomb matrix elements, A_{20} is connected to the dipole matrix elements.

The description of the photoionization process in the framework of the dipole approximation limits the possible values of the orbital angular momenta of the outgoing photoelectrons through the selection rules. Thus, in the case of the $4d$ ionization, the electrons can leave the atom as ϵp or ϵf continuum waves. In the nonrelativistic approximation, i.e. when the spin-orbit interaction in the continuum is neglected, there are only the two outgoing waves ϵp and ϵf and the photoionization cross section is determined by the single-particle radial matrix elements $R_{4d,\epsilon p}$ and $R_{4d,\epsilon f}$ [6]. Using the density-matrix and statistical-tensor formalism, Berezhko et al [7] showed, that the alignment tensor depends only on the ratio of the dipole amplitudes

$$A_{20}^{5/2} = -\frac{1}{5} \sqrt{\frac{2}{7}} \frac{2 + 7\lambda^2}{1 + \lambda^2}, \quad A_{20}^{3/2} = -\frac{1}{10} \frac{2 + 7\lambda^2}{1 + \lambda^2} \quad \text{with } \lambda = \sqrt{\frac{2}{3}} \frac{R_{4d,\epsilon p}}{R_{4d,\epsilon f}}. \quad (2)$$

In the nonrelativistic approximation the ratio of the alignments for the different final states is a fixed number

$$A_{20}^{5/2}/A_{20}^{3/2} = \sqrt{8/7}. \quad (3)$$

The extrema of the alignment can be easily derived, when either the εp or the εf wave completely vanishes. For $R_{4d,\varepsilon p}=0$, $A_{20}^{5/2}=-0.214$ and for $R_{4d,\varepsilon f}=0$, $A_{20}^{5/2}=-0.748$ [6].

Theoretical A_{20} values in dependency of the photon energy were published by several authors. Hartree-Fock calculations were performed by Kennedy and Manson [6] and by Berezhko et al [7]. Cherepkov [8] carried out calculations using the random-phase approximation with exchange (RPAE). All these authors treated the photoionization process in the nonrelativistic approximation.

RESULTS

Fig. 2 shows $A_{20}^{5/2}$ together with other experimental data and theoretical curves. The agreement between all experimental data is very good up to 142 eV photon energy. At higher energies a considerable discrepancy between our results and those of Southworth et al. [4] can be seen. The earlier data has large uncertainties and doesn't show a pronounced minimum.

The overall shape of all theoretical curve is similar, showing a clear minimum at higher energies. Whereas the RPAE calculation of Cherepkov gives the position of the minimum at 6 eV lower energy than experiment, all other calculations predict the minimum at either 30 eV lower energy Hartree-Slater model of Ref. [7] or at 30 eV higher energy Hartree-Fock model of Ref. [7] and Ref. [6]. To get a better idea about the course of the A_{20} curve, we modified the RPAE curve by stretching it to higher energies to match the minimum of the experimental data. In this way we obtain a good agreement with a slight deviation around 145 eV. This deviation might be due to the fact that the 4p threshold is approx. at 146 eV photon energy and this was not taken into account during the calculations.

As described above, A_{20} can reach two extrema for vanishing p- or f-waves. (cf. Eq. (3)). Due to the potential barrier for f-electrons near threshold ($E_{\text{bind}}(4d_{5/2})=67.54$ eV), the outgoing p-waves dominate the photoionization. At increasing energies, the f-electrons overcome the barrier and carry almost all the cross section in the maximum of the shape resonance (~ 100 eV). In the Cooper minimum $R_{4d,\varepsilon f}$ changes sign, i.e. only the p-wave is present at ~ 176 eV. Whereas the first two extrema were confirmed by the previous experiments, we could prove the existence of the A_{20} minimum in the Cooper minimum of the cross section.

SUMMARY

Using the framework of the two-step model of Auger decay we determined the alignment A_{20} of the $4d^{-1} 2D_{3/2}$ and $2D_{5/2}$ photoions at different excitation energies including the very important region of the 4d photoionization Cooper minimum around 180 eV. By obtaining an A_{20} value of $-0.73(4)$ at 176 eV photon energy, we could experimentally prove for the first time, the vanishing of the εf component of the outgoing electron wave. This is in good agreement with theoretical predictions, taking into account a small deviation in the position of the predicted minimum. An important implication of the present result is that with $R_{4d,\varepsilon f}=0$ at 176 eV all dynamical parameters of photoionization have fixed values at this energy.

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Figure 2. Alignment A_{20} of the Xe $4d^{-1} 2D_{5/2}$ hole state. The stars show the extreme values of A_{20} in LS-coupling for vanishing f-wave (at threshold and in the Cooper minimum) and vanishing p-wave in the cross section maximum (cf. Eq. (3) and text). The dashed curve was obtained by stretching the calculation of Cherepkov to match the A_{20} minimum.

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Angular Distributions of Molecular-Field and Spin-Orbit Split Core Levels of Sulfur 2p Photoemission in OCS: A Sensitive Probe of the Molecular Environment

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INTRODUCTION

The photoelectron spectra (PES) of inner-shell electrons in molecules can be subtly perturbed by the molecular environment in which they are embedded. Large spin-orbit splittings of core orbitals in heavier atoms are commonly observed in molecular PES, but the much smaller molecular field splittings require high energy resolution for their experimental observation.

The angular distributions of photoelectrons are sensitive probes of the potential field experienced by the departing electrons. In the case of molecules, the angular distributions of electrons leaving inner-shell orbitals can be altered due to scattering from neighboring atoms into many partial waves, and they are also influenced by molecular vibration and rotation. To date, only experiments on spatially oriented diatomic molecules have been able to probe the molecular (body-frame) environment in angle-resolved photoemission studies [1]. In such experiments, the photoelectrons are detected in coincidence with ionic fragments of the molecule at selected angles. It is, however, very difficult to obtain sufficiently high count rates together with high energy resolution in such coincidence experiments.

EXPERIMENT

Non-coincidence PES measurements of angular distributions, with their high count rates and high energy resolution, can provide an alternative to coincidence techniques by fully resolving the effects of spin-orbit and molecular-field splittings. We measured angle-resolved PES of sulphur 2p of the carbonyl sulphide (OCS) molecule with completely resolved spin-orbit, vibrational, and molecular field splittings, and provided a supporting theoretical interpretation for the experimental anisotropy parameters [2].

The experiment was carried out at beamline 10.0.1. The photon beam, monochromatized by a spherical grating monochromator operating at about 10,000 resolving power, interacted with the target molecular gas in an experimental station equipped with a Scienta SES-200 electron energy analyzer designed for angle-resolved gas-phase electron spectroscopic measurements. The analyzer, which is rotatable in the plane perpendicular to the propagation direction of the linearly polarized incoming photon beam, was set to provide an electron energy resolution of about 25 meV, resulting in an overall instrumental broadening of 30 to 35 meV.

Figure 1 shows the S 2p PES, excited by 191 eV photons, taken at different angles relative to the polarization plane. The molecular field splitting into three different components (marked by A, B and C) as well as the vibrational splitting are clearly resolved. Spectra similar to Fig. 1 show that the angular distributions of the components B and C are different over broad photon energy range, an effect specific to the molecular environment.

THEORY

The origins of the spectral features reported in Fig. 1 can be understood quantitatively on basis of the specific forms of the wave functions describing the spin-orbit, vibrational, and molecular-field split core-excited ionic states of good total electronic angular momentum along the internuclear axis. The measured $\beta(B)$ and $\beta(C)$ values are shown by theoretical analysis to provide the anisotropy parameters $\beta(2p\sigma)$ and $\beta(2p\pi)$, which are generally inaccessible separately due to the near degeneracy of these inner-shell ionic states. The latter values, furthermore, provide body-frame information in the absence of explicit sample alignment.

Figure 1. Sulphur 2p photoelectron spectra of the OCS molecule excited by 191 eV photons. The molecular field split components are marked by A, B and C.

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Auger decay of the C 1s⁻¹2π* resonance in carbon monoxide: vibrationally and angularly resolved spectra

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INTRODUCTION

Resonant photoexcitation of carbon 1s electrons to the lowest empty molecular orbital, 2π*, gives rise to the dominant pre-edge feature in the C 1s photoabsorption spectrum. The C 1s→2π* excitation displays a vibrational progression corresponding to the population of different levels of the excited state, in which the strongest v=0 peak is accompanied by transitions to the higher levels, v=1 and 2, with rapidly decreasing intensity. In previous experiments [1,2], it has been possible to completely resolve the vibrational structure of the Auger decay spectra of the lowest level of the 1s⁻¹2π* state, whereas the decay spectra of the higher levels have been obtained only with considerably lower experimental resolution. Vibrationally resolved Auger electron spectra from the higher vibrational levels provide richer and more precise information about the shapes of the potential energy curves and transition intensities to different final ionic states. The present experiment provides such information, which is compared with the latest theoretical results. In addition, angular distributions of the individual vibrationally resolved peaks in the Auger electron spectra have been obtained.

To obtain a more complete picture of the Auger decay processes in resonantly excited CO, we employed two complementary experimental techniques -- high-resolution angle-resolved measurements at the resonance maxima using hemispherical electron energy analyzer and electron time-of-flight (TOF) measurements in combination with two-dimensional mapping of the photon and electron kinetic energy.

EXPERIMENT

The experiment was carried out at the undulator beamline 9.0.1 at the ALS (later relocated to 10.0.1). VUV radiation was monochromatized with a spherical grating monochromator using a grating with a groove density of 2100 lines/mm. For the high-resolution measurements, an end station based on the Scienta SES-200 hemispherical electron analyzer and designed for angle-resolved gas-phase studies was used. The analyzer is rotatable in a plane perpendicular to the propagation direction of the beam of linearly polarized photons, allowing studies of electron angular distribution. An electron energy resolution of 25-30 meV (at 40 eV pass energy) was used for these measurements. A photon bandwidth of about 60 meV was used when recording the Auger electron spectra and a smaller bandwidth of 45 meV was used for additional lineshape studies.

The data set for two-dimensional imaging was collected using two electron time-of-flight analyzers, mounted 125.3° apart and perpendicular to the photon beam [3]. The photon energy was scanned over the resonance in 20 meV steps using 60 meV bandwidth.

Figure 1. Electron energy spectra of the decay from the C $1s'2\pi^*$ $v=0,1,2$ resonances, taken at the magic angle relative to the polarization plane. Also shown is a nonresonant photoelectron spectrum measured at $h\nu=280$ eV.

Figure 2. Electron energy spectra of the decay from the $v=2$ level of the C $1s'2\pi^*$ resonance, taken at 0° and 90° relative to the polarization plane. Lower panel shows the anisotropy parameter β .

RESULTS

Auger electron spectra were measured at selected photon energies, corresponding to the C $1s \rightarrow 2\pi^*$ absorption maxima, using the hemispherical analyzer. The spectra are shown in Fig. 1, together with a photoelectron spectrum taken well below the resonant absorption energy. The spectra were measured at 54.7° relative to the polarization plane of the light and are scaled to equal intensity for the ease of comparison. The overall intensity of the spectra taken at the $v=1$ and 2 absorption peaks is about 13% and 1.4%, respectively, of the intensity of the spectrum taken at the strongest $v=0$ peak.

The vibrational envelopes of the spectra in Fig. 1 can be compared with theoretical simulations [4]. There is excellent agreement between theory and experiment, indicating that the calculated potential energy curves describe the core-excited and final ionic states very well.

Fig. 2 shows angle-resolved Auger electron spectra from the weakest $n=2$ level of the resonance. The anisotropy parameter β varies significantly within the vibrational envelopes of the low-binding energy states. These CO' states are also accessible by direct photoionization and we therefore ascribe the variations in β to the contribution from and interference with the nonresonant photoionization process. The states at higher binding energies are not accessible by direct photoionization and the spectator Auger decay to these states provides the only opportunity for electron spectroscopic studies. There are a number of strongly overlapping ionic states present in this energy region, with bonding and antibonding character. The present high-resolution spectra allow us to identify the character of these states and develop the theoretical model correspondingly.

The comparison of the Auger decay spectra from different levels of the excited state allows better assignment of these states. It can be seen from Fig. 2 that the β parameter

displays strongly oscillating behavior in the high binding energy region. From these oscillations, we were able to determine the angular properties for the Auger transitions to individual electronic states.

TWO-DIMENSIONAL IMAGING

An intensity map of electron emission following photoexcitation of CO across the C $1s \rightarrow 2\pi^*$ resonance is shown in Fig. 3. The map is constructed from a series of electron energy spectra recorded at small steps over a broad range of photon energies. The X and Y axes of the map represent the binding energy of emitted electrons and the energy of absorbed photons, respectively.

2D images provide a direct means to observe lifetime vibrational interference effects by following the intensities of individual vibrational peaks in the Auger electron spectra as a function of photon energy. The intensity of the $v'=1$ line of the $1^2\Sigma^+$ transition reaches its second maximum (corresponding to the $v=1$ absorption peak) at lower photon energy than does the intensity of the neighboring $v'=0$ and 2 lines. Also, the minimum between the first and second maxima is very shallow compared to the minima in the intensity of the $v'=0$ and 2 lines. Similar behaviour can be seen in the vibrational envelopes of the $1^2\Pi$ and $2^2\Sigma^+$ final states. These effects are clear indications of significant vibrational lifetime interference between different Auger decay pathways, which naturally emerges in the single-step treatment of the excitation-deexcitation processes.

Figure 3. Intensity map of electron emission over the C $1s \rightarrow 2\pi^*$ photoexcitation region as a function of electron (X axis) and photon (Y axis) energies. The area between dashed lines is reproduced above the main panel, emphasizing low-intensity areas. The right-hand panel shows the integrated electron yield over the given energy range. Assignment of final states is given above the map.

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Beamline 10.0.1 – an undulator beamline for high-resolution spectroscopy in the 17-340 eV range

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INTRODUCTION

Beamline 10.0.1 was installed to support programs in high temperature superconductivity research and in atomic and molecular spectroscopy. The beamline was constructed and saw its first light in June 1998. A new 10cm period undulator was constructed by the ALS Insertion Device Group and installed in the sector 10 straight section of the ALS storage ring during the spring 1998 shutdown. A specification for the personnel safety shutter/photon shutter assembly was developed by the ALS Mechanical Engineering group and the fabrication contract awarded to Oxford Instruments. The shutter assembly was also installed during the spring shutdown. The majority of the rest of the beamline was moved from Beamline 9.0.1 during the period of March – June 1998. New mirrors were fabricated to replace the horizontally focusing M1 mirror that remained with BL9.0.2 and to produce small horizontal foci in the two side branches of the beamline.

OPTICAL LAYOUT

The optical layout of beamline 10.0.1 is similar to that of its predecessor, BL9.0.1. Spherical mirrors and gratings deflect, focus, and disperse the radiation from the U10 undulator.

Figure 1. Schematic layout of Beamline 10.0.1 optics in plan and elevation views. The numbers indicated at the top of the figure indicate the distance of the center of the optical element from the center of the undulator along the optical path. Three different experimental end stations are available with horizontal foci at different distances from the refocusing optics as indicated.

Radiation from the undulator is horizontally focused by the water cooled M1 mirror to a point 28.4m downstream from the mirror. While this location is actually outside of the ALS building, it was chosen to provide a highly collimated beam with a maximum width of 1.5mm at the position of the ion beam experiment on the central branch line. The long focal length of the mirror also plays a role in the demagnification of the M4 and M5 mirrors for the side branches. The water cooled M2 mirror focuses the undulator radiation vertically and forms an 8:1 demagnified image of the source at the entrance slit

of the monochromator. The demagnification is crucial to the performance of the beamline as it permits all of the undulator radiation to be passed through the small entrance slit required for high spectral resolution. The entrance slit opening is variable over 0 – 150 μ m to allow a suitable compromise between intensity and resolution.

One of three water cooled diffraction gratings can be positioned in the beam path following the entrance slit, depending on the photon energy required. The low energy grating with a ruling density of 380 lines/mm covers the photon energy range from 16 to 61 eV, the medium energy grating with a ruling density of 925 lines/mm covers the range from 40 to 150 eV, and the high energy grating with a ruling density of 2100 lines/mm covers 90 to 340 eV. The energy range of each grating is limited both by the geometry of the beam path and the length of travel of the exit slit. The exit slit, which translates along the beam path to remain in the focus of the grating as it is rotated to select the appropriate wavelength or photon energy, has a variable opening from 0 to greater than 500 μ m. The exit slit is the first uncooled component of the beamline. Following the power filtering of the upstream mirrors and the dispersion of the gratings, the power density of the photon beam at the exit slit is sufficiently reduced to allow the use of uncooled optics.

The variable radius M3 mirror vertically refocuses the light and forms an image of the exit slit into the experimental apparatus. The mirror is bent by a flexural hinge with a large piezo crystal. The radius of the mirror is variable from 35-65m allowing the focus to be moved between the end-stations. Two horizontally focusing deflection mirrors can be inserted into the beam to deflect it at a 14° angle into one of two side branches of the beamline. These mirror use the image of the first horizontal mirror in the beamline (the M1 mirror) as a virtual object and form a demagnified image 2.5m and 4.0m downstream for the outboard and inboard branches respectively.

Table 1. Parameters for the optical elements within beamline 10.0.1.

Mirror	Coating	Cooling	Deflection	Deflection	r (m)	r' (m)	R (m)
M1	Ni	Water	Horizontal	9°	16.0	28.4	391.1
M2	Ni	Water	Vertical	9°	18.4	2.3	51.2
325 l/mm	C	Water	Vertical	15°	1.45	4.00–4.77	21
925 l/mm	C	Water	Vertical	15°	1.45	4.00–4.77	21
2100 l/mm	Ni	Water	Vertical	15°	1.45	4.00–4.77	2
M3	Ni	None	Vertical	6°	1.8-2.6	2.5 – 8.5	35-65
M4	Au	None	Horizontal	14°	-15.3	2.5	49.0
M5	Au	None	Horizontal	14°	-15.3	4.0	88.9

FLUX OF BEAMLINE 10.0.1

No significant changes are expected in the flux of beamline 10.0.1 relative to its predecessor, beamline 9.0.1 as they use the same source, mirror angles, mirror coatings, slits, and gratings. The transmitted flux of the beamline was evaluated for slit settings corresponding to a resolving power ($E/\Delta E$) of 10,000. The flux of the undulator was calculated at 400 mA of stored current in the storage ring at 1.9 GeV. Geometrical factors corresponding to the masking of the beam by the entrance and exit slits and the overfilling of the grating at some energies were included in the calculation. Reflectivities

of the mirrors were obtained from the CXRO web site (www-cxro.lbl.gov) and the grating efficiency calculated by a scalar theory formula. Combining all of these factors together yields the data presented in figure 2. The two curves for each grating correspond to the flux on the central and side branches and result from the reflectivity of the 7° horizontal focusing mirror. Note that this mirror has a cut off starting at 140 eV where the reflectivity drops from approximately 80% to less than 20% above 200 eV. Notice that the flux is greater than 10^{12} photons per second over most of the range covered by the beamline.

Figure 2. Flux of radiation from beamline 10.0.1 at a resolving power ($E/\Delta E$) of 10,000. Details of the factors included in the calculation are described in the text. There are two curves for each grating (as indicated on the figure by their line densities; 380, 925, 2100 lines/mm). The upper curve corresponds to the flux on the central branchline and the lower curve the flux on either of the side branch lines.

RESOLUTION OF BEAMLINE 10.0.1

The resolution of beamline 10.0.1 should be unchanged from the previous beamline 9.0.1 since none of the resolution determining elements have been changed. The resolution of a spherical grating monochromator is determined by the size of the slits, the dispersion of the grating and contributions from various aberrations. In figure 3 the resolution of beamline 10.0.1 is calculated for slit settings of 10 μ m. In addition to contributions from the slits, the effect of the coma aberration from the grating is included in the resolution evaluation. Contributions from the slits and coma are indicated separately by the two lighter lines for each grating and the two are added in quadrature to yield the total resolution of the beamline.

Figure 3. Contributions of 10 mm slits and coma to the resolution of beamline 10.0.1 for each of the three gratings. The contributions of the slits are shown by the light lines which increase with photon energy and the contributions from grating coma by the light lines which dip near the center of the range of the grating. The sum of the two contributions is shown by the heavier line.

It is apparent that there is a minimum in the coma contribution for each grating near the center of its range. This coma zero occurs when the positions of the slits and grating angle are at the Roland circle geometry which occurs at approximately 29, 70 and 162 eV for the 380, 925 and 2100 line/mm gratings respectively.

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Construction and Commissioning of the High Energy Resolution Spectrometer (HERS) for the Study of Highly Correlated Materials

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INTRODUCTION

This endstation was designed to study highly correlated materials, including the high temperature superconductors with unprecedented resolution. As many feel that the most useful clues to understanding these fascinating materials will come from angle-resolved photoemission data (ARPES) the 100 fold increase in momentum resolution afforded by the HERS endstation will provide many of the clues to understanding the High T_c materials.

THE ANALYZER

The electron energy analyzer is a commercial unit purchased from Gammatdata-Scientia AB. As Fig. 1 demonstrates, the energy resolution from this instrument is excellent. Fig. 1A we display the photoemission spectra of the fermi-edge function from a polycrystalline gold sample at temperature of 10 K. With thermal broadening of $4.4 \cdot kT$ or 4 meV at 10 K, the combined analyzer and beamline energy resolution is 8 meV. Fig. 1B is the photoemission spectrum of the Ar $3p_{3/2}$ core level taken using 25 eV synchrotron radiation from beamline 10.0.1.1. The full width at half maximum of the peak is 8 meV. Taking into account the natural line width and Doppler broadening of the Ar 3p line, the total contribution from the beamline and the analyzer is 3 meV.

In addition to the excellent energy resolution, the analyzer also demonstrated very good angular resolution. When operating in the angular mode, the analyzer lens system focus changes so that the lens diffraction plane is at the entrance slit to the analyzer. This allows the two-dimensional focusing of the hemispheres to maintain the angle with which the electrons left the sample. Using the proper image-capturing equipment we can at one time collect and energy analyze electrons leaving the sample within a cone of $\pm 7^\circ$ with 0.2° resolution. This angular resolution is an order of magnitude increase in resolution over previous equipment apparatus. In Fig. 2, we show the

Fig. 1. Energy resolution demonstrated by the HERS analyzer and beamline 10.0.1.1. A. Au fermi-edge measured at 10 K using 25 eV photons. The combined analyzer and beamline resolution is 7 meV. B. Ar $3p_{3/2}$ photoemission line at 25 eV photon energy. The combined energy resolution here is 3 meV.

results of the angular mode testing. The electron source is a thin wire illuminated by 55 eV photons from the synchrotron beam. This wire is parallel to a slit array positioned 25 mm above it. The slits are 100 μm wide and spaced 500 μm center to center, which gives a spacing between slits of 1.3 degrees. This spectrum was collected using 5 eV pass energy. As can be seen in the figure, the angular resolution is excellent even at kinetic energies approaching the pass energy. Fitting a Gaussian to the individual peaks gives an angular resolution of $\pm 0.15^\circ$ when one accounts for the width of the source and width of the slit. While the intensity is uneven over several channels, we believe this is an artifact due to inhomogeneous graphite coating on the slit array.

An important feature of the endstation is the ability to rotate the analyzer about the incoming beam. The main chamber, where the electron energy analyzer is mounted rotates 120° about the incoming beam. Because the radiation from the storage ring is polarized in the plane of the ring, this rotation allows one to vary the polarization incident on the target from s to p while maintaining a constant emission angle from the sample. Two differentially pumped rotary seals mounted to the chamber allow the rotation while maintaining good vacuum. The chamber base pressure is less than 3×10^{-11} torr and there is no appreciable pressure change when the analyzer is rotated.

SAMPLE MANIPULATOR

The manipulator consists of two important parts. The first is the x, y, z stage. For this part we made use of existing technology and purchased a commercial mill table. The mill, while quite large, works very well in this application allowing very precise sample movements of 0.001" over the 37" of travel from the sample prep chamber to the analysis position in the main chamber. The sample polar rotation is accomplished by a differentially pumped rotary feedthrough to which the liquid helium cooled cryostat is mounted. The azimuthal rotation is cable driven through a rotary feedthrough. The rotational accuracy for both axes is 0.5° . With the LHe cooled cryostat the sample temperature can be controlled from 10 K to 450 K with better than one degree accuracy.

Also deserving of special mention is the sample transfer system. The reactive nature of the sample surface dictates that the experiments be performed at less than 5×10^{-11} Torr, in order to study surfaces that are representative of the bulk. Additionally, the samples cannot be baked. These two criteria require an excellent sample load lock

Fig. 2. The angular resolution of the HERS analyzer. The sample is a slit array of 100 μm wide slits spaced 500 μm center to center. The electron source is a 250 μm thick wire illuminated by 55 eV photons from beamline 10.0.1.1. Accounting for the angular size of the source and the slits, the demonstrated resolution is 0.3° . A. The image of slit array collected by the analyzer. B. A narrow cut at 25 eV kinetic energy showing the angular resolution and uniform intensity across 12 degrees.

system. The HERS system consists of three intermediate vacuum stages, which in practice allows the transfer of a fresh sample from atmosphere and on to the cryostat in 2 hours without baking while maintaining the prep chamber pressure of 4×10^{-11} torr.

Future Direction

With the initial commissioning of the endstation completed, work is now beginning on the high- T_c superconductors. Our initial experiments (detailed by Zhou in this compendium) are very encouraging. We see the promise that a 100 fold increase in momentum resolution holds for a qualitatively new understanding of correlated materials. In addition to the cuprates, we also plan to study the isostructural compounds nikelates, manganates and ruthenates. These materials have their own equally fascinating physics, which the HERS will help to understand.

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Electronic Structure of the Stripe Phase in $\text{La}_{1.28}\text{Nd}_{0.6}\text{Sr}_{0.12}\text{CuO}_4$

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INTRODUCTION

The stripe phase first proposed to explain neutron data from Nd-substituted $\text{La}_{1.28}\text{Nd}_{0.6}\text{Sr}_{0.12}\text{CuO}_4$ (Nd-LSCO) represents a new paradigm of charge carriers in a solid.[1] Unlike conventional metals where the charge distribution is homogeneous, the stripe phase envisage microscopic antiferromagnetic domains separated by one-dimensional domain walls (stripes) consisting of hole carriers and frustrated spins. The implication of this charge segregation propensity on the conduction as well as the superconducting mechanism is at the heart of the current debate in high- T_c research today. So far, much of the stripe information stems from interpretation of the incommensurate neutron scattering peaks. Very little is known about the electronic structure of these materials. Here we report angle-resolved photoemission data that directly probe the electronic structure and charge dynamics of the stripe phase.

Experimental

Angle-resolved photoemission spectroscopy (ARPES) measures the single particle spectral function $A(k, \omega)$ weighted by the photoionization cross section. The ARPES data have been recorded at the beamline 10.0.1.1 HERS endstation of the Advanced Light Source.[2] 55eV (rather than the typical 20-25 eV) photon energy was used for more efficient k -space sampling. Using the angular mode of the Scienta analyser, the momentum resolution was 0.02π , improved from traditional value of 0.14π (the unit of the momentum is $1/a$ with a being the lattice constant). The energy resolution is detuned from its optimal 7 meV to 16 meV so that a few thousand spectra with sufficient statistics can be obtained during the lifetime of a cleaved surface. For example, the 500 spectra presented in Fig. 1 were recorded within the first 3 hours after the cleaving. The vacuum during the measurement was $2-5 \times 10^{-11}$ Torr. The Nd-LSCO sample was grown using the travelling floating zone method. The same class of samples has been used for neutron scattering experiments.[1]

Results and Discussion

Fig. 1 presents typical ARPES spectra of Nd-LSCO sampled from the first and fourth quadrants of the Brillouin Zone (BZ) at a temperature of 20 K. Using the angular mode of the analyser, we can sample nearly a whole quadrant along k_x with 48 points at the same time, which correspond to the spectra in one panel (1 to 10); the whole Brillouin zone is then measured by taking various k_y cuts. It is clear from the figure that the spectra do not contain peak structure anywhere in the

BZ - a behavior which is quite different from the Fermi Liquid. Nevertheless, the data still show edge or cusp-like structures with clear angular dependence. As k_x moves from 0.10π to 1.17π , a broad feature moves from 200 meV or deeper towards the Fermi level E_F and stays there for an extended region near $k_x = \pi$. The detailed discussion of the peculiar electronic structure will be described elsewhere.

Figure 1. Angle-resolved photoemission spectra taken on Nd-LSCO at 20K. The measurement scheme is depicted in panel 12 which covers part of the first and fourth quadrants. Each of the panels 1-10 represents a cut along (0,0) to (π ,0) direction with k_x covering from 0.10π to 1.17π , while panels 1 to 10 represents 10 cuts along (0,0) to (0, π) direction, with k_y covering from -0.14π to 0.51π . Panel 11 shows the same spectra in panel 2 but with the high energy background removed.

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First spin-resolved gas-phase studies at the ALS

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To perform spin-resolved gas-phase experiments we have developed a new spectrometer system consisting of a time-of-flight (TOF) electron energy analyzer [1,2] combined with a retarding field Mott detector [3]. This instrument allows very effective data acquisition, because all electron lines in the TOF spectrum are spin-analyzed simultaneously with a high signal to noise ratio.

In a first investigation we have measured the spin polarization of the Xe $5p^{-1} 2P_{1/2,3/2}$ and $4d^{-1} 2D_{3/2,5/2}$ photolines parallel to the photon beam. The 5p measurements were primarily used to calibrate the polarization sensitivity (S_{eff}) of the Mott detector. The measurements were performed with linearly polarized light at the AMO undulator beamline 10.0.1 of the ALS storage ring.

Using linearly polarized light one component of the spin polarization vector, the so called dynamical polarization, can be measured. The origin of this electron spin polarization is a quantum mechanical interference effect, as opposed to the transferred spin polarization which originates from spin polarized photons and can be measured only with circularly polarized light. We measured the dynamical polarization in the photon energy range 80-210 eV. Comparison with theory shows a good agreement with RPAE calculations of Cherepkov [4] and also with a semiempirical prediction under 140 eV [5].

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High-Resolution (6-12 meV) Threshold Photoelectron Spectroscopy of Argon from 28 to 49 eV

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INTRODUCTION

We have measured the threshold photoelectron (TPE) spectrum of argon at high resolution (6-12 meV) using synchrotron radiation on beamline 10.0.1.2 of the Advanced Light Source over a wide spectral range (28-49 eV) encompassing the $(3s)^{-1} \text{Ar}^+$ main line, the entire associated satellite ionization region, and the onset region of the doubly ionized Ar states ^3P , ^1D and ^1S . These basic features are displayed in the overall high-resolution spectrum shown in Fig. 1.

Figure 1. Overall view of the high-resolution threshold photoelectron spectrum of Ar in the 28-49 eV region.

RESULTS AND DISCUSSION

It is now well known that the satellite ion states in atoms and molecules arise from correlation effects involving the simultaneous ejection of one electron and the excitation of another electron upon the absorption of a single photon. In the case of Ar, TPE spectroscopy has proven very useful in studying the valence satellite ionization region.¹⁻³ Numerous satellite ion and resonance states have been discovered and assigned. In this work, because a higher resolution was achieved (by a factor of 4 or more) than in any previous study, we observe many new satellite ion and resonance states. In some cases we observed satellite ion states predicted on the basis of

expectation but not actually observed as resolved peaks. An expanded view of our high-resolution TPE spectrum of Ar in the main satellite ionization region is shown in Fig. 2.

Figure 2. Expanded view of the high-resolution threshold photoelectron spectrum of Ar in the main satellite ionization region.

One interesting aspect of this TPE study is the first observation of a number of rather broad peaks immediately preceding the $(3s)^{-1}$ main line of Ar^+ as shown in Fig. 3. We tentatively identify these as being due to the formation of neutral $(3s^1 3p^6) nl$ Rydberg states converging on the $^2S_{1/2}$ ion state. We believe these states are detected by us as near threshold (3 meV) electrons via autoionization of the $(3s^2 3p^5) ll's'$ Rydberg state forming the Ar^+ ($^2P_{3/2}$) ion following fluorescence from the initially formed Rydberg states. A complete analysis of the TPE spectrum is currently underway.

Figure 3. Neutral Ar resonances preceding the $(3s)^{-1}$ main line of Ar^+ in the threshold photoelectron spectrum.

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High-Resolution Carbon 1s Photoelectron Spectrum of Small Molecules

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INTRODUCTION

A challenge for inner-shell photoelectron spectroscopy has been the study of organic molecules in which the carbon atoms have similar ionization energies even though they are quite distinct chemically. Only recently has it been possible to resolve the contributions from these carbons in the carbon 1s photoelectron spectrum of this molecule and to correlate the ionization energies with the reactivity.[1] The very high resolution capabilities of the Advanced Light Source present a long-awaited opportunity to examine inner-shell photoelectron spectra of such molecules and to gain chemical insights that were previously inaccessible.

The complete analysis of such a spectrum requires an understanding of a number of factors: the vibrational excitation that occurs during ionization, the line broadening that results from the finite lifetime of the core-ionized state, and the distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole). In addition it is necessary to understand the instrumental features that affect the spectrum. These include the calibration of the energy scales of the monochromator and electron-energy analyzer, the resolution of the photon beam, the resolution of the electron-energy analyzer, and the variation of the analyzer transmission with electron energy.

Our program during 1998 aimed at providing a basis for this understanding with extension of our earlier work on CH₄, CO, CO₂, CF₄, and H₂C=CH₂ to include HCCH, CH₃CH₃, CH₃C≡CH, CF₃C≡CH, CH₃C≡CCH₃, CF₃C≡CCF₃, CF₃CH₂CH₃, and H₂C=C=CH₂. Although analysis is still in progress for much of the data, interesting results have been obtained for ethyne (HCCH), propyne (CH₃C≡CH) and methane (CH₄). These are summarized below.

CARBON 1s PHOTOELECTRON SPECTRUM OF ETHYNE [2]

When core-ionization takes place in a molecule, there is typically vibrational excitation of the resulting ion, leading to vibrational structure in the photoelectron spectrum. The carbon 1s ionization spectrum of ethyne shows additional structure because there are two closely spaced molecular orbitals (1σ_g and 1σ_u) resulting from combination of the equivalent atomic carbon 1s orbitals. This effect can be seen in the spectrum shown in Fig. 1, measured using the high-resolution beamline for atomic and molecular physics. In this spectrum the principal peak is due to the transition to the vibrational ground state of the ion. The most prominent part of this peak results from

Figure 1. Carbon 1s photoelectron spectrum of HCCH

ionization of the $1\sigma_g$ orbital and the shoulder at lower ionization energy from the $1\sigma_u$ orbital. The u-g split shoulder on the high-energy side of the peak results from the $v = 1$ excitation of the carbon-carbon stretching mode. It is apparent that the cross section for $1\sigma_u$ ionization is less than that for $1\sigma_g$ ionization.

That the intensities for these two ionizations are not the same is related to the existence of a σ_u shape resonance in the photon energy range studied here, and is of especial interest because of on-going discussion of the criteria for identifying such shape resonances. In the spectrum shown in Fig. 1 the intensity for $1\sigma_g$ ionization is enhanced, since the transition $1\sigma_g \rightarrow k\sigma_u$ is allowed by dipole selection rules but the transition $1\sigma_u \rightarrow k\sigma_u$ is not. We have mapped out the ionization intensity ratio ($1\sigma_u/1\sigma_g$) as a function of photon energy, and these results are shown in Fig. 2a. Combining these with measurements of the carbon 1s ionization cross section [3], we obtain cross sections for the ionization of the $1\sigma_g$ and $1\sigma_u$ orbitals. These are shown in Fig. 2b, where they are compared with theoretical predictions of the cross sections [4]. Both theory and experiment show a cross section for $1\sigma_u$ ionization that decreases monotonically with increasing photon energy and a cross section for $1\sigma_g$ ionization that has a peak. The theoretical ionization intensity ratio ($1\sigma_u/1\sigma_g$), shown as the solid curve of Fig. 2a, reproduces the trend of the data. Although there is not quantitative agreement between theory and experiment, it is apparent that the theory includes most of the basic physics of the process.

These results support the assignment of a σ_u shape resonance at a photon energy of about 310 eV; they also make clear the importance of having detailed information for making such an assignment.

CARBON 1s PHOTOELECTRON SPECTRUM OF METHANE [5]

Carbon 1s photoelectron spectra have been measured for CH_4 at photon energies of 302, 320, and 330 eV and for CD_4 at 330 eV with an instrumental resolution about half the natural line width. The spectrum of CH_4 at 330 eV is shown in Fig. 3. The spectra have been analyzed to obtain vibrational spacings, vibrational intensities, and the lifetime of the carbon 1s core hole state. The vibrational intensities vary with photon energy, in

Figure 2. a. The ratio of the cross sections for ionization of the $1\sigma_u$ and $1\sigma_g$ orbitals in ethyne. b. Cross section for carbon 1s ionization in HCCH. Circles: total single-hole cross section. Triangles: cross section for ionization of $1\sigma_u$ (open) and $1\sigma_g$ (closed). Lines are theoretical cross sections for ionization of $1\sigma_u$ (dashed) and $1\sigma_g$ (solid).

Figure 3. Carbon 1s photoelectron spectrum of CH_4

agreement with earlier results [6]. At 330 eV, the observed vibrational intensities for both CH_4 and CD_4 can be understood only if anharmonic effects (consistent with the predictions of theory) are included. On the other hand, the vibrational spacings in CH_4 show no evidence for anharmonicity (in contrast with theoretical predictions). In CD_4 the observed anharmonicity in the vibrational energy spacings is about half of the predicted value, but the experimental and theoretical values differ only by an amount comparable to the experimental uncertainty. The measured values of the lifetime show a dependence on photon energy; this is attributed to failure of the theory of post-collision interaction to predict correctly the observed electron spectrum near threshold. At 330 eV, the measured Lorentzian lifetime, 93-95 meV, agrees with predictions of simple theory, but not with the prediction of more complete theory. It is also observed that there are systematic discrepancies between the observed line shapes and those predicted by the theory of post-collision interaction.

CARBON 1s PHOTOELECTRON SPECTRUM OF PROPYNE [7]

In propyne, $\text{CH}_3\text{C}\equiv\text{CH}$, the three carbons are chemically inequivalent. The $\text{CH}\equiv$ unit is the site for electrophilic attack and is the basic end of the molecule. The central carbon, while susceptible to attack is not so reactive as the $\text{CH}=\text{}$ carbon. The CH_3 carbon, less reactive than the others, is the acidic end of the molecule. The inner-shell photoelectron spectroscopy of this molecule provides a basis for a better understanding of its chemistry, and, by extension, that of more complex molecules. Such knowledge can enhance our ability to predict properties of molecules and to design molecules with particular properties.

Measurements of the carbon 1s photoelectron spectrum of propyne by Cavell showed only a single asymmetric peak. Although he analyzed this in terms of three components, each representing a contribution from one of the carbon atoms, Cavell expressed reservations about both the positions and the assignments of each component. It was, therefore, difficult to draw firm conclusions about the chemistry of the molecule from these measurements.

With the high-resolution capabilities of the Advanced Light Source, it has been possible to resolve the contributions from the three inequivalent carbons in propyne. The spectrum for this molecule is shown in Fig. 4, where it is compared with that of ethyne (above) and ethane (below). Shown as a dashed line in the center spectrum is a representation of the earlier spectrum measured by Cavell. The additional structure that is revealed at higher resolution is striking.

Figure 4. carbon 1s photoelectron spectra of ethyne, propyne, and ethane

The three peaks in the propyne spectrum can be assigned to the three carbons by comparison with the model spectra of ethyne and ethane. Comparison with the spectrum of ethane shows a strong resemblance between the peak labeled "c" in propyne and the ethane spectrum, and we are therefore confident in assigning this peak to the CH₃ group in propyne. The vibrational pattern of peaks "a" and "b" are similar to the structure observed for ethyne, allowing us to assign these two peaks to the acetylenic part of the molecule. These assignments are in accord with theoretical calculations of both their shapes and positions, and these calculations allow us to assign peak "a" to the CH carbon and peak "b" to the central carbon of propyne.

The results shown here for propyne indicate that, with the high-resolution capabilities now available, the techniques of x-ray photoelectron spectroscopy can be extended into studies of hydrocarbons. A richness of detail is observed, both in vibrational structure and in the variation in ionization energy. The former provides an important test of ab initio theory and the latter provides insight into a variety of fundamental chemical phenomena.

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Photo Double-Ionization of Deuterium Chloride Studied by Threshold Photoelectrons Coincidence Spectroscopy

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INTRODUCTION

Photo double-ionization (PDI) of DCl has been investigated in the 35-38 eV energy range using synchrotron radiation on beamline 10.0.1.2 of the Advance Light Source (ALS) by the threshold photoelectrons coincidence (TPEsCO) method. The TPEsCO spectrum of DCl, encompassing the formation of the ground ($X^3\Sigma^-$) and first-excited ($a^1\Delta$) states of DCl^{2+} , was recorded at good resolution (~ 13 meV) using a pair of penetrating-field electron spectrometers (see Fig. 1, upper panel). In addition, the threshold photoelectron (TPE) spectrum of DCl for the formation of singly charged DCl was recorded simultaneously in the same energy range (see Fig. 1, lower panel).

Figure 1. Threshold photoelectrons coincidence spectrum of DCl (upper panel) and threshold photoelectron spectrum of DCl (lower panel).

RESULTS AND DISCUSSION

As can be seen in the TPEsCO spectrum in Fig. 1 (upper panel) a clear vibrational progression is observed in both systems confirming the TPEsCO results for HCl¹, thus supporting the quasi-bound nature of these states². The adiabatic double-ionization potentials ($v^{2+}=0$) for these states are found to be 35.650 eV ($^3\Sigma^-$) and 37.145 eV ($^1\Delta$) with an identical vibrational separation ($v^{2+}=0-1$) of 0.137 eV in both systems. The peaks observed in the TPE spectrum in Fig. 1 (lower panel) most probably represent vibrational structure in the formation of satellite DCI⁺ ion states converging on one or more excited, doubly-charged DCI states.

The implications of these results are as follows. In the TPEsCO spectrum of DCI the first two vibrational bands in the ($X\ ^3\Sigma^-$) system and the first three vibrational bands in the ($a\ ^1\Delta$) system are intense, well-defined and well-resolved while higher vibrational bands in both systems are much weaker, poorly defined and only barely recognizable as band systems. This suggests that both states are predissociated by tunneling effects, in basic agreement with theoretical calculations on the tunneling lifetimes of the vibrational levels of these states in DCI²⁺.³ The number of vibrational bands observed in the ($X\ ^3\Sigma^-$) system (four) is supported by theoretical calculations that show⁴ that the fifth vibrational level of the DCI²⁺ ($X\ ^3\Sigma^-$) state is coincident in energy with the maximum in the potential energy (dissociative) barrier and thereby should not be bound. The observed vibrational intensity distributions within the ($X\ ^3\Sigma^-$) and ($a\ ^1\Delta$) DCI²⁺ systems are significantly different from the calculated Franck-Condon factors³ for direct transitions from the ground state of DCI suggesting an additional route is operative in the TPEsCO spectrum. Such an indirect mechanism is possible by resonance autoionization of singly charged DCI states lying in this energy region as supported by the structured TPE spectrum shown in the lower panel of Fig. 1. The influence of autoionization processes may also be the origin of the structured peaks lying between 36.3 eV and 37.1 eV in the TPEsCO spectrum. Continued analyses of these results are underway and will be compared with the findings in the PDI of HCl.¹

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The high brightness and low emittance that characterize the ALS make it an ideal facility for the study of photon-ion interactions. A common objective of the collaborative experiments to be conducted at the photon-ion end-station is a deeper understanding of the complex multi-electron interactions that govern inelastic processes occurring in ionized plasmas, which comprise more than 99.99% of the known mass in the universe. The end-station has been designed for absolute measurements, which are important for benchmarking theoretical calculations of x-ray opacities. These are critical to the modeling of astrophysical, fusion, pulsed-power and x-ray laser plasmas. Systematic studies along isoelectronic and isonuclear sequences of ions will permit a fine-tuning of their electronic structure and therefore provide a sensitive probe of the electron-electron interaction.

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Beamline 10.3.1 Abstracts

CHEMICAL STATE AND ELEMENTAL DISTRIBUTION OF METAL IMPURITIES IN POLYCRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT

The work presented here directly measures the chemical state and elemental distributions of metal impurities in polycrystalline silicon used for terrestrial-based solar cells. The goal of this project was to determine if a correlation exists between poorly performing regions of solar cells and metal impurity distributions as well as to ascertain the chemical state of the impurities. Synchrotron-based x-ray fluorescence mapping and x-ray absorption spectroscopy, both with a spatial resolution of $1\mu\text{m}^2$, were used to measure impurity distributions and chemical state, respectively, in poorly performing regions of polycrystalline silicon. The Light Beam Induced Current method was used to measure minority carrier recombination in the material in order to identify poor performance regions. We have detected iron, chromium and nickel impurity precipitates and we have recognized a direct correlation between impurity distributions and poor performing regions in both as-grown and fully processed material. Furthermore, we have results, which indicate that the Fe in the polysilicon material is in oxide form, not a silicide form. These results provide a fundamental understanding into the efficiency-limiting factors of polycrystalline silicon solar cells as well as yielding insight for methods of solar cell improvement.

INTRODUCTION

Polycrystalline silicon can be used to fabricate solar cells with a moderate solar conversion efficiency and low fabrication costs. Although these cells are presently manufactured for terrestrial-based applications, an improvement in the efficiency of these cells would greatly increase their commercial viability. Presently, polycrystalline solar cells have efficiencies of 13-15% as compared to more expensive, single crystalline solar cells with efficiencies of 17-20% [1]. The primary cause for lowered efficiencies is localized regions of high minority carrier recombination, which possess high concentrations of dislocations [2-4]. However, it is known that minority carrier recombination at "clean" dislocations is relatively weak but greatly increases by decoration or precipitation of transition metal impurities [5-8]. This suggests the dislocations in high recombination regions of polycrystalline silicon are decorated with transition metals. Past work, [9], has provided indirect evidence that metal impurities are precipitated in regions of high carrier recombination while other work, [10], has revealed metal impurity agglomerations at dislocations in polycrystalline silicon. However, no direct evidence has been provided to relate high minority carrier recombination with transition metals in this material. In fact, carbon or oxygen may play an important role since these impurities are found in high concentrations in most polycrystalline silicon materials, $\approx 10^{18}$ atoms/cm³.

The first *direct* evidence of a relationship between metal impurities and poor performance is provided in this work and has recently been published [11]. In this work, we have performed mapping of metal impurity distributions using the x-ray fluorescence microprobe, beamline

10.3.1 at the Advanced Light Source (ALS), with which we have obtained a direct correlation between metal impurities, such as Fe, Cr and Ni, and poor performance regions of the material. Additionally, we have results on the chemical state of Fe in this material, specifically the Fe is in the form of an oxide, not a silicide. These results have serious implications in regards to strategies for material improvement.

EXPERIMENT

Boron doped polycrystalline silicon grown by an electromagnetic casting method [12] was used in this study. In order to locate poor performance regions, minority carrier recombination was mapped across the as-grown material with the Light Beam Induced Current (LBIC) method, using 880nm wavelength light. The frontside of the samples were analyzed using synchrotron-based x-ray fluorescence (XRF) mapping in order to determine metal impurity content and distribution. The XRF equipment is located at the microprobe beamline, 10.3.1, in the ALS. It uses 12.5keV monochromatic radiation to excite elements in the sample with a spatial resolution of $1\mu\text{m}^2$ and a Si-Li detector to measure fluorescence x-rays from the sample, all in atmospheric conditions. The XRF microprobe sensitivity is impurity and matrix specific but, for example, the system can detect a single Fe or Cu precipitate/agglomerate in silicon greater than 10-20nm in radius. The sampling depth for 3d transition metal impurities in silicon is approximately $50\mu\text{m}$. It should be noted that the sensitivity of the microprobe drops considerably for elements with an atomic number < 16 . X-ray absorption studies were carried out at beamline 10.3.2 in the ALS. A four crystal Si monochromator produces a tunable monochromatic x-ray beam, which is focussed to a $1\mu\text{m}^2$ spot with a pair of grazing incidence mirrors. A Si-Li detector was used to detect fluorescence x-rays and quantify absorption for specific elements. Detail of the absorption apparatus is given in [13].

RESULTS AND DISCUSSION

LBIC mapping of minority carrier recombination across the polycrystalline silicon sample revealed localized regions of high carrier recombination. A typical LBIC map in a portion of the cast polysilicon is shown in Figure 1 where dark regions indicate areas of high carrier recombination. Note the regions of high recombination located approximately in the center of the LBIC scan area.

X-ray Fluorescence (XRF) spectra were taken at $1\mu\text{m}^2$ points in the region of Figure 1 as denoted by the black box. No impurity-generated x-ray fluorescent radiation was

detected in regions of low minority carrier recombination. However, x-ray fluorescent radiation associated with Cr, Fe and Ni was detected in regions of high carrier recombination. Concentrations of impurities at each $1\mu\text{m}^2$ spot were calculated by data analysis of the collected spectra and comparison to standard samples with known concentrations of impurities. Impurity maps were produced in the region denoted by the black box in Figure 1. Figure 2 is an impurity map of Fe in this region. Maps of Ni and Cr revealed the exact same distribution as the Fe, indicating a preferred precipitation site exists for these impurities. By comparison of Figures 1

Figure 1: Light Beam Induced Current map of carrier recombination across a portion of multicrystalline silicon. Dark regions indicate high carrier recombination. The black box denotes the area analyzed with x-ray fluorescence.

and 2, one can clearly see a correlation between metal impurity distributions and minority carrier recombination. These results indicate metal impurities are the cause for high carrier recombination regions in polycrystalline silicon and, therefore, play a significant role in the performance of the material as a solar cell.

At each high impurity content region of Figure 2, a single precipitate or a number of precipitates may reside in each $1\mu\text{m}^2$ spot. If only one precipitate is assumed present, the diameter can be calculated from the measured impurity concentrations and assuming the precipitate is located at or near the surface. For instance, the measured concentration of 5×10^{16} atoms/cm² for Fe shown in Figure 2 would suggest one precipitate with a diameter of 288nm is present in that area. However, considering earlier work [10,14], the impurities in Figure 2 are more likely a fine dispersion of smaller impurity precipitates.

We have also performed x-ray absorption studies on this polysilicon material. Spectra were taken with a $1\mu\text{m}^2$ spot on regions of high Fe content. A summation of spectral scans at the Fe K absorption edge was taken in the Fe-rich region of Figure 2, as shown in Figure 3.

Additionally, for purpose of comparison, we also provide the summed spectrum of a standard sample of an elemental Fe film and a $\alpha\text{-Fe}_2\text{O}_3$ powder. The elemental Fe standard has a body centered cubic crystal symmetry while the $\alpha\text{-Fe}_2\text{O}_3$ standard has a hexagonal crystal symmetry with the Fe in a +3 charge-state. The spectra shapes of the Fe in polysilicon and Fe in $\alpha\text{-Fe}_2\text{O}_3$ are closely matched, especially in the near edge region, indicating the Fe in polysilicon has a similar symmetry as $\alpha\text{-Fe}_2\text{O}_3$. Both of these absorption spectra are significantly different than the Fe film standard. Considering iron silicide is in either a cubic, tetragonal or orthorhombic crystal symmetry while $\alpha\text{-Fe}_2\text{O}_3$ possesses a hexagonal crystal symmetry, the absorption spectra of iron silicides would be significantly different than the spectra obtained for Fe in polysilicon. Therefore, our results indicate the Fe in the polysilicon is not in an iron silicide state but rather in an oxide state. Further work is planned to produce iron silicide standards (FeSi and FeSi_2) for direct comparison of x-ray absorption spectra.

Figure 2: Fe distribution in polycrystalline silicon. The mapped area directly corresponds to the area in the black box of Figure 1. Note the correlation between metal impurity distributions and carrier recombination.

Figure 3: X-ray absorption spectroscopy of Fe in polysilicon, Fe in Fe_2O_3 and elemental Fe. Note the similarity between the Fe in polysilicon and Fe in Fe_2O_3 .

The chemical state of metals in polysilicon drastically alters the removal of impurities from the material and, in turn, improvements in performance. For example, the binding energy of a Fe atom to a Fe oxide phase is drastically higher than a Fe atom to a Fe silicide phase, [15]. This constitutes a lower concentration of dissolved Fe impurities in the presence of a Fe oxide particle as compared to a Fe silicide particle during an annealing treatment. This lower concentration would decrease the flux of impurities out of the material during impurity removal and severely hinder material improvement. For instance, a 20nm diameter precipitate of FeSi₂ in silicon would require minutes to hours for complete dissolution at moderate temperatures while a precipitate of the same size of α -Fe₂O₃ would require days to weeks to fully dissolve. Therefore, the identification of Fe oxide in polycrystalline silicon indicates improvement of polysilicon solar cells is an arduous task and perhaps preventative measures are required.

CONCLUSIONS

In summation, metal impurities were found in polycrystalline silicon used for solar cells. The distribution of impurities correlated directly with poor performing regions of the material. These results are the first direct proof that metal impurities significantly affect the performance of polycrystalline silicon solar cells. Furthermore, our results indicate that the chemical state of Fe in this material is Fe oxide rather than the expected Fe silicide. This is the first indication that impurity removal from silicon is severely limited by the chemical state of the impurity precipitate.

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Development of a Fast Scanning X-ray Microprobe

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INTRODUCTION

The x-ray microprobe at beamline 10.3 of the ALS has recently been upgraded with a new scanning stage and data acquisition system that substantially improves the capability of the beamline. The previous system acquired data in a "step and shoot" mode with no data analysis while images were being acquired. The new system has two modes of data acquisition – "step and shoot" and "slew scanning". Both modes allow a real time display of two-dimensional maps of elements selected for analysis. In the "step and shoot" mode a spectrum from the fluorescence detector is collected at one point and then the stage is moved to the next point in the scan and the next spectrum is taken. On the other hand, in the "slew scanning" mode the sample is scanned repeatedly through the beam in a raster mode and the fluorescent x-rays are detected and stored with a position tag. Elemental maps are produced and displayed as the system is scanning. Since the whole scan area is scanned in several minutes, this mode provides on-line analysis of the whole image field so that experimenters can optimize their beam time and quickly produce publishable results. In both modes the complete energy spectrum from the fluorescence detector is stored for each pixel so the data can be analyzed later for elements that were not looked for while collecting the data. The spectral data are processed with a peak fitting routine to provide elemental images that are calibrated using elemental standard samples.

SYSTEM DESCRIPTION

The system is based on a two-dimensional scanning stage that has high resolution (100 steps/micron) position encoders on both stages. The horizontal scanning stage uses a solenoidal magnet to move the stage and a DC motor moves the vertical stage. In the "step and shoot" mode of data acquisition the system acquires data at one point and then moves to the next point. The complete spectra from the Si(Li) detector and the current in two ion chambers (one upstream of the sample and the other downstream of the sample) are recorded at each point. Elemental maps for many different elements can be selected and then displayed as the scan progresses. This mode is used for scanning small areas of the sample around areas of special interest where a detail spatial profile is desired.

In the "slew scanning" mode, the scanning parameters for the stages are downloaded into a programmed controller by the data acquisition computer and then the raster scan data is collected by the system hardware with minimal software overhead. Each x-ray event is tagged with the position of the stages when the event occurred. As the scan progresses the computer stores each event in the correct spectra for each pixel. It also updates the elemental image maps for the elements of interest. This scanning mode has two major advantages. It allows the data in the whole image field to be monitored in real time so that the scan can be stopped when sufficient statistics have been accumulated or modified if the scan parameters are incorrect. In the "slew scanning" mode the data are averaged over the length of each pixel. This produces a more accurate map of the sample area than in the "step and shoot" where it is possible to miss areas of rapidly changing concentration if the pixel size is not about the same as the beam spot size. Typical

scanning parameters in this mode are a sample area of 100 micron x 60 micron with a pixel size of 2 microns and a scanning speed of 5 msec/pixel. With these parameters the system scans the full area in less than two minutes. The system scans the area repeatedly or until the desired number of scans is complete. The fluorescent x-rays are detected with a Si(Li) detector and the data is collected on a SUN computer with a modified data acquisition system from Princeton Gamma Tech. Since the intensity of the x-ray beam from the ALS varies during the experiment, the beam current is also recorded for each pixel as the stage scans. This allows the data to be normalized. The absolute elemental concentrations are determined by running elemental standards from NIST that are run before or after a sample run. The spectral data are processed after the scan with a peak fitting program based on a program from Mark Rivers of the University of Chicago. Quantitative elemental maps are produced using the calibration spectra from the elemental standards.

RESULTS

The system uses a SUN computer system and software and hardware from Princeton Gamma Tech. Samples are usually mounted in between two layers of thin polypropylene on a 35-mm slide frame. The horizontal-vertical scanning stage is mounted on another linear stage to allow the sample to be positioned at the focal plane. In addition, the stage system is mounted on a rotary stage to allow for stereo and tomographic imaging.

Figure 1 is from a scan of a pair of crossed 25-micron diameter gold-covered tungsten wires. The sample is at 45 degrees to the incident beam and the detector is at 90 degrees to the beam. The Fig. 1a is the spatial profile of the total fluorescence image. The shadowing of the fluorescence signal on the horizontal wire by the vertical wire is visible on the right side of vertical wire. Fig 1b shows the zinc elemental image of the same area. This shows that the two spots on the lower right of the horizontal wire are from zinc particles on the wire.

Figure 1a. Image of two 25 μ m diameter Au-coated tungsten wires showing the shadowing by the vertical wire.

Figure 1b. Image of zinc over same area.

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Elemental Distributions in Cancerous Lung Tissue

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We have performed x-ray fluorescence (XRF) mapping to determine elemental distributions in cancerous lung tissue. Our studies compare tissue samples from three people who developed similar types of lung cancer: 1) a Chernobyl clean-up worker, 2) a person who lived in the area of radioactive fall-out associated with the Chernobyl disaster and 3) a person who developed the same type of lung cancer but who was not involved with the disaster. We are investigating whether or not a correlation exists between this cancer and elemental distributions as well as particulate shape and size. Located below is an optical micrograph of lung tissue from the third person. The cancerous regions are white while the healthy regions are dark. XRF scans were performed on this tissue with the box indicating the scan region. A wide variety of elements were detected, notably particles of Fe, Cu, and Zn. Furthermore, strong correlations between Fe and Zn, S, K and Cl as well as Ca and P were seen. On the right hand side of the figure are the specific maps for Fe, Cu, and Zn, aligned to show their correspondence to the boxed area in the optical micrograph. A correlation exists between all three elements in a diagonal region in the lower part of the box. This area is associated with the large white area in the optical micrograph, which is cancerous tissue. In other samples Zn, Ti, Cr, Fe, Ni, and Co particles are seen in both healthy and diseased regions. These particles are often in the 10 – 20 μm range, although some

Figure showing an optical micrograph of lung tissue sample #3 with the box indicating the scan region. On the right hand side of the figure are the specific maps for Fe, Cu, and Zn, aligned to show their correspondence to the boxed area in the optical micrograph.

are larger. In some cases, the particles are composed of several elements. In addition, broad but relatively weak correlations are seen in some larger areas involving P, S, K, and Ca. Future work will focus on obtaining more detailed maps over larger areas of all samples, and determining the distribution of size, shape, and composition of the observed particles, their relationship to the healthy and diseased portions of the samples, and their relation to disease.

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Evaluation of the X-ray Microprobe for Analysis of Sediment Cores

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INTRODUCTION

Marine, lacustrine and estuarine cores can provide a wealth of information about natural and human-driven processes. Furthermore, because these cores usually contain a long and continuous record of these processes, they often prove more useful than discontinuous terrestrial deposits. However, in most cases geochemical analyses of the cores have been limited to discrete samples which are removed from the core at a specified sampling interval. The disadvantage of this approach is that it is often difficult to use the discrete analyses to reconstruct the time evolution of changes in geochemical properties. Also, the analyses are usually limited to a relatively small number of elements. We are developing a method for obtaining elemental geochemical analyses directly from continuous sections of core. This approach allows us to achieve high spatial resolution, which can be translated into high temporal resolution. Furthermore, by using monochromatic polarized x-rays, we can extend the analyses to a much wider range of elements. Finally, by developing the appropriate software, we should be able to obtain the analysis in real time which would allow us to go back and examine any important features at higher resolution and at greater compositional sensitivity.

EXPERIMENT

Last summer, we analyzed a composite sample made up of segments from cores collected from two saltwater ponds associated with San Francisco Bay, near Mare Island. The Mare Island site is heavily contaminated with transition and heavy metals from decades of shipbuilding and maintenance. The sediment was contained in a "u-channel" which is a three-sided, plastic channel with a square cross-section, 2.5 cm on a side, and a length of 1 meter. The fourth, open-side of the u-channel was covered with a thin (1/8 mil) Mylar covering in order to keep the moisture content high enough to avoid the formation of a powdery surface and the loss of depth resolution.

The u-channel was placed in a traveling stage that allowed us to move the u-channel in steps as small as 0.1 mm across the 5 micron x-ray beam spot. The analyses were calibrated using thin film standards, but additional work needs to be done to make corrections for thicker samples. The x-ray data were reduced using a Sun workstation.

RESULTS

The first example is a scan of sulfur from the two ponds. The surface of each core is on the left in both cases. Both cores show considerable variation in sulfur concentration. Of particular interest are the peak at 290 mm in Core 1 and the peaks between 680 mm and 710 mm and between 760 mm and 800 mm in Core 2. In each case the changes in concentration appear to occur over very short depth intervals making these peaks prime candidates for higher resolution studies using the ALS x-ray microprobe.

A second example is the analysis of calcium and phosphorous. Again, we see large changes in concentration over short depth intervals, especially in Core 2, but what is of particular interest is that the variations of these two elements are very closely correlated. This correlation implies co-precipitation of these two elements in this pond and suggests that the conditions in the pond were often favorable to formation of the calcium phosphate mineral known as apatite.

Our third example is the analysis of iron, copper and arsenic/lead. Since iron is a major element and copper and arsenic/lead are trace elements, we would not necessarily expect these elements to be closely correlated which is what we see for the most part. However, the consistent peak in all three elements at the bottom of Core 1 suggests that this level represents a thin layer of heavy metal contamination that would need to be remediated as part of any clean-up effort.

CONCLUSIONS

These results clearly demonstrate that it is possible to use a u-channel of sediment mounted on a traveling stage to obtain non-destructive elemental geochemical analyses from continuous core segments with high spatial resolution to sub-PPM concentrations. In the near future we intend to extend this approach to cores representing a variety of depositional environments and sediment types from both lakes and oceans.

We also plan to develop an on-line data reduction capability so that we can obtain our analyses while the measurements are in progress. This will enable us to obtain results from standards and samples during the run so that we can identify interesting regions and study them at higher resolution.

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Mapping of metal contaminants in photovoltaic grade silicon by X-ray fluorescence

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INTRODUCTION

Photovoltaic grade polycrystalline silicon is widely used for solar cell fabrication because of cost considerations. However, the conversion efficiency of such cells is still clearly lower than that of more expensive, high quality monocrystalline cells. The primary cause for the poorer performance is regions of strong carrier recombination, caused by high densities of extended crystal defects. It is generally accepted that transition metals play an important part since it is known that "clean" extended defects cause only weak carrier recombination while transition metal decoration increases the recombination activity greatly [1-3]. Therefore, identification of transition metals in solar grade silicon and assessment of their impact on the recombination properties is crucial to further improving the performance of polycrystalline solar cells.

EXPERIMENTS

Boron doped polycrystalline Si material grown by the rapid growth on substrate (RGS) method was used in the study. Minority carrier recombination was mapped with the light beam induced current (LBIC) and electron beam induced current (EBIC) methods. On the basis of high spatial resolution EBIC maps, regions of high carrier recombination were chosen for x-ray fluorescence mapping. Prior to the XRF measurements, the samples were carefully cleaned with Piranha clean. The measurements were carried out on the XRF equipment at beamline 10.3.1. The equipment uses a focused 12.5 keV monochromatic radiation and a Si-Li detector to measure the fluorescence from the sample. The sampling depth for 3d transition metals in silicon is approximately 50 μm . The spatial resolution was about $1.5 \times 2 \mu\text{m}^2$, which allows to detect a single Fe precipitate greater than 10-20 nm in radius.

RESULTS AND DISCUSSION

Fig. 1 shows an EBIC recombination map of a polycrystalline silicon sample. Dark regions correspond to high recombination, bright regions to low recombination. Note the dark region with a bright center in the central part of the image. X-ray fluorescence measurements taken in the region denoted by the box revealed a small

Fig 1 EBIC image of a portion of a polycrystalline silicon sample. The box denotes the area analyzed with x-ray fluorescence

Fig. 2: Fe distribution in the area marked by the box in Figure 1.

amount of iron slightly above the background noise level in this region. (Fig.2). No other transition metals were detected.

Unlike previously reported results on polycrystalline silicon [4,5], in most samples with regions of high carrier recombination the transition metal content was below the detection limit of the XRF system. This indicates an improvement of the metal impurity level in the photovoltaic grade silicon. Despite the reduction of metal content, carrier recombination may still be high since, according to past work [2], small amounts of transition metals may be sufficient to increase the recombination activity of extended defect considerably. Another possible cause for high carrier recombination is precipitation of oxygen or carbon since these impurities are present in very high concentrations ($\approx 10^{18} \text{ cm}^{-3}$), but are not detected by the XRF system. Therefore, an upgrade of the system for detection of light elements would be very helpful for future studies.

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Out-Diffusion and Precipitation of Copper in N- and P-Type Silicon

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Abstract

The use of copper for metallic interconnects in ULSI technology has revived the interest in the precipitation kinetics of copper in silicon. We have investigated copper of various contamination levels in n- and p-type silicon. While the interstitial copper concentration was measured with Transient Ion Drift (TID), the precipitated copper concentration was detected by X-Ray Fluorescence (XRF). The existence of the precipitates as well as their morphology was investigated by Transmission Electron Microscopy (TEM). In n-type silicon no interstitial copper was detected, whereas the concentration of precipitated copper was close to the copper solubility at the diffusion temperature. Contrary, in p-type silicon interstitial copper was observed after quench, and only few copper precipitates were found if the copper contamination was chosen below a certain critical level, which was found to be in the range of 10^{16}cm^{-3} . At higher contamination levels, precipitation prevails and the concentration of precipitated copper reaches the solubility level at the diffusion temperature. Despite the difference in the precipitation kinetics of p- and n-type silicon, the precipitates found in p-type form the same thin {111}-platelets as are known after quench in n-type. Analysis of the experimental data suggests that the copper kinetics is dominated by bulk precipitation in n-type silicon and by out-diffusion in p-type silicon. If the concentration of the positively charged copper exceeds the acceptor concentration, type inversion may occur. We discuss a possible Fermi level effect as a criteria for out-diffusion and precipitation.

Introduction

Introduction of copper interconnects in silicon integrated circuit technology has drastically increased the danger of unintentional introduction of copper into silicon substrates. Consequently, understanding of the behavior of copper in silicon and evaluation and prediction of its potential effect on device performance has become an increasingly important problem of semiconductor materials science and device technology. The experience of copper research accumulated in the past 35 years has demonstrated that the task of understanding the physical properties of copper in silicon is much more difficult than for most other transition metals. This is caused by interstitial copper being positively charged in silicon [1] and retaining a high diffusivity in the silicon lattice even at room temperature [2]. Copper homogeneously distributes in the bulk of the wafer during high temperature anneals and forms interstitial point defects, complexes, precipitates, or diffuses to the surface of the wafer upon cooling down. The detrimental effect of copper to devices depends on which of these reaction paths becomes preferential. Thus, prediction of the detrimental role of copper in integrated circuits and evaluation of the feasibility of its gettering require fundamental physical understanding of properties of copper in silicon. The previous attempts to solve this fundamentally challenging and technologically relevant problem met with only limited success, mainly because none of the groups involved in copper research had the combination of analytical tools necessary to access copper in all possible states and to follow its reaction from the interstitial state to a stable state in the lattice.

Today two mechanism of copper in silicon are proposed. Since the 1980s Transmission electron microscopy (TEM) studies suggested that in n-type silicon most of copper precipitates in the bulk after high-temperature anneal and quench to form Cu_3Si platelets on the {111} planes. Comparison of the electrical properties of these platelets as measured with Deep Level Transient Spectroscopy (DLTS) and computer simulations of the resulting spectra have revealed that these precipitates form band like states within the band gap of the silicon matrix ranging from $E_c-0.35\text{eV}$ to $E_c-0.15\text{eV}$ [3]. Furthermore, they show that the copper precipitates are positively charged if the Fermi level is below their neutrality level at $E_c-0.2\text{eV}$ and neutral or positively charged if the Fermi level is above this critical level. However, recent experimental studies of Shabani *et al.* [4] and McCarthy *et al.* [5] demonstrated another possible behavior of copper, copper diffusing to the surface within 48 to 72 hours after high temperature in-diffusion of copper into p-type samples. In n-type silicon, out-diffusion was observed only if the sample temperature was raised to 300°C - 400°C in a second annealing step. Up to now no explanation for this difference in the behavior of copper in n-type silicon and p-type silicon could be provided as to what is the reaction path of copper in silicon, what is the reason for the difference in its behavior in n-type and p-type silicon.

During the last two years, our research team achieved significant progress in studies of interstitial copper in silicon. We introduced Transient Ion Drift (TID) as a technique that is capable of measurements of low concentrations of interstitial copper in the bulk of silicon [6]. Complementary, copper precipitates can be detected and mapped by X-Ray Florescence (XRF). Utilizing the synchrotron-based XRF microprobe at the ALS copper bulk concentration of 10^{16} cm^{-3} can be measured. This corresponds to the observation of isolated copper precipitates with a diameter of 20nm, or smaller precipitates with a higher density [7]. The research reported here utilizes the unique experimental capabilities of our group and the ALS to investigate the properties of copper in silicon in order to approach the first comprehensive and predictive model of the behavior of copper.

Results and Discussion

In Fig. 1 we plot the maximum interstitial copper concentration as measured with TID vs the solubility of copper at in-diffusion temperature. The copper has been introduced into the silicon wafer by in-diffusion at high temperatures followed by a quench.

Three different p-type samples are presented with a doping concentration of $4*10^{14}$, $4*10^{15}$ and $2*10^{16}$ boron atoms per cm^3 , respectively. A most significant effect is the observation of two regimes: A lower copper contamination regime and a higher copper contamination regime. In the lower copper contamination regime, up to a critical copper solubility concentration at diffusion temperature in the range of 10^{16} cm^{-3} , the maximum interstitial copper concentrations as measured with TID increases with the solubility concentration. However, beyond that critical copper contamination level the interstitial copper concentration decreases with increasing solubility concentration. The critical amount of in-diffused copper is identical for the samples doped with $4*10^{14}$ to $4*10^{15}$ boron atoms per cm^3 and is found to be at $1*10^{16}$ copper atoms per cm^3 . Nevertheless, the critical concentration of copper contamination is shifted to $3*10^{16}$ copper atoms per cm^3 for the sample doped with $2*10^{16}$ boron atoms per cm^3 .

In Fig. 2 we plot the concentration of precipitated copper as measured with XRF vs the solubility of copper at diffusion temperature for one n-type sample doped with $2*10^{15}$ phosphorus atoms per cm^3 and three p-type samples with doping concentrations again ranging from 10^{14} to 10^{16} boron atoms per cm^3 . Because of the detection limit of XRF only samples with an initial contamination of at least 10^{16} copper atoms per cm^3 are measured. It can be seen that the amount of precipitated copper for the n-type sample follows the solubility concentration of

Fig. 1: Interstitial copper concentration as measured with TID for boron doped samples of $4 \cdot 10^{14} \text{ cm}^{-3}$, $4 \cdot 10^{15} \text{ cm}^{-3}$ and $2 \cdot 10^{16} \text{ cm}^{-3}$.

Fig. 2: Precipitated copper concentration as measured with XRF for a phosphorus doped sample of $2 \cdot 10^{15} \text{ cm}^{-3}$ and for boron doped samples of $4 \cdot 10^{14} \text{ cm}^{-3}$, $4 \cdot 10^{15} \text{ cm}^{-3}$ and $2 \cdot 10^{16} \text{ cm}^{-3}$.

copper at diffusion temperature. The same is true for the p-type samples with boron concentrations of 10^{14} cm^{-3} and 10^{15} cm^{-3} . The concentration values of precipitated copper are very homogeneously distributed as measured with the XRF microprobe with a spatial resolution of about $1 \mu\text{m}^2$. In particular no profile of precipitated copper has been found. This indicates that all the copper that has been in-diffused has precipitated in the bulk very fast. On the contrary, the detected concentrations of precipitated copper for the sample doped with $2 \cdot 10^{16}$ boron atoms per cm^3 does not follow the solubility concentration of copper at in-diffusion temperature. Only if the initial copper concentration is above the critical copper concentration for this particular sample of $3 \cdot 10^{16} \text{ cm}^{-3}$, as found in Fig. 1, the amount of precipitated copper equals the in-diffused concentration of copper. Yet, after in-diffusion of copper to an amount that equals the critical concentration of this sample the concentration of precipitated copper is below the detection limit, i.e. much below its initial concentration. Thus the difference of copper between the initial copper concentration and the later found concentration of precipitated copper has diffused out of the sample.

This data show that for silicon doped with $2 \cdot 10^{16}$ boron atoms per cm^3 out-diffusion is dominant for the lower copper contamination regime and precipitation is the dominant reaction path for the higher copper contamination regime. Unfortunately the detection limit of XRF equals the critical copper concentration of the lower doped samples, i.e. the samples doped with less than 10^{16} boron atoms per cm^{-3} . Therefore we can only measure the precipitated copper concentration for the higher copper contamination regime of these samples. We see that for the lower doped samples, as was observed for the higher doped sample, precipitation is dominant if the initial copper concentration is above the critical copper concentration of these samples. Yet, with TID we recognize a qualitative similar behavior of the copper in both regimes for all p-type wafers. This suggests that for the lower doped samples the lower contamination regime is also dominated by out-diffusion. Future work at the ALS with a lower XRF-detection limit for copper in silicon, as is intended, will be able to decide about this behavior for low doped samples.

The question that remains is why is out-diffusion being the dominant path in the lower copper contaminated region, and why does copper "change its mind" and precipitation becomes the dominant reaction path in the higher copper contaminated region? A hypothesis, which was put forward in our recent conference presentations [8, 9] is that the coulomb repulsion between positively charged copper ions and positively charged copper precipitates in p-Si might retard copper precipitation. The precipitation becomes possible in n-type silicon or in p-type silicon if the position of the Fermi level determined by the concentration of shallow dopants and copper

donors becomes so high in the band gap that either copper ions or copper precipitates change the sign of their charge and coulombic repulsion between the two disappears. This hypothesis represents a principally new physical mechanism, which was never discussed before with applications to copper, and is one of the issues to be addressed in future experiments.

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X-ray Fluorescence Microprobe Analysis of a Contaminated Soil

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INTRODUCTION

Contaminated soils present a major global health problem especially in urban areas with dense populations. Heavy metals are common contaminants and understanding their behavior in soils is central to our ability to predict the extent of their environmental hazard. The environmental and health consequences of elevated concentrations of soil Pb resulting from human activities is of great concern because of its toxicity at very low concentrations, especially to children.

The solubility and potential biological availability of Pb and other heavy metals in soils is influenced by a number of mechanisms including solid phase interactions with soil constituents and spatial distributions both on a micro-scale and larger. Lead, e.g., can adsorb to soil phyllosilicates, hydrous oxides, and organic matter as well as form separate solid phase compounds like lead phosphate.¹ Identifying elemental associations on a micro-scale is important for assessing these solid phase forms. Understanding spatial distribution of Pb and other toxic elements in soil is also very important since hazardous conditions from contamination may not be related to an averaged concentration found in bulk soil but to possible exposure to extremely high concentrations in micro regions.

The sampling site was a heavy metal contaminated, residential area in Oakland, CA. Apparently, paint from old buildings that burned down in the late 1960's resulted in soil contamination. Initially, the site was investigated because local residents expressed a desire to develop a community garden on this plot of land. Preliminary x-ray fluorescence (XRF) analysis of the soil yields the following ranges of concentrations for a number of various locations at the site: 195-64510 mg Pb/kg, 243-32414 mg Zn/kg, 45-165 mg Ni/kg, 164-10414 mg Cr/kg, and 5900-110,000 mg Ti/kg soil. In comparison, the range of means for U.S. soil as it pertains to Pb, Zn, Ni, Cr, and Ti are 7-26, 34-84, 13-30, and 20-85 and 1800-3600 mg/kg respectively^{2,3}. In general, the site had heavy metal concentrations far greater than the means for the U.S. and showed a very heterogeneous distribution dependent on location.

The objectives of this project are to determine the spatial distribution and elemental associations of Pb as well as other potentially toxic metals in a contaminated urban soil. These results will provide important information which will help in our interpretation of the chemical solubility and biological availability of these elements studied in another part of this overall project. The high spatial resolution and low detection limits of the x-ray fluorescence microprobe at Beamline 10.3.1 at the Advanced Light Source provides excellent capabilities for the detection of elemental association in undisturbed soil systems.

EXPERIMENTAL

Intact soil cores were collected from various locations in a contaminated residential area in Oakland and at various soil depths. The cores were imbedded with LR White acrylic resin. Samples were cut into approximately 2 cm wide x 0.5 cm thick x 3 cm long blocks, polished, and mounted on the microprobe stage. Using the x-ray fluorescence microprobe, four vertical scan lines spaced 0.18 mm apart horizontally, ran vertically along the sample in 0.18 mm steps. Data for only one core is presented in this report.

Figure 1 shows the Pb, Cr, and Ti distributions and concentrations in an Oakland soil sample that was collected 22.5 to 25.4 cm below the soil surface. The x, y, and z axes are in units of mm, cm, and $\mu\text{g}/\text{cm}^2$ respectively. Figure 2 shows linear regression analyses of a) Cr vs. Ti, b) Ti vs. Pb, and c) Cr vs. Pb with R^2 values of 0.733, 0.389, and 0.485, respectively. Ti and Cr concentrations were the most highly correlated in the soil matrix. Figures 1b and 1c show the actual distribution of Cr and Ti. It can be seen that Cr and Ti were concentrated between 25.0 and 25.4 cm below the soil surface.

Figure 1. a) Pb, b) Cr, and c) Ti distributions in a soil sample which was collected approximately 22.5-25.4 cm below the soil surface.

Figure 2. Linear regression analysis of a) Cr vs. Ti ($R^2=0.733$), b) Ti vs. Pb ($R^2=0.389$), and c) Cr vs. Pb ($R^2=0.485$) from x-ray microprobe analysis.

However, at approximately 24.7 cm, Ti had an elevated concentration which was independent of Cr. This suggests that these metals originated from two sources or that Cr is more mobile than Ti and has migrated from its previous location which was in close proximity with the Ti at 25.0 cm. Pb and Ti were concentrated in the area between 24.5 and 25.4 cm below the soil surface as shown in Figures 1a and 1c. However, Pb was fairly dispersed in this region and Ti was localized. These two metals were not as well correlated ($R^2=0.389$) as Cr and Ti ($R^2=0.733$). These results imply that the Pb and Ti contamination originated from two sources or that lead is slightly more mobile than titanium in the soil.

The titanium in the soil is likely to have originated from titanium dioxide which comes in two crystalline forms, both of which are used for interior and exterior paints.⁴ Titanium dioxide is a very stable compound. Through the use of a sequential extraction technique⁵, Pb has been found to be highly associated with carbonates. Lead carbonate and other lead pigments are used in paint pigments and usually prevents the growth of microorganisms.⁴ Crocoite (PbCrO_4) that is associated with litharge (PbO), a drier used in nails and varnishes, are possible sources of Cr and Pb.⁶ Thus, these results along with the support of other chemical and biological methods provide an important tool for accessing potential hazards from heavy metal contamination of soils.

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Beamline 10.3.2 Abstracts

A Novel Attenuation Mechanism of Zinc within Aquatic Plants: Complexation on Root Borne Manganese Nodules

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The ability of plants to grow and prosper in contaminated soils of contrasting properties is intriguing yet enigmatic. Aquatic plants, such as those within wetlands, have in particular been recognized for their ability to sequester trace element contaminants [1]. Identification of direct mechanisms involved in plant accumulation and tolerance is essential not only for discerning physiological adaptations by plants to metal contaminated soils but also for exploiting specific plant attributes to maximize efficiency in metal binding. Furthermore, the specific binding mechanisms of trace elements within plants has important implications for the delineation of potential bioavailability and/or release of toxins upon changing physicochemical conditions within aquatic environments. While accumulation of metals in the shoots of plants has been explored extensively [2], the role of plant roots is ill defined despite their ability to sequester toxins at high levels. Iron (hydr)oxide coatings, or plaque, formed on plant roots are suspected to directly hinder the uptake and translocation of phytotoxins [3]; however, the direct mechanisms of metal immobilization have yet to be determined. Moreover, manganese has been given only cursory attention although it is a ubiquitous, redox sensitive element that forms reactive (hydr)oxides as well. Here we describe the critical and unforeseen role of manganese in contaminant attenuation and cycling within aquatic plants. The formation of discrete manganese oxide nodules on root surfaces of aquatic plants, which subsequently induced local sequestration of zinc (an acute toxin of aquatic organisms), was revealed using x-ray microprobe analysis.

The novel technology of phytoremediation has prompted countless studies to determine optimal species for maximal accumulation [4], chemical modifications to improve accumulation and translocation [5] and, most recently, the mechanisms allowing for this phenomenon [6-7]. Due in part to the modern emergence of synchrotron radiation techniques (e.g., x-ray absorption fine structure spectroscopy), metal speciation in plant biomass is currently being ascertained [7]. Recent studies, however, focus on aerial portions of plant-metal complexation yet contaminant concentrations in the roots are generally several fold higher. Accordingly, our research focuses on the mechanisms underlying the sequestration of toxins within the rhizosphere of aquatic plants.

A number of grass species (e.g., reed canarygrass) have demonstrated tolerance and accumulation of heavy metals [8]. *Phalaris arundinacea* L. (reed canarygrass) belongs to the grass family and is indigenous to aquatic environments. Accordingly, reed canarygrass samples underwent acid digestions, which revealed extensive concentrations of metals and metalloids including As, Fe, Mn, Pb and Zn. Consistent with previous investigations, concentrations of trace elements (As, Pb, Zn) in the plant roots are several fold higher than in shoots. Root tissue concentrations for As, Fe, Mn, Pb and Zn are 96.2, 15100, 1500, 892, and 1050-mg kg⁻¹, respectively. Scanning electron microscopy (SEM) discloses the extensive nature of a plaque on the exterior of the grass roots (data not shown). Coatings exist predominantly as casts or fillings in cavities of the epidermal cells, which are composed predominantly of Fe with lesser amounts of As, Mn, Pb and Zn.

A cross-sectional map from the interior of the root through the epidermis and plaque was constructed for manganese and zinc using a synchrotron based x-ray microprobe (Fig. 1). Scans

Figure 1. Microprobe map of Mn and Zn concentration distributions on and within grass roots. White line represents the root epidermis and relative elemental concentrations increase with color brightness. (A) Spatial distribution of Mn along a transect from root center to exterior of plaque. (B) Spatial distribution of Zn along the same transect as that for Mn.

were performed on beamline 10.3.2 at the Lawrence Berkeley National Laboratory Advanced Light Source (LBNL-ALS). The scan covers a 250 x 250- μm section of the root with data collection at 5- μm increments. The two elements were mapped simultaneously along the same transect such that direct spatial associations and distributions were ascertained. The distribution of Mn is concentrated in discrete oxidized zones on the exterior of the epidermis. Concentrations of Mn diminish in areas adjacent to these zones and are negligible in the interior of the root. The spatial distribution of Zn on grass roots corresponds remarkably with the distribution patterns for Mn. Zinc concentrations are elevated at the discrete sites of Mn deposition, while concentrations decrease elsewhere. Concentrations of Zn and Mn are strongly correlated aside from the interior cell wall where Zn concentrations are slightly higher.

The morphology of the Mn-Zn precipitate on the plant root is analogous to that of seafloor ferromanganese nodules. Nodules have been discovered in a variety of environments including marine and freshwater systems, soils, desert varnish and streambeds [9]. Seafloor ferromanganese nodule formation is initiated by precipitation of a hydrated iron oxide on a nucleating agent (pumice, rocks, glass, clays) followed by cyclic deposition of Mn oxides [10]. Structural similarities between iron and manganese (hydr)oxides, such as ferrihydrite and birnessite, make them amenable to epitaxial growth thus allowing for nodule formation and oscillatory intergrowths of Fe and Mn bearing minerals. The specific and high affinity of birnessite for contaminants such as cadmium and zinc is well documented [11]. Zinc, although

an essential micronutrient to most biota, is a ubiquitous contaminant and toxic when present at excessive levels. Similarly, as a result of radial oxygen diffusion, plant roots serve as nucleating agents for the deposition of a hydrated iron hydroxide plaque, which subsequently provides a reactive substrate for manganese oxidation and precipitation. Consequently, discrete manganese nodules are produced on the root surface by way of epitaxial growth and auto-catalysis and may then provide a surface for attenuation of toxins such as zinc.

In conclusion, our research introduces and elucidates an unprecedented process behind the unique ability of aquatic plants to accumulate trace elements. A crucial and unforeseen mechanism underlying this phenomenon involves the formation of manganese nodules on the root epidermis and subsequent sequestration of zinc. Accordingly, the expansive distribution of ferromanganese nodules may now be augmented to include microscopic, and perhaps macroscopic, nodules on the epidermis of plant roots. Additionally, the ability for plant roots to serve as nucleating agents for hydroxide precipitation and nodule formation, as well as contaminant sequestration, has been introduced. Therefore, contrary to current belief [12], Zn attenuation on plant roots may be predominantly due to specific adsorption on to Mn oxide nodules rather than adsorption onto Fe oxides.

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Development of Monocapillary X-ray Optics for Synchrotron Applications

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Monocapillary x-ray optics are a candidate technology for producing micron and submicron beams of x-rays for a variety of microanalytical applications. At the ALS, these optics can be used to perform diffraction and fluorescence analysis of materials with submicron spatial resolution. Capillary optics are formed by re-drawing a glass tube, at high temperature, to produce a pre-selected optical figure. We have brought on-line an advanced capillary puller that is capable of drawing a wide range of figures in a reproducible fashion. We can routinely achieve a desired figure to within a slope error of 50 to 300 microradians, depending on the quality of the glass starting material.

The performance of these optics has been characterized at the ALS on the basis of their efficiency, spot size, and divergence. Early experiments used the output directly from a bending magnet on Beamlines 10.3.1 and 10.3.2. These optics typically had entrance diameters from 25 to 100 microns and exit diameters of less than 3 microns. More recent activities have explored the feasibility of advanced optical systems that rely on pre-focusing mirrors to concentrate the radiation onto the entrance of the capillary optic. We designed and tested a series of optics that take the output from the Kirpatrick-Baez (K-B) mirror pair on Beamline 10.3.2 and condense it further to produce a submicron beam of x-rays. Figure 1 shows the shape of a representative capillary optic. Typically, the tip of the optic is beveled to allow the sample to be placed very close to the exit of the capillary optic.

Figure 1. Internal diameter of typical optics is matched to the convergence angle of the Kirpatrick-Baez focusing mirrors on 10.3.2. The tip of the capillary optic is beveled at 45 or 60 degrees so that the capillary tip can be placed close to the sample and still allow the fluorescent or diffracted x-rays to reach a detector.

We tested these optics during two experimental series in 1998 and demonstrated that the output from the K-B mirror pair is efficiently coupled into the capillary optic. We measured the x-ray beam diameter by scanning a wire through the beam at various distances from the capillary tip. Figure 2 shows representative results obtained with the capillary optic shown in Figure 1, at a distance of about 50 μm from the exit of the capillary. The measured diameter of 0.37 μm FWHM is about a factor of four lower than the 1.4 μm diameter FWHM produced by the K-B mirror pair. Depending on the capillary design and distance from the exit of the capillary, we have measured beam diameters from 0.2 to 0.6 μm FWHM. A typical efficiency for these optics (defined by the ratio of the ion chamber signal produced by the K-B mirror pair to the signal produced by the combination of the K-B mirror pair and the capillary optic) ranges from 30 to 50%. For the capillary shown in Figure 1 we measured an efficiency of 40%. Thus, given a 50 μm stand-off distance, this capillary produced an increase in flux of 6X while reducing the beam diameter by a factor of 4. The beam divergence was measured to be about 6 mrad which currently limits the distance between sample and the capillary tip to less than about 50 μm , in order to preserve the small spot.

Future effort will be devoted to further reducing the spot-size and divergence of the x-ray beam produced by these optics. Additionally we will be conducting a series of microdiffraction and fluorescence experiments to demonstrate applications that are of interest to the semiconductor, optoelectronic, and advanced materials industries.

Figure 2. Beam profile measured by scanning a wire through the x-ray beam at a distance of about 50 μm from the capillary tip. This optic had an efficiency of 40% and a divergence of 6 mrad.

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Grain Orientation Mapping of Passivated Aluminum Interconnect Lines with X-ray Micro-Diffraction.

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INTRODUCTION

Electromigration is the physical movements of atoms in metallic interconnect lines passing current at high electron density (typically in the range of 10^5 amp/cm²). Significant material movement results in voids that consequently lead to breakage and circuit failure in the metal lines. This problem gets more severe as the line dimensions continue to shrink on integrated circuits. In spite of much effort in this field (1,2,3), electromigration is not understood in any depth or detail, but is strongly associated with the physical material properties (stress and strain) within the interconnect material. X-rays have been used to measure these properties in materials on the macro scale - this work describes the start of a program to perform similar measurements on the micro scale and its applicability to the electromigration problem. X-rays are quite well suited to such measurements as they are able to penetrate several microns into matter. This is important as interconnect lines are invariably encased in an insulator such as silicon dioxide (this is known as passivation). X-rays are thus able to probe the buried samples in their natural environment. Sample sizes are typically the grain sizes and are on the micron length scale. With the use of the x-ray micro probe techniques developed at the ALS, sample wires can be studied on a grain by grain basis.

EXPERIMENTAL CONSIDERATIONS

X-ray diffraction usually involves the determination of the x-ray diffraction angle with fixed photon energy. In such a case the sample is rotated through the Bragg condition. This is appropriate for large samples and large x-ray beams where the sphere of confusion of the goniometer (typically several tens of microns) is small compared to the sample interaction volume. When working on the micro scale, we have adopted the alternative approach that fixes the sample position, but still generates x-ray diffraction as the sample can be illuminated with polychromatic radiation from the ALS bend magnet synchrotron source. The sample can be considered to consist of many grains in random orientation. To see diffraction from such random individual grains requires the use of white light. This will generate a Laue pattern that can be used to determine grain orientation. The photon energy and position of the Laue spots will allow determination of the strain within the individual grain. This can also be carried out on a grain by grain basis. The data is intended as input for micro mechanical modeling calculations.

In summary there are two goals of this program to characterize micro crystals

1. grain orientation mapping
2. strain measurements on the separate grains.

This present work describes our progress towards the first goal of grain orientation mapping.

EXPERIMENTAL

Figure 1 shows the experimental setup. The synchrotron source of size typically $300 \times 30 \mu\text{m}$ FWHM (horizontal and vertical) is located some 31m distant from the apparatus. The source is imaged with demagnifications of 300 and 60 respectively by a set of grazing incidence platinum-coated elliptically bent Kirkpatrick-Baez (K-B) focusing mirrors (4). Imaged spot sizes have been measured as 0.8 micron FWHM in size. Photon energy is either white of energy range 6-14 keV or monochromatic generated by inserting a pair of Si(111) channel-cut monochromator crystals into the beam path. A property of the four crystal monochromator is its ability to direct the monochromatic primary beam along the same direction as the white radiation. Thus, the sample can be irradiated with either white or monochromatic radiation. The x-ray probe motion on the sample between white and monochromatic modes has been measured to be less than $0.5\text{-}\mu\text{m}$. White radiation is required for Laue experiments, which allow for crystal grain orientation determination. Monochromatic radiation is to be used for d-spacing measurements to determine stress/strain determination of single grains in the metal line.

Figure 1 Schematic layout of the K-B mirrors and the four crystal channel-cut monochromator

Figure 2 Schematic layout of the arrangement around the sample

The sample was an aluminum line deposited to $0.5\text{-}\mu\text{m}$ thickness and $0.7\text{-}\mu\text{m}$ width on an oxidized silicon substrate. The line was passivated with a plasma-enhanced chemical vapor deposition (PECVD) nitride at 300°C to $0.3\text{-}\mu\text{m}$ thickness. Laue patterns were collected using white radiation and a x-ray CCD camera. The exposure time was 1.0 sec and sample-to-CCD distance was 19.63 mm. Fig. 2 shows the arrangement of the sample with the CCD x-ray detector positioned vertically above it. As the x-rays are horizontally polarized, x-ray diffraction in the vertical plane is the more efficient.

Figures 3A and 3B show the raw data CCD image Laue patterns from the silicon substrate and aluminum line. The 2 images are displaced from each other by 1 micron along the wire length and differences are apparent due to the illumination of different aluminum grains. (The grey areas to the edge of the left and top of the images are defects in the phosphor coating on the CCD and should be ignored.) The dominant spots in the Laue pattern are from the silicon substrate, but when these are digitally subtracted the aluminum Laue pattern is apparent. These aluminum spots are highlighted and indexed in the figures. We have developed an automatic indexing code that can accept as input, the geometric positions of the Laue spots and can output the spot index and grain orientation matrix. The code achieves this by systematically working through the Miller indices and

obtaining a best fit to the spot positions for the applicable geometry. The photon energy range (~6-14keV) and aluminum unit cell size allows us to restrict the Miller indices range to 7 and less. The code is able to automatically index patterns for both the single grain Laue case and also for the 2 grain overlapped Laue case. Figures 3A and 3B show that there are 3 grains present in the aluminum line within the 2 micron distance along wire length measured. In both cases there are 2 overlapped grains illuminated by the 0.8 micron x-ray spot, with the grain indicated by "O" being present in both positions. It is clear that the x-ray spot has moved from one side of the "O" grain to the other. This grain has dimensions of about 1 micron and is typical for this sort of system.

Figure 1. Laue patterns from 0.7 micron wide aluminum wires on a Si (100) substrate. The two images are displaced by 1 micron along the wire length. The intense spots are from the silicon substrate and the weaker spots (highlighted) are from the aluminum grains. Both images contain 2 aluminum grains within the 0.8 micron x-ray spot. The aluminum spots have been automatically indexed and are assigned to separate grains using the square, circle and diamond shape scheme.

CONCLUSION AND FUTURE DEVELOPMENT

We have demonstrated that x-ray micro-diffraction is capable of determining the crystallographic orientation of individual grains in passivated interconnect lines. Orientation mapping has been achieved using automated indexing code that can accept input positions from the aluminum Laue patterns.

Having demonstrated that we can automatically index aluminum lines, we can proceed to the next stage of the project where samples having different processing conditions and various grain orientation maps can be investigated with respect to their electromigration behavior. After this the strain from grain to grain has yet to be measured. A new instrument capable of carrying this out is under construction at this time.

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Iron and Manganese as proxies for oxygenation and diagenesis in foraminifera

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During the late Quaternary, ocean conditions in Santa Barbara Basin (SBB) switched between two primary states: 1. Laminated or varved sediments, which formed during periods of low oxygen and contain low-oxygen tolerant benthic foraminifera; and 2. massive bioturbated sediments, representing periods of greater oxygenation in the basin, and which contain foraminifera preferring higher oxygen conditions. Laminated sediments occur as a result of suboxic (<0.1 mL/L oxygen) bottom waters in the basin below ~475 m, combined with highly productive surface waters that generate abundant organic material, consuming the small supply of oxygen that enters the basin (Kennett, et al., 1994). Using the degree to which these sediments were laminated, Behl and Kennett, (1996) assigned a bioturbation index ranging from 1 to 4. A bioturbation index of 1 was associated with varved sediments in which benthic oxygenation was <0.1 ml O₂ per liter while a bioturbation index of 4 indicated the oxygenation was >0.3 ml O₂ per liter.

In most marine sediments the interstitial fluids are derived from the sea water in the overlying water column. This interstitial complex of sediments, rocks, and water is the site of numerous physical, biological, and chemical reactions that can change both the mineral phases and the composition of the water. These changes are commonly grouped together under the term diagenesis. In early diagenesis most of the chemical changes that occur are dependent on the redox environment which is in turn controlled by the amount of organic carbon undergoing decomposition or preservation. This process of oxidation is a result of catabolic microbial reactions that break down organic molecules into simple molecules or inorganic elements. Further more there is a diagenetic sequence of the catabolic processes which is dependent on which oxidizing agent is consuming the organic carbon. Oxygen is the preferred electron acceptor as the organic matter is metabolized and donates electrons to the oxidizing components. However, if there is no oxygen present a succession of secondary oxidants will be used. The two most common of which are Manganese (Mn) and Iron (Fe). In the case of iron, Fe³⁺ undergoes reduction to Fe²⁺ as is shown in the equation below where (C) represents organic matter:

The purpose of this study is to develop a technique by which Fe³⁺ and Fe²⁺ can be measured in benthic foraminifera from Santa Barbara Basin so that we can use the results as a proxy for the oxygen content of the basin. As a result of diagenesis, Fe and Mn coatings can be found on foraminifera. Preliminary results of X-Y scans on several foraminifera from anoxic layers in SBB show that these coatings do contain relatively high levels of Fe. MicroXANES scans on the regions of high Fe concentration were also conducted. Representative results from one such scan are shown in Figure 1. Figure 1 shows an Fe microXANES spectrum from a foraminifera alongside an Fe₂O₃ microXANES spectrum from a Fe₂O₃ standard. Clearly the Fe in the foraminifera is at the lower oxidation state of Fe²⁺ which would be indicative of a reducing environment which we would expect from the low oxygen content of the sediments from which the foraminifera came. In on going work we continue to look for relative changes in the levels and speciation of the Fe and Mn in the diagenetic coatings of the foraminifera. We expect to see variations in these results based on the oxygen content of sediments from which the foraminifera come.

Figure 1: MicroXANES scans of Fe² coating of a foraminifera from anoxic bottom water conditions in Santa Barbara Basin and a MicroXANES scan of an Fe²O³ standard.

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Kinetics of Formation of Mixed Metal Hydroxides on the Surfaces of Clays

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BACKGROUND AND INTRODUCTION

Recent time-resolved, traditional XAFS measurements made at the NSLS in studies by Donald Sparks' group at the university of Delaware made an important contribution to the understanding of metal ion retention in the environment[1][2][3][4]. It was found that, under certain conditions of pH and concentration, nickel forms nickel-aluminum hydroxides on the surfaces of a number of clays. These hydroxides are quite resistant to dissolution and being less soluble severely reduce the mobility of Ni in the environment. It is thought that the same behavior will apply to a large number of other metal contaminants; the main criteria being that the ionic radius should be reasonably close to that of the aluminum cations. It was found that, like many cation-mineral reactions, there was a very rapid rate in the first part of the reaction, which lasted about 25 minutes. This was followed by a much slower rate until the experiment was considered to be complete and the last measurement made after 250 hours. The rapid part of the reaction is usually attributed to adsorption and complex formation whereas the slow second part is generally thought to be due to the formation of surface precipitates or to the incorporation of the cation(s) into the bulk.

The measurements were made by exposing pyrophyllite clay to Ni ions in solution for a specific length of time and then washing immediately to assure that further reaction had been arrested. The sample was then measured using XAFS. Although, to our knowledge, this was the first time that such measurements had been made to obtain kinetic information using XAFS it was not possible to obtain analyzable data at metal/clay reaction times of less than 15 minutes. This is because the average concentration of Ni on the clay surface over the area of sample measured was too low to provide sufficiently good statistics to give speciation information.

The data analysis of the traditional XAFS data, including a full structural analysis suggested that the Ni was forming three-dimensional surface precipitates of nickel aluminum hydroxide. The X-Ray Fluorescence and the Micro-XAFS capabilities[5] at beamline 10.3.2 were used to take a closer look at the precipitates of these mixed metal hydroxides and their micro-structure, at shorter exposure times than it had previously been possible to measure.

RESULTS

XRFM measurements of one of the low coverage structures are shown in Figure 1. This particular pyrophyllite clay substrate had been exposed to Ni solution for ten minutes. It can be seen that some form of Ni aggregation or precipitation is already forming at these short reaction times.

Figure (1) Map of Ni Kedge fluorescence for a low coverage phase (10 minutes reaction time of clay surface with Ni ions) showing regions of local concentration of Ni.

Figure (2) μ -XAFS measured in regions of local concentration, shown in (1). Results from the μ -XAFS indicate that the precipitates which begin to form at low coverage resemble those from the highest loading. This has important implications for the transport of low concentrations of contaminants.

It was possible to make μ -XAFS measurements on these precipitates which, after a 10 minute exposure to the Ni solution, appeared to be a few microns in size. This data are shown in Figure 2 along with data taken using the conventional technique of the longest reaction time (250 hours).

These initial data indicate that the precipitates formed at these low coverages are of similar type as those formed at the higher coverages. This suggests that the mixed-metal "binding" of contaminants occurs close to the onset of adsorption which, in itself, has important implications for metal transport in the environment. More extensive studies are planned [4] in order to check the reproducibility of these initial results. This particular example shows how, in the case where there is aggregation and thus local concentration on the micron scale, μ -XAFS can be more

sensitive than the macroscopic technique and why the parameter describing absorber 'dispersion' is more meaningful than the macroscopic value of the concentration.

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Major and Minor Element Variations in Speleothems as a High Resolution Paleoclimatic Record

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Cave calcite deposits or speleothems collected from California Caverns in Calaveras County, California show strong potential for preserving a high resolution paleoclimate record. Geochemical variations along speleothem growth axes combined with precise U-series dating will provide a continuous high temporal resolution record of precipitation and temperature changes in California as far back as the last glacial maximum (LGM), about 18,000 years ago. Major and minor element x-ray fluorescence analysis performed on beamline 10.3.2 at the Advanced Light Source will be combined with O ($^{18}\text{O}/^{16}\text{O}$), C ($^{13}\text{C}/^{12}\text{C}$), and Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopic analyses of microdrilled samples. The high spatial resolution and elemental sensitivity of this beamline provide an ideal tool for the detection of temporal variations in speleothem composition. As a typical speleothem growth rate is about 50 $\mu\text{m}/\text{year}$, the x-ray beam allows at least an annual time resolution. The age of the samples will be precisely determined using $^{230}\text{Th}/^{234}\text{U}$ TIMS analysis. Previous studies have shown that oxygen isotope ratios can be used to determine past temperature changes (Dorale et al., 1992). Carbon and strontium isotopic variations will be interpreted as indicating changes in groundwater flow path related to changes in recharge rate. A continuous record of major and minor element variations will provide a valuable supplement to this isotopic data.

The main sources of speleothem Sr and C, soils and bedrock, commonly have distinct isotopic signatures. Soil carbon isotopic variations may be caused by shifts between C_3 and C_4 vegetation. However, we have chosen a site in which vegetation has been constant over the time scale of interest. Therefore, C and Sr isotopic variations likely reflect changes in solute transport and water-rock interaction due to hydrologic changes. Initial results suggest that the two main sources of speleothem C and Sr, overlying soils and bedrock, have distinct isotopic signatures. Therefore, through the measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ for all soil, bedrock, and cave calcite samples, we can, check for any vegetation induced changes as the two systems would be expected to co-vary under constant C_3 influence. The C and Sr isotopic systems will thus be useful for determining changes in water-rock interaction. Past changes in flow regime should be reflected by the degree to which water in equilibrium with the soil equilibrated with the bedrock before the signal was preserved in a speleothem. Banner et al. (1996) determined that in a cave system in Barbados, during times of high precipitation, groundwater flow through the bedrock was mainly conduit flow and hence the water retained more of a soil signature, whereas during times of low precipitation, diffuse flow dominated and the water contained more of a bedrock component. In order to interpret C and Sr isotopic variations along speleothem growth axes, we will apply the model of Johnson and DePaolo (1994) which relates the temporal isotopic evolution of groundwaters to solute transport and water-rock interaction. It is likely that both major and minor element variations between speleothem growth bands also reflect the hydrologic conditions at the time of formation. If the concentration of these elements varies between the soil and bedrock, we should see more of a soil component during times of high precipitation and more of a bedrock component during times of low precipitation. Through the

use of the soft x-ray beamline 10.3.2 at the ALS, we have initially examined the temporal variation of Ca, Mg, Sr, and Fe within a stalactite. Figure 1 shows the variations in iron concentration along a speleothem growth axis. The bands of high iron concentration most likely correspond to detrital layers deposited by flood waters. The bands are visible in the sample as well, but the elemental analysis helps us distinguish these bands from similar reddish bands caused by the presence of organic acids. Figure 2 shows that the iron bands are indistinguishable from the Fe_2O_3 standard. Thus, these iron bands were deposited in an oxidizing environment.

Figure 1. X-Ray Fluorescence map of Fe in a stalactite. Bands of high Fe concentrations are shown by the light areas.

Figure 2. The absorption spectra of Fe in the stalactite is compared to an Fe^{2+}O^3 standard.

The initial results are promising, but more samples need to be analyzed. In addition, we need to measure these elements in stream water in the drainage basin, in the soil, in cave drip waters, and in the limestone bedrock in order to fully understand the complex interactions governing the concentration of these elements in the calcite. High resolution time series such as these are very important in understanding the natural variability of the climatic, hydrologic, and ecologic systems in California on long time scales. This information may help lead to improved climate models and hence improved predictions about future climate changes. Speleothems potentially contain the most complete record of past environmental change in central California, and their study will provide a valuable complement to other climate records.

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MicroXANES Characterization of Temporal Changes in the Zinc Environment of Zebrafish (*Danio rerio*) Embryos

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Introduction

Zinc is critical to the growth, development and differentiation of all species¹. Thus, for example, zinc deficiencies during development are often teratogenic, with effects ranging from mild developmental retardation to embryo death, depending on the severity of the deficiency². Despite its obvious importance, the molecular-level function of zinc in embryonic development is poorly understood. There are hundreds of zinc proteins, each with a different Zn site, and each likely to be present in variable amounts as a function of developmental stage. Precise definition of Zn distribution is therefore a daunting task.

Embryos that develop without maternal nutrition must possess all of the nutrients required for normal development at the time of fertilization. Such “closed” systems make excellent models to study the migration and speciation of zinc during development. Recently, Vallee and colleagues working with *Xenopus laevis* (African Clawed Toad) oocytes³ and Berg and colleagues working with *Danio rerio* (Zebrafish) embryos⁴ have reported that a large amount of zinc (~1 mM) is stored within the embryos at the time of fertilization. Subsequent studies using ⁶⁵Zn were performed on the *X. laevis* embryos to follow the distribution of zinc during embryonic development⁵. The results of these experiments showed that the zinc remained associated with the lipovitellin protein in yolk platelets until the organism reached the tadpole stage of development (~48 hours after fertilization). The interpretation of these results was that zinc did not play a role in the early stages of development but was stored in the lipoproteins until a much later stage of development, at which time it was distributed to other zinc metalloproteins as needed.

Due to the relatively large concentration of zinc in the embryos, such samples are directly amenable to study via x-ray absorption spectroscopy (XAS). XANES (x-ray absorption near edge structure) spectra measured on intact embryos of various stages during early development for both zebrafish and *X. laevis* demonstrated that significant changes occurred in the bulk zinc environment within the first hour after fertilization, and that the zinc environment remained dynamic throughout the first 12 hours. These results were in contrast to the previous studies on *X. laevis* made using ⁶⁵Zn labeled vitellogenin.

Results

Taking advantage of the small spot size and high brightness of beamline 10.3.2, zinc microXANES spectra have been measured in the yolk and blastomere regions of the zebrafish embryos at different stages of development. Figure 1 shows the XANES and difference spectra from the yolk of the 4-cell, 128-cell and high stage embryos, while figure 3 contains XANES and difference spectra from the blastomeres of the 4-cell and high stage embryos. Despite the high noise level in these spectra, it is apparent that the yolk XANES in the latter stages of development are different from the yolk XANES of the 1-cell embryo. Comparing the trends observed in the embryo yolk XANES with

those of zinc model complexes⁶, the persistent positive difference at ~9663 eV and negative difference at ~9670 eV suggests that there is an increase in low-Z (N/O) ligand zinc sites found in the yolk at the later stages of development. The XANES spectra measured in the blastomere regions of the 4-cell and high stage embryos also show some differences. However, when difference spectra are calculated by subtracting these blastomere XANES from the XANES spectrum for the 1-cell yolk, the differences appear to be quite similar. The negative difference at ~9663 eV and the positive difference ~9670 eV suggests that the zinc sites in the blastomere have a larger number of sulfur ligands than the sites found in the yolk of the 1-cell embryo. Future efforts will focus on improving the signal to noise ratios in these spectra, so that direct comparisons may be made with spectra of crystallographically characterized zinc model complexes.

Figure 1: Zinc XANES (top) and difference spectra (bottom) measured with a 4 μm^2 beam positioned in the yolk of fertilized zebrafish embryos. These spectra show that changes occur in the zinc environment of the yolk within the first hour of development.

Figure 2: Zinc XANES (top) and difference spectra (bottom) measured with a 4 μm^2 beam positioned in the blastomeres of fertilized zebrafish embryos. The differences observed in the blastomeres are opposite those observed in the yolk, suggesting that there are distinctly different zinc environments localized in the yolk and blastomeres of the embryos.

Given that the 1-cell yolk is not only different from the yolk of the later stage embryos but also from the blastomeres, it can be ascertained that the changes observed in

the intact embryo XANES were due to changes in the zinc sites within both the yolk and the blastomeres. Since the changes observed in the yolk manifested themselves opposite of those from the blastomeres, it can also be inferred that the zinc sites in the blastomeres are dominated by sulfur ligands, while the zinc in the yolk tends toward a larger percentage of low-Z (N/O) ligands.

Since the microspectroscopy line is equipped to measure fluorescence signals from more than one element simultaneously, it has also been possible to measure Fe K α maps for the zebrafish embryos. The elemental maps suggest that the iron is highly localized within the blastomeres. The quantity of iron was sufficient to measure microXANES spectra in the blastomere region of the embryo. Figure 3 shows the preliminary Fe microXANES spectra from the 4-cell and 128-cell embryos. While this data demonstrates that it will be possible to deduce the oxidation state and coordination environment from such XANES measurements, future measurements will need to be signal averaged for a significant amount of time given that the iron concentration in the embryo is less than 500 μ M.

Figure 3: Fe XANES spectra measured in the blastomeres of newly fertilized (1-cell) and two-hour old (128-cell) zebrafish embryos.

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Spatial Correlation of Trace Elements with Zoning Patterns in Agates

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INTRODUCTION

Autonomous pattern formation is now recognized as a universal phenomenon common to many physical, chemical, and biological systems. Commonly patterns are observed over several different length scales. The key to understanding how systems self-organize to create patterns lies in detailed analysis of the mechanisms that operate over the different length scales. Banded agate has often been cited as an example of such pattern formation. Variation in size, orientation, defect density, and composition of chalcedony fibers have been associated with banding patterns, and many of these have been documented by studies.

Because chalcedony, a fibrous variety of quartz, typically contains only extremely low concentrations of impurity elements, few tests have been made to determine whether chemical variations exist within the fine-scale banding ranging typically from <10 to >100 μm and whether such variations may record periodic fluctuations in fluid chemistry.

EXPERIMENT AND PRELIMINARY RESULTS

As a preliminary study, we examined several thin slices (< 20 μm thick) of banded agate at beam line 10.3.2. The distribution of Al, Fe, Ca, Zn, and Si was mapped over several optically visible bands corresponding to variations in size and orientation of chalcedony fibers. This was done using an incident monochromatic beam of 10.5 keV and rastering the sample over the area of interest whilst collecting the fluorescent photons at specific energies corresponding to the elements of interest. Results are shown in the figures below. These clearly demonstrate that thin bands with larger fiber size are depleted in Fe and enriched in Al relative to the zones composed of smaller fibers. In addition there is an indication that Ca varies spatially with a zoning pattern that is commensurate with the others, but suggesting that the maxima in concentration do not coincide exactly with minima for Fe and Al. This is an intriguing new finding, and raises the question of whether significant changes in fluid composition accompany the pattern formation.

For iron, which was the most easily detectable element in the agate, it was also possible to measure the microXAFS to determine its oxidation state. This is shown in figure 2 and, by comparison to standard iron compounds it appears that the oxidation state is 3+ both inside and outside of the bands.

These preliminary findings would not have been possible with electron-probe techniques, in which minimum detection limits are too high to allow quantitative mapping. Secondary ion mass spectroscopy has been used to document variations in Al, but heavier elements pose difficulties. Thus spectro-microscopy at a synchrotron source offers the best means of characterizing micro-scale chemical variations, and further provides the opportunity for determining the oxidation state of certain trace elements and possibly even information on local structure.

Figure 1: (A) Shows fluorescence map of Fe K α radiation over the agate bands shown at corresponding distances in the optical micrograph shown in (B). The Fe concentration in the sample is a few tens of ppm: Within the bands about 20 ppm and outside about 35 ppm.

Figure 2: This near edge region of the Fe between the bands indicates that it is in the Fe 3+ oxidation state. The concentration here is about 35 ppm. Better statistics are required for a complete speciation determination.

The results of this work are of interest not only for understanding agate, but more generally for unraveling the mechanisms by which patterns form in mineral systems. Such zoning patterns exist in a wide variety of minerals, including those produced biogenically.

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Spatially Resolved XAS Measurements of Particulates in Lung Tissue

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INTRODUCTION

Lung tissue samples obtained from Russian nuclear industry workers have been observed to have numerous particles imbedded in them. The particles are typically in the micron to ten's of micron size range and many contain heavy metals. X-ray fluorescence microprobe (XFM) and spatially resolved XAFS studies were carried out on beamline 10.3.1 and 10.3.2 respectively, to determine the size, composition, and chemical state of these particles. The overall goal is to try to correlate the properties of these particles and their chemical nature to the health effects on these industrial workers.

EXPERIMENT

Lung tissue samples were obtained from autopsies of Russian nuclear industry workers who had died of cancer. The workers were typically male, had been exposed to metallurgical refining for many years, and were, generally, heavy smokers. Lung tissue samples were mounted on a thin plastic film and dried in air. The samples were typically 5 mm by 10 mm and 2-3 mm thick. Preliminary XFM measurements were taken on BL 10.3.1 at the ALS with the collaboration of Scott McHugo, Al Thompson, and Keith Jackson of the CXRO at LBNL. Measurements reported here were taken on the new microfocus line (BL 10.3.2) at the ALS built by MacDowell et al. [1]. BL 10.3.2 uses a 4 crystal monochromator followed by KB focusing mirrors[1]. It has been shown to achieve a beam size of 0.8 by 0.8 microns with flux densities of 10^7 photons/ sec in the energy range of 4 - 11 keV.

XFM measurements were taken over selected areas in the sample including both diseased and healthy tissue. An area of about 100 μ by 100 μ was scanned in 5 μ steps and a Si(Li) detector was used to identify the atomic species present. An excitation energy of 12 keV was used so that elements up to As could be identified from their K α lines.

An area was chosen which contained small particles containing Cu and Fe. We used this area for spatially resolved XAFS measurements. The focused beam was used and XAS spectra were

collected at the Fe and Cu K edges. Points of interest were first located by rastering the sample in 5 μ steps over a region identified as being of interest from results taken at 10.3.1.

Once the particles of interest were found, five scans were done at each edge, over a range of -50 to +400 eV. Each scan took about 40 minutes. Improvements in the software (permitting regions to have different stepping increments) now enable scans with the same degree of extractable speciation information in them as those previously taken to be measured in approximately 30% of the time it took previously.

RESULTS AND CONCLUSIONS

Numerous micron sized particles have been seen in both healthy and diseased lung tissue. Several different elements were seen overall, some in isolated particles and others associated in the same particle or region. Heavier elements may also be present which could not be seen because of the excitation energy (12 keV) used here. An area was located which contained Fe and Cu. The maps for this area are shown in Figure 1. The μ -XAFS spectra, using a micron sized beam, were obtained in this area for both edges. The μ -XAFS spectra were consistent with oxidized states for each element of 3+ for Fe and 2+ for Cu, respectively. These studies demonstrate the feasibility of characterizing the chemical state of micron sized particles in human tissues.

Figure 1. : Fluorescence maps of Copper K α and Iron K α in the region of interest

Figure 2. Oxidation states of Cu and Fe were determined by observing the edge position in relation to standard compounds.

These results are preliminary but are potentially very significant because they may help in providing key information about the role of small metal particles in pulmonary disease. To be more definitive will require an extensive set of measurements with many samples whose medical history is well understood. This, in turn, will require a much higher level of manpower and support than is currently available.

These results were presented as part of a poster at the recent XAFS X Conference that also included x-ray XFM results taken at 10.3.1. We believe that we have now demonstrated the potential for this work and are in the process of putting a team together to prepare a proposal to use both XFM and spectromicroscopy to study heavy elements in human tissue and relate them to disease. We are trying to identify someone in the US who can work with us on the health effects and coordinate with our colleagues in Russia where there is an extensive team there who can obtain samples and medical histories. Presently we are manpower limited to do much more. We would like to develop a significant program in this area to look at the correlation to health effects of other small particles, both airborne and *in situ*, such as calcifications, where it is believed that particle size, morphology, and correlated distributions of calcifications may play a role in some types of breast cancer. We believe that once these results start to be made available to the wider community it will spur additional medical imaging applications using synchrotron radiation.

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Speciation of Arsenic in Soils

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In this study we used beamline 10.3.2 to collect arsenic micro-XAFS spectra from a natural soil collected near Panoche Creek, California. By using the microprobe to scan the surface of a polished section of the soil, ~ 1 mm thick, two distinct iron containing areas were found (diameters < 200 μm) only 500 μm apart: one of the areas is dominated by iron and sulfur, while the other is dominated by iron oxide. The XANES spectra reveal that the speciation of arsenic in the two features is different, consisting of two arsenic oxidation states. Thus, by using the micro-XAFS technique, we are sampling two areas separated by a mere 500 microns, that are completely distinct in their chemical nature. This data clearly illustrates the power of this micro beam technique in its capacity to spatially resolve different chemical species. Such information cannot be determined using the more traditional bulk XAFS technique, which would give an average spectrum of the arsenic environment in the soil. This micro-XAFS technique yields the detailed information that is critical for modeling and managing arsenic in the environment.

As XANES collected from two distinct mineralogic features in soil. The FeS feature is a region in the soil less 200 μm in diameter that is relatively high in Fe and S. The FeO feature is a similar feature (500 μm away) in which S is not present. The step size in the spectra is 0.5 eV.

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Speciation of Zn in a smelter-impacted soil

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INTRODUCTION

More than hundred years of ore-processing activities have severely impacted the natural environment, and specifically soils resulting in some heavy polluted areas losing the vegetation cover [1]. Determining the chemical form of toxic metals is of fundamental importance for assessing the chemical risk posed by their presence in agricultural fields, forest soils, and gardens, and developing effective remediation strategies in the most contaminated areas.

Micro-EXAFS and micro-SXRF were used to study the speciation and spatial distribution of Zn in a smelter-impacted soil located in the North of France in the vicinity of an ancient Zn, Pb, and H₂SO₄ plant. This plant was active during the first half of the 20th century, and was the third largest smelter in the world. Surrounding soils have been contaminated by Zn- and Pb-rich fly ashes originating from high-temperature smelting process and containing predominantly franklinite (ZnFe₂O₄), willemite (Zn₂SiO₄) and unidentified Pb compounds. Zn and Pb were progressively released in soil solutions during the weathering of slag materials, and dissolved species precipitated or were taken up by soil constituents. The profile concentrations of Zn and Pb with depth indicate that Zn is much more mobile than Pb: At about 110 cm depth, the Zn concentration still reaches 500 ppm as compared to a geochemical background of 70-100 ppm (Fig. 1). EXAFS and SXRF measurements were carried out on samples collected at 40-50 cm depth in order to assist us in the identification of Zn-precipitated and Zn-sorbed phases.

EXPERIMENT

Measurements were performed on the 10.3.2. station [2]. A polished 30 µm-thick soil section indurated in epoxy was rastered in 6 µm steps through the focused monochromatic X-ray beam, and the selected K α fluorescence was integrated for one second per point corresponding to a total data collection time of approximately 8 h. A typical energy dispersive fluorescence spectrum obtained after ~ 8 h is shown in Fig. 2. The total signal is heavily dominated by the Fe and Mn fluorescence-yield of the soil matrix and, in EXAFS spectroscopy, the desired Zn signal makes only ~ 2 10⁵ counts while typically 10⁶ good counts are suitable to get an acceptable precision of 10⁻³. In spite of this curse due to the present flux limitation on this station (~ 10⁸ ph/s/µm²), EXAFS spectra with an acceptable S/N ratio were successfully obtained by averaging 8-10 spectral sweeps of ~ 1 hour each thanks to the high stability of the spectrometer optics.

RESULTS AND DISCUSSION

Fig. 3 shows the spatial distribution of Mn, Fe, and Zn in a (Fe,Mn)-rich zone of the soil clay matrix. Highest Zn concentrations were encountered in Fe-rich grains, but Zn is also partly associated to Mn. Mn and Zn-µEXAFS spectra were collected in a Mn-rich zone, and a Fe-EXAFS spectrum was collected on a Fe-rich grain. Metal-bearing phases were identified from the comparison of EXAFS spectra with a large database of references. Fig. 4 shows that Fe grains have a δFeOOH-like structure and that the Mn rich concretion is made of a phylломanganate, birnessite-like, compound. The Zn-EXAFS spectrum closely resembles the Zn-sorbed birnessite model compound in which Zn is bounded at layer vacancy sites [3] (Fig. 5). This experiment

demonstrates the potential of coupled μ SXRF and μ EXAFS measurements to directly determine metal species on a very small spatial scale in chemically and structurally heterogeneous natural systems.

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Fig. 1: Concentration of Zn and Pb in the $<100 \mu\text{m}$ soil fraction (ppm).

Fig. 2: X-ray fluorescence spectrum.

Fig. 3: Gray-scale map of the distribution of Fe, Mn, and Zn in the soil matrix. Zn is partly associated to Fe in Fe-rich grains and to Mn in the Mn-rich concretion. Size of the map: $1 \times 1 \text{ mm}$.

Fig. 4: micro-EXAFS measurements from the Mn- and Fe-rich regions. lines: exp. spectra; dots: reference spectra.

Fig. 5: Structural model for Zn-sorbed birnessite (After Silvester et al., 1997).

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Studies of Adsorption of Contaminants onto Viscous Liquid Barriers

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Contaminants in the subsurface can be contained by injection of viscous liquid barriers [1,2]. These barriers, formed by injection of a low viscosity liquid which gels after placement in the subsurface, reduce the permeability of the porous media surrounding the contaminants and thereby inhibiting the flow of potentially toxic agents to groundwater. There are several chemical formulations that are used in liquid barriers technology. Recent work [3] has suggested the use of injectable colloidal silica barriers that contain magnetite. The addition of magnetite would facilitate the precise placement of the grouting liquid during the gelling process. The stabilized colloidal silica-magnetite fluid, called a ferrofluid, can be held in position during the gellation process using permanent or electromagnets, thus providing a means of precise placement of the barrier.

To evaluate the long term stability of this type of barrier, an understanding of the interaction of the entrapped contaminants with the barrier material is needed. The interaction of the contaminant species with the barrier can result in either surface adsorption, chemical transformation, or diffusion through the barrier. Any of these phenomena can effect the mobility of the contaminant in the subsurface.

To understand the interaction process, information on the contaminants, for example Cs and Cd, on the surface of the barrier is needed. Microscale measurements of elemental distribution of contaminants on the barrier surface would reveal both the adsorption patterns and chemical speciation of the contaminants. This, along with macroscale measurement of barrier integrity, would reveal information on the stability and the longevity of subsurface barriers. Detailed knowledge of chemical-barrier interactions would lead to the development of more effective barrier systems.

Initial investigation by μ -XAFS of the ferrofluid barrier material gelled in the absence of a magnetic field has shown detailed iron self-organization patterns on the barrier surface (see Figure 1). The patterns are a combination of small circular accumulations and longer striated patterns. Initial measurement of the iron in the circular shaped areas may indicate a non-magnetic form of iron. Barrier material exposed to cesium shows adsorption in a network or web pattern, not associated with the striated iron patterns (Figure 2). We can see that the Fe still shows striated 'self-organization'. The cesium, however, shows quite a different distribution. It appears to have a web-like or network structure that spreads over the organized iron without any apparent directional favor of its own. Additional measurements would be required to determine the speciation of the iron and cesium in the scans to understand the details of the barrier-cesium interaction.

Future work will look this interaction in detail and would also include investigation of other contaminants. In addition, iron patterns formed in the barrier in the presence of a magnetic field would be investigated. Also of interest is observation of changes in the surface characteristics either by chemical erosion or dissolution and patterns in the iron after long term exposure studies which would aid in the evaluation of long-term barrier stability.

Figure 1 Elemental Scan of Fe in ferrofluid colloidal barrier material gelled in the absence of a magnetic field showing self organization

Figure 2. Magnetite in silica after exposure to CsCl solution

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Studies of Mineral Heterogeneity Using the Advanced Light Source

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Reactive transport simulations have been used in coupling thermohydrologic and chemical (THC) processes to describe the evolution of geothermal fields and potential nuclear waste repositories, ore deposits, and transport at environmentally contaminated sites. Reactive transport models generally use a simplified set of volume-averaged mineral and geochemical parameters as input and then predict the evolution of fluid chemistry and mineralogy along transport pathways. However, naturally heterogeneous distribution of porosity and mineralogy may make volume-averaged representations of those parameters inappropriate, if mineralogy and porosity are correlated. As a result, simulated fluid chemistry may change significantly when represented by volume-averaged vs. non-averaged mineral and porosity distributions. For example, a change in the abundance of ferric minerals can have a noticeable effect on the redox potential of the fluid. As a result of changes in fluid chemistry, mineral dissolution or precipitation can occur. Volumetric mineralogical changes in turn can cause changes to porosity and permeability in the hydrologic framework.

To evaluate this problem, we are working on two dissimilar rock systems. One part of this work addresses the question of the scale of mineralogical heterogeneity that should be included in reactive transport models of THC behavior in fractured volcanic tuffs at Yucca Mountain, Nevada. As a first step, we have determined the compositional heterogeneity of the tuff in order to formulate a means of representing the heterogeneity in a statistical manner (random, fractal, ordered repetition, etc.). We have chosen representative regions of distinct physical properties that represent different types of heterogeneity, including fracture-matrix regions and replacement-alteration regions. The chemical element maps that are produced from probing these regions using the x-ray fluorescence microprobe (beamline 10.3.2) provide a unique means of quantifying the degree of chemical variation across small areas (on the order of less than 1 cm²) that can be compared to larger scale heterogeneities (on the order of 10 m²). Simulations that incorporate small-scale mineralogical differences are then run to determine the sensitivity of model results to these differences. Model output to date suggests the mineralogical results are sensitive to the heterogeneities, implying they must be incorporated in a representative way in larger scale reactive transport simulations in order to obtain realism in modeling the natural system.

A second part of this work addresses the extent to which different fluid chemistries influence the development of mineralogical heterogeneity during recrystallization from the same original bulk composition. We are examining samples of rock which have experienced a uniform temperature and pressure history, but which exhibit different mineralogy. The mineralogy appears to reflect differences in the composition of the co-existing fluid phase from location to location, on the scale of millimeters. By mapping the past distribution of fluid heterogeneity based on differing mineral chemistry, we will be able to establish the scale at which fluid chemistry influences on mineral composition are significant and must be accounted for in reactive transport models.

Acknowledgments

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Beamline 11.3.2 Abstracts

Actinic detection of defects in Extreme Ultraviolet Lithography Mask Blank

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INTRODUCTION

Optical projection lithography has been the workhorse of the semiconductor industry for making integrated circuits for the past three decades. However, it is widely believed that optical lithography will finally run out of steam for circuit fabrication with $<0.1\ \mu\text{m}$ critical dimensions and that a new lithographic approach is needed to sustain the further scaling of integrated circuits[1]. Extreme ultraviolet Lithography (EUVL) is one of the leading candidates to follow optical lithography in the next century[2]. Utilizing 11-14 nm radiation with an all-reflective projection optical system, EUVL is expected to provide resolution down to 30 nm with reasonable depth of focus and adequate wafer throughput[3].

The mask architecture that is being actively pursued for EUVL is a reflective mask, consisting of absorber patterns on top of multilayer reflective coatings on a robust substrate[4]. Since a defect on the mask will disrupt the image of the circuit pattern on the wafer, the capability to produce defect free masks is crucial in any advanced lithographic technology. A recent simulation study suggests that a defect as small as 80 nm on the EUVL mask is "printable"[5]. This tight defect specification necessitates a very stringent control on the level of defects in mask making: the mask blank needs to be free of any printable defect and the absorber circuit pattern also needs to be free of any printable defect. While repair technologies are being actively studied for defects in the absorber pattern[6], defects in the mask blank are essentially impossible to repair. Therefore, producing low defect density EUVL mask blanks and inspecting them represents a very important technical challenge to meet for the commercial viability of EUVL technology.

While there are several inspection strategies for EUVL mask blanks such as visible light scattering and scanning electron microscopy, these probes tend to have a limited probing depth into the multilayer coating. Furthermore, the connection between the visible light scattering cross section and the EUV response is not well understood. Therefore, to capture all the printable defects in the EUVL multilayer mask blank, an inspection method at the operating wavelength (at-wavelength inspection) is necessary, at least at the developmental stage of the technology. Only an at-wavelength inspection technique can provide reliable feedback to the low defect density multilayer deposition technique and can qualify other inspection techniques for commercial EUVL system.

DEVELOPMENT OF EUV SCANNER FOR AT-WAVELENGTH MASK INSPECTION

As a proof-of-principle at-wavelength inspection system for EUVL mask blanks, we have built an EUV scanner based on raster scanning a focused EUV beam along the Mo/Si multilayer coated mask blank.[7] As shown in Figure 1, when the focused EUV beam is incident on a defect, the amplitude and phase of the reflected radiation is perturbed by the defect. This perturbation manifests itself as an intensity reduction in the specularly reflected beam (bright field) and scattering of photons into non-specular directions(dark field). The scattered radiation

Figure 1. Concept behind the current actinic scanner is shown. When the focused radiation is incident on a defect, intensity of the specularly reflected beam is reduced (bright field) and photons are scattered into a non-specular direction (dark field).

is captured by microchannel plate detector. The microchannel plate has an opening at the center so that the specularly reflected beam passes through the opening and can be captured by a bright field detector situated behind the microchannel plate. The focusing of the incoming EUV radiation is achieved by a pair of glancing angle bendable mirrors in the Kirkpatrick-Baez configuration.

The system is installed at BL 11.3.2 at the ALS, which is the dedicated beamline for EUVL mask blank defect inspection. Thusfar, we have concentrated on studying properties of various programmed defects on an EUVL mask blank. Specifically, we studied defects beneath the multilayer (substrate defects or "phase" defects) or defects on top of the multilayer ("opaque" defects). Figure 2 and Figure 3 shows the bright field and dark field inspection results from an array of phase programmed defects (Figure 2) and opaque programmed defects (Figure 3). The phase programmed defects were made by fabricating a small bump on the silicon substrate before the multilayer deposition. When the multilayer is deposited, the multilayer deposition over the bump is conformal, resulting in a coherent bump in the multilayer. This will produce a localized phase shift in the reflected wavefront. The opaque programmed defects were made by depositing and patterning a small absorber island (in this case aluminum). Because the absorption is very strong in the EUV spectral region, any particle on top of the multilayer coating will significantly reduce the intensity of the reflected beam.

As shown in Figure 2, detection of scattered photons in the dark field shows a superior sensitivity to phase defects. Strikingly, the dark field signal is quite weak for opaque defects as shown in Figure 3. Correlating the signal strength between the bright field and the dark field can provide a clue to whether a defect is a phase (substrate) defect or an opaque defect.

In a recent experiment with programmed defects, we also demonstrated that we can detect a defect as small as 100 nm in lateral dimension. The sensitivity of our system depends critically on the spot size we can achieve. The best spot size achieved so far is $10\text{ }\mu\text{m}^2$ in area, which results in approximately 0.1% change in the bright field for a 100 nm diameter opaque defect.

Figure 2. (a) The bright field scan of the 25 nm high programmed defect sample. The size of the programmed defect ranges from 1.5 by 8 μm to 0.5 by 0.5 μm as indicated in the figure. (b) The dark field scan of the same region as 3(a) Note the phase defects appear very distinctively in the dark field

Figure 3. (a) The bright scan of the opaque programmed defect sample. The sample was fabricated by depositing and patterning absorber material such as aluminum to simulate particles on top of the multilayer coating. The size of the defects are similar to that shown in Figure 2. (b) The dark field scan of the same region as 5(a). The visibility of defects are low compared to that of phase defects even though the scale has been adjusted.

FUTURE EXPERIMENTS

Based on the system learning that we acquired during 1998, we are planning to do a series of experiments. Specifically, experiments for cross correlating results obtained with a visible light scattering defect inspection tool and our EUV scanner will be performed. It is anticipated that this kind of correlation study will reveal the EUV response of various defects found on the EUVL mask blank and also test the sensitivity of the visible light scattering inspection system to EUV specific defects. Another crucial experiment that is being planned is a defect counting experiment. A relatively larger area of an EUVL mask blank will be scanned and the statistics of defects found on the mask blank will be compiled.

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Beamline 12.0.1 Abstracts

A Spectromicroscopy Study of the Al/GaS Interface: An Evidence of Band Bending Lateral Inhomogeneities.

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ABSTRACT

Spectromicroscopy study has been performed to find evidence of lateral inhomogeneities in the band bending for the Al/GaS system. Micro-images of the interface tuned to the Al 2p core levels revealed localized chemical inhomogeneities in proximity of the edge of the Al overlayer. A careful analysis of the photoemission spectra supports these conclusions and relates the inhomogeneities to band bending variations.

INTRODUCTION

In the past 50 years, the problem of interface barriers, both for Schottky barriers and heterojunctions has been one of the main topics in solid state physics [1,2,3]. This problem is still open and, in particular, there is no complete explanation of how interface phenomena affect the barriers. Many models and theories were developed over the years to tackle the problem and to obtain a unified picture [4,5,6]. The attention to this problem is due not only to the technological impact of semiconductor devices but also to many relevant fundamental questions. A good theory for explaining the barrier requires in fact knowledge of both the interface electronic structure and of the “absolute” interface energy scale (e.g., the mid-gap energy) [7,8].

The main objective of the present work is to detect lateral inhomogeneities of the band bending via high resolution spectromicroscopy and to show that the elementary Schottky picture breaks down when the interface is probed with sufficient spatial and energy resolution. Spectromicroscopy studies in this domain with high lateral resolution are still quite scarce [9].

EXPERIMENT

The single crystal GaS are grown at Ecole Polytechnique Fédérale of Lausanne (Switzerland). GaS is a layered compound so cleavage is easy and yields near perfect surfaces. The samples were cleaved in ultra high vacuum at a base pressure $\sim 3 \times 10^{-9}$ mbar. The interfaces were obtained by evaporating $\sim 100\text{\AA}$ thick aluminum metal on a half masked sample at 10^{-9} mbar. An Al-overlayer edge width obtained with this method ranged from 2-15 μm . The spectromicroscopy was performed at a base pressure of 1.0×10^{-10} mbar. The elemental and morphological information is obtained via photoemission microscopy performed at MAXIMUM at BL 12.0.1 at the ALS, Berkeley. The MAXIMUM microscope has achieved unprecedented lateral resolution of 0.1 μm and a nominal energy resolution of 0.25 eV at 130 eV photon energy.

RESULTS

A $20 \times 20 \mu\text{m}^2$ microimage of an Al/GaS interface obtained at Al $2p_{3/2}$ core level by focusing 130 eV undulator beam down to a submicrometric size on the sample is shown in the fig.1 (a). Al overlayer signal inhomogeneities are clearly visible in the image along the entire overlayer border - see the bright “bubbles” on the image - suggesting

Figure 1. (a) $20 \times 20 \mu\text{m}^2$ microimage tuned at the Al $2p_{3/2}$ core level of the Al/GaS. The bright areas correspond to the Al covered area while the dark areas correspond to the metal-free area. (b) and (c) Ga 3d spectra obtained at along the dashed A and B lines in (a), respectively.

possible chemical reactions between the substrate and the overlayer. Fig. 1 (b) and (c) are two correlated series of Ga EDCs obtained along lines A and B of fig. 1a. By comparing the two, we see the difference in the band bending along line A and B. Note that line A crosses one of the bright Al overlayer border areas of fig. 1a, whereas line B does not. Valence-band GaS spectra (not shown here) exhibit the same shifts -- i.e., they are related to the GaS band bending changes. From best-fit peak positions we derived the interface band bending. The maximum shift for the GaS features along line A is ~ 150 meV, whereas the Al $2p$ fits give a value of 50 meV for the shift of these levels. This rules out any charging effects. Furthermore, it implies a difference in the Schottky barrier height variations along two lines where Al reactivity to the substrate is different. Also, Fig 1(b) and (c) shows that metallic gallium feature originates at higher kinetic energy, whose intensity increase on going from pure GaS to the Al-rich region indicating the reactivity of Al overlayer with the substrate is thickness dependent.

This band bending and Schottky barrier behavior is related to local chemical inhomogeneities. In fact, a careful analysis of spectra for the bright border regions along line “A” reveals a different chemical composition with respect to the other regions and in particular to the border portion of line B.

CONCLUSION

Our results establish a correlation between local chemical reactions and inhomogeneities in the band bending and in the Schottky barrier. Bright areas were found in the Al 2p microimages along the border of the Al overlayer. The local chemical composition was different in these bright areas with respect to the other border areas. In parallel, the band bending changes (as the Schottky barrier changes) across the Al 2p border were different for the bright areas and for the other border areas. The size of bright areas are up to 5 μm^2 . Similar border features were found for other III-VI compounds, but their size is growth dependent [11].

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EUV Exposure of ETS Components

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INTRODUCTION

The Engineering Test Stand (ETS) is an advanced, prototypical lithography tool being developed in the EUVL (Extreme Ultraviolet Lithography) Program. In the ETS there are many components whose responses to prolonged exposures of EUV radiation must be determined. Such exposure responses include the effects of residual gases on multilayer mirror (MLM) reflectivity, multilayer mirror stability, and gas desorption from resist-coated silicon wafers. During 1998 we completed a series of experiments to help answer some of these important ETS/EUV exposure issues. This abstract outlines the work that was done. Details of the results obtained are not given because of their business-sensitive nature in the EUVL Program.

EXPERIMENTAL SYSTEM

All experimental runs were performed using a demountable, ultrahigh vacuum chamber that could be attached to a port on the existing EUV Interferometry chamber on Beamline 12.0.1.2. Our chamber had a movable, 100 μm diameter aperture located at the EUV beam crossover point downstream from the Interferometry chamber. This aperture provided vacuum isolation from the upstream beamline. This isolation was important when doing simultaneous EUV + gas exposures of ETS components, since it allowed the use of high exposure pressures (up to 10^{-4} Torr) in the experimental exposure chamber while keeping the Interferometry chamber at its normal operating pressure of $\sim 10^{-8}$ Torr. The experimental chamber was totally dry-pumped and had a residual gas analyzer (RGA), ion gauge, gas inlet system, and photodiode for measuring EUV powers. A removable end flange on the chamber supported all the internal sample manipulators and specialized diagnostic equipment. The internal fixturing attached to this flange was changed to perform different experiments. An existing, upstream grating monochromator or "blank" reflecting surface on Beamline 12.0 was used to select either a single wavelength band or the complete undulator spectrum as the input EUV beam. As measured by the *in-situ* photodiode, energy fluxes in excess of $\sim 10 \text{ mW/mm}^2$ were achieved in sample positions in the experimental chamber. The base pressure in the system after an overnight bake was approximately 1×10^{-9} Torr with hydrogen being the dominant background gas.

EXPERIMENTS

I. Mo/Si Multilayer Mirror Contamination

Several experimental runs were devoted to determining the effects of exposing Mo/Si multilayer mirrors (40 bilayer pairs, Si capping layer, maximum initial peak reflectivity of $\sim 67.8\%$ at 92.24 eV) to EUV in the presence of different, low molecular weight gases, some of which contained carbon. Exposure pressures up to $\sim 10^{-4}$ Torr and nominal beam powers of 10 mW/mm^2 at 92.3 eV ($\sim 1\%$ bandwidth) were used. The change in multilayer mirror reflectivity was measured *in-situ* with the photodiode and *ex-situ* sputter-through

Auger Electron Spectroscopy (AES) was used to help determine the change in the near surface composition of the mirrors. The possible effects of sample beam heating and theoretical change in mirror reflectivity with contamination were modeled.

II. Mo/Be EUV Exposure

An extended experimental run was made with Mo/Be multilayer mirrors mounted in a position in the experimental chamber, which maximized EUV energy flux to the samples. These data runs were performed to help determine the radiation stability of the mirrors and the “raw” undulator power reflecting off the blank was used. The reflectivities of the mirror samples before and after the exposures were measured on the Calibration and Standards Beamline 6.3.2. Sputter-through AES of all samples was also performed.

III. Filter EUV Exposure

The radiation hardness of EUV filters was also studied. Both “raw” undulator radiation and EUV at 92.3 eV (~1% bandwidth) were used for the exposures. Both the EUV transmission and physical integrity of the test filters were measured before and after exposures. The surface compositions of all samples were determined by AES.

IV. Resist Desorption

The EUV-induced desorption of three different resists was studied over an energy flux range of ~ 0.1 to 1.5 mW/mm² with EUV light at 92.3 eV. The pressures and residual gas spectra for all resists were detected during all desorptions. Desorptions were performed such that the residual gas analyzer could be operated in both line-of-sight and non line-of-sight modes. An *in-situ* calibration of the mass spectrometer response together with measurement of the desorption area after the runs permitted quantitative desorption rates to be determined. Within experimental accuracy, it was found that the peak desorption pressures were proportional to energy flux for each resist.

SUMMARY

A wide range of applied, EUV exposure experiments for the EUVL Program were performed on Beamline 12.0.1.2. These experiments have provided data essential for the planning and refinement of optical components and operating procedures for the ETS.

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Extreme ultraviolet interferometry: at-wavelength testing of optics for lithography

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INTRODUCTION

Extreme ultraviolet (EUV) lithography is a promising and viable candidate for circuit fabrication with 0.1-micron critical dimension and smaller. Recently voted by a group of semiconductor industry leaders as the most viable next-generation lithography candidate, EUV lithography research is conducted by a large-scale collaborative effort involving three national laboratories (Lawrence Berkeley, Lawrence Livermore, and Sandia National Laboratories, collectively called the *Virtual National Laboratory, or VNL*) and the industry-sponsored EUV Limited Liability Corporation (EUV LLC), which includes Intel, Motorola, and Advanced Micro Devices. A number of other groups around the world are also involved in EUV lithography research, including both Japanese and European efforts.

Operating near 13-nm wavelength, optical systems for EUV lithography require multilayer-coated, all-reflective elements with a system numerical aperture of 0.1 or higher. In a region of the spectrum where all materials are highly absorptive, the mirrors utilize molybdenum/silicon multilayer coatings to achieve reflectivities near 70% at normal incidence. The suggested wavefront aberration tolerance for these sophisticated systems, composed of aspherical elements, is only 0.27 nm, or one-fiftieth of an EUV wavelength [1]. This places extremely high demands on the fabrication of EUV mirror substrates and multilayer coatings, and even higher demands on the metrology tools required to characterize them.

The EUV wavefront is determined by a combination of the geometric figure of the mirror surfaces and the properties of the multilayer coatings, which are deposited across mirror areas of several square inches. While advanced visible-light interferometric techniques possessing the required measurement accuracy are being developed [2], phase effects arising from multilayer coating defects and thickness errors are measurable only at the EUV operational wavelength. Final alignment and qualification may require *at-wavelength*, using EUV light, to successfully predict the imaging performance of an optical system. These factors motivate the development of high-accuracy EUV wavefront-measuring interferometry now in progress at the ALS.

A NOVEL EUV INTERFEROMETER DEVELOPED FOR HIGH-ACCURACY

Researchers from LBNL's Center for X-Ray Optics have built a prototype EUV phase-shifting point-diffraction interferometer (PS/PDI) [3, 4, 5] at ALS beamline 12.0.1.2. By spatially-filtering undulator radiation, the interferometer takes advantage of the high brightness from the ALS to generate coherent EUV light.

The PS/PDI is a common-path interferometer that incorporates pinhole diffraction to generate reference wavefronts of extraordinarily high spherical accuracy. A schematic of the optical design of the PS/PDI is shown in Fig. 1. Open-stencil pinholes smaller than 100-nm diameter are used to test the latest high-quality EUV optics. A coarse grating beam splitter placed before the test optic divides the beam into multiple diffractive orders that are brought to spatially separated

0.64-nm RMS ($\lambda_{\text{EUV}}/21$), 4.31-nm peak-to-valley

Figure 1. The extreme ultraviolet phase-shifting point diffraction interferometer (EUV PS/PDI) is designed to measure EUV optical systems with sub-angstrom accuracy. Probing the combined surface figure of the multilayer-coated, reflective elements *at-wavelength*, the PS/PDI reveals aberrations on the angstrom scale. Here an interference pattern from the measurement of an off-axis sub-aperture of a 10x Schwarzschild objective shows that nearly diffraction limited performance has been achieved, with RMS wavefront aberrations below one-twentieth of an EUV wavelength in a numerical aperture of 0.088.

foci in the image-plane. One beam, the *test* beam, containing the aberrations of the test optical system, is allowed to pass through a large window in an opaque mask placed in the image-plane. A second beam, the *reference* beam, is spatially filtered by a pinhole smaller than the diffraction-limited resolution of the test optic, and becomes the spherical reference wave. These two beams overlap to produce an interference fringe pattern that is detected by an EUV CCD detector. The interference pattern may be interpreted as a coherent comparison of the aberrated test beam with the nearly-perfect spherical reference beam. The fringe pattern thus reveals the aberrations in the test optic. Translation of the grating beam splitter is used to introduce a controlled relative phase-shift between the test and reference beams, allowing phase-shifting interferometry techniques to be employed.

NEW OPTICS AND NEW MEASUREMENT CAPABILITIES

The focus of the interferometry research in 1998 was on the measurement of new 10x Schwarzschild objectives fabricated to the same tight figure and finish specifications as the coming generation of four-element EUV lithographic optics. Additional research was conducted to calibrate the performance of the interferometer and to advance several new interferometric testing strategies.

Of the two new optics measured in 1998, both systems had wavefront figure errors below 1 nm rms, with one as low as 0.64 nm—better than its design specification. One such wavefront is shown in Fig 1. Favorable comparisons have been made of EUV and visible-light interferometric measurements performed on the same optical systems.

In an effort to characterize and extend the accuracy of the interferometer, a two-pinhole *null test* interferometer calibration was developed. Such a test filters the aberrations from the test optic using a pair of tiny pinholes, and produces the interference of two nearly-perfect spherical reference waves in a configuration similar to Young's famous experiment. Measurement of the residual aberrations allows the accuracy of the interferometer to be probed and geometric effects to be identified. Previous null-test experiments had verified the accuracy of the interferometer from 100-nm diameter pinholes as 0.5 Å rms ($\lambda/250$ at 13.4-nm wavelength). Continued experiments have since pushed this level to 0.4 Å rms ($\lambda/330$) using 80-nm diameter pinholes [6]. Since the pinhole functions as a spatial filter for the aberrated test beam, it is expected that as higher quality-optics are tested, the reference wavefront quality can be further improved.

As smaller pinholes are used to improve the measurement accuracy, the strength of the reference beam decreases and the fringe contrast suffers. This year, new strategies were implemented to improve the interferometer's fringe contrast from below 10 percent to over 80 percent. Fringe contrast has a significant impact on both measurement precision, and the ease with which the interferometer can be aligned. Combined with the increased fringe contrast, new features in the window/pinhole masks and new real-time analysis methods have reduced the time required for alignment of the interferometer from hours to minutes.

Due to the short wavelength of EUV light EUV optics are especially vulnerable to *flare*. Flare is the unwelcome distribution of light around bright image features caused by roughness in the projection optics. Of primary concern is a difficult-to-measure range of mid-spatial-frequency roughness accounting for surface errors of sizes between the large-scale *figure* errors and small-scale *finish* errors. To date, a great effort has been spent to reduce roughness and mitigate the flare problem; part of that effort has been in improved metrology, including at-wavelength scatterometry [7] and other complementary measurement techniques. Recently, the spatial-frequency-response of the PS/PDI has been extended into the mid-spatial-frequency regime, with the ability to measure sub-mm sized features with hundreds of cycles across the aperture. The advances in the PS/PDI's flare measurement capabilities have been made possible by a recently-developed noise-suppressing analysis method and improved window/pinhole mask designs.

REMARKS FOR FUTURE WORK

In 1999, a new PS/PDI is being built on a branchline of beamline 12.0.1. The new interferometer is designed to measure a large-field, four-mirror EUV lithographic optical system with 0.1 NA. This so-called *projection-optics box* (POB) [8], represents the combined efforts of the Virtual National Laboratory and presents the interferometry team with its first opportunity to measure and align an EUV optical system suitable for commercial applications. The POB has a four-mirror ring-field design, and contains aspherical optical elements. Continued interferometry research efforts will explore the extension of the PS/PDI to higher numerical apertures, and different configurations, and will include further collaborations with our VNL partners in the development and testing of EUV optics.

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Photoemission spectromicroscopy studies of ELO GaN surface

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ABSTRACT

Photoemission spectromicroscopy is employed to investigate the surface electronic inhomogeneities of epitaxy lateral overgrowth (ELO) GaN material. The surface morphology obtained via photoemission microscopy is in confirmation with AFM. Localized EDCs for Ga 3d-core level obtained on clean GaN demonstrates Fermi level pinning for different growth areas. Hydrogen adsorption destroys this Fermi level pinning. The magnesium deposition on GaN results in Magnesium Island where reactivity of magnesium with nitrogen is higher compared with Ga thus leaving Ga in a metallic form.

INTRODUCTION

The wide band gap III-V nitrides have attracted much attention because of their great significance in both scientific research and practical applications [1]. Among them GaN is the most interesting materials because of its suitable direct band gap of 3.4 eV at room temperature, notable chemical inertness, and great physical hardness, high temperature stability [2]. However, the development of III-V nitride materials has suffered from the lack of suitable substrate to produce low-dislocation-density using MOVPE or MBE. Currently, the promising technique is the ELO growth of GaN where GaN/sapphire or SiC layer patterned with SiO₂ is used as a substrate to produce stripes of GaN with remarkable reduction in dislocation density [3].

In this work we are investigating surface electronic structure of GaN grown with the above technique. We have investigated electronic surface structure of clean GaN, hydrogen adsorbed GaN, and GaN with an overlayer of Mg. The later two investigation is driven by the fact that hydrogen is one of the precursor used in the growth process while magnesium is used as a p-type dopant.

EXPERIMENT

The ELO GaN used in the experiment was grown on a sapphire basal plane by MOVPE at North Carolina State University. The ELO GaN surface morphology was characterized by atomic force microscopy (AFM). The sample was annealed cleaned at 850°C. The synchrotron radiation-based spectromicroscopy technique has been employed to study the electronic inhomogeneities on the surface. The strength of this technique is its chemical and surface sensitivity. The photoemission spectromicroscopy is thus performed at MAXIMUM at beamline 12.0.1 at the ALS, Berkeley. The microscope has SO optics to focus the beam to less than 0.1 micron. Thus, the microscope is capable of acquiring chemical and electronic information from a localized area.

RESULTS AND DISCUSSION

A 30 x 30 μm^2 photoemission microscopy image at step size of 0.3 μm acquired at Ga 3d core level at 104.5 eV using 130 eV photon is shown in fig. 1a. The image reveals three distinct areas i.e. (a) meeting fronts where two strips meet each other, (b) an opening areas between masks (homoepitaxial growth), and (c) areas above masks (lateral overgrowth). The fig. 1b shows the series of energy distribution curve acquired at corresponding positions shown in the fig. 1a. The

high resolution EDC's clearly demonstrate the Fermi level pinning. The curve a that is from meeting front area is shifted by 0.15 eV compared to curve b and c. Thus, EDC's suggest the different Fermi level behavior for GaN strip and the meeting front. A $30 \times 30 \mu\text{m}^2$ of GaN surface exposed to 1000 Langmuir atomic hydrogen acquired at Ga 3d peak shown in fig. 2a. Compared with the image of clean GaN, the hydrogen espouser brings dramatic change in the surface electronic structure. The V-shaped meeting fronts in clean GaN are changed to W shape upon hydrogen exposure. The center of the meeting fronts has less hydrogen adsorption than the other areas hence the core level attenuation is smaller.

Figure 1 (a) Micrograph of ELO grown clean GaN surface obtained at Ga 3d core level at $h\nu = 130 \text{ eV}$ (b) A set of Ga 3d EDCs obtained at positions marked in (a)

Figure 2 (a) Micrograph of ELO grown GaN surface exposed to 1000 Langmuir hydrogen obtained at Ga 3d core level at $h\nu = 130 \text{ eV}$ (b) A set of Ga 3d EDCs obtained at positions marked in (a).

The set of EDC obtained at different areas marked in fig. 2a doesn't show any Fermi level pinning. The comparison of fig. 1 and 2 brings forth the fact that the growth fronts in clean GaN have different electronic environment, which gets destroyed upon hydrogen adsorption. A 10 ML Mg deposited on GaN grows with S-K mode and island formation. The core level Ga 3d EDCs in the Mg islands shifts toward higher kinetic energy compared to smooth areas. The bend bending is Ga 3d peak is observed in going from Mg island areas to between-island areas. Also, it is observed that islands are rich in metallic Ga indicating higher reactivity of Mg with GaN leaving behind Ga in metallic form. (Results not shown).

CONCLUSION

The photoemission spectromicroscopy was successfully employed to investigate inhomogeneities of surface electronic structure of ELO GaN material. The set of EDCs obtained at Ga 3d core level demonstrate meeting fronts have different Fermi level pinning behavior compared to opening areas and overgrowth areas. The hydrogen adsorption destroys this Fermi level pinning behavior. We propose that the selective adsorption of hydrogen in meeting fronts may be due to two reasons: (1) the different dislocation density in meeting front area (2) in meeting front regions the GaN surface is oriented {112-2} where as flat regions are oriented along {0001}[5]. This difference in the surface orientation in two regions may lead to difference in the surface free energy, which thus leads to selective hydrogen adsorption. The S-K growth of Mg on GaN leads to islands formation leaving behind metallic Ga. The difference in the Fermi level pinning behavior in Mg reach islands and in between-island area arises from the difference in reactivity of Mg with GaN in two areas.

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Photoemission spectromicroscopy studies on epitaxial lateral overgrowth GaN surfaces

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INTRODUCTION

Gallium nitride (GaN) materials are very useful for fabricating electronic and electro-optic devices, such as high power electronics, blue and ultraviolet light emitting diodes (LED), detectors, and laser devices.^{1,2,3} However, the development of III-V nitride materials and devices has suffered from the lack of the availability of low-dislocation-density, lattice-matched substrates for device synthesis. Recently, epitaxial lateral overgrowth (ELO) technique⁴ produces GaN with a remarkable reduction of the dislocation density to about 10^4 per cm^2 or less. This method starts with a layer of GaN on sapphire (or SiC) which is then patterned with SiO_2 stripes of about $15\text{ }\mu\text{m}$ wide separated by $3\text{ }\mu\text{m}$ windows. The final MOVPE growth starts in the windows growing up and over the SiO_2 stripes because the film will not “seed” on it. Between two adjacent final stripes is where the growth fronts meet and coalesce. It is above the middle of the SiO_2 stripes.

EXPERIMENTS

In this work, synchrotron-radiation-based photoemission spectromicroscopy was performed to investigate the inhomogeneities in the electronic structures of the ELO GaN surfaces. MAXIMUM microscope⁵ on beamline 12 at ALS is used for the studies, which operated at photon energy of 130 eV. The photon energy is quite appropriate for semiconductor investigations. Data are collected in two modes: (a) the scanning mode where a 2-D image is acquired by measuring the photoelectrons in a given kinetic energy window, and (b) the microprobe mode where an energy distribution curve (EDC) is acquired at the position of interest. The spot size has been measured to be $0.1\text{ }\mu\text{m}$. A cylindrical mirror analyzer (CMA) is used to detect the energy-resolved emission.

RESULTS

The AFM image of the ELO GaN surface (sample M287) is depicted in the $100\times 100\text{ }\mu\text{m}^2$ image of Fig. 1(a). The line scan along the horizontal line across the image is shown in Fig. 1(b). The scanning-mode measurement of the photoemission signal with the spectromicroscope is used to obtain an overview. Figure 2(a) is the image and (b) is the line profile. The $100\times 100\text{ }\mu\text{m}^2$ image is acquired with a step size of $1\text{ }\mu\text{m}$ by recording the signal from Ga 3d core-level emission peak at a kinetic energy of 104.6 eV. In the image, bright areas correspond to stripes of GaN and dark areas are stripes due to the meeting-fronts grooves. The photoemission signal (PESS) line profile shows the same general features as the AFM data shown in Fig. 1. The PESS signal has a bit wider

“V” groove than the AFM micrograph, about 4.2 and 3.6 μm , respectively. The contrast mechanism producing the spectromicroscopy image is largely due to the angular dependence of the photoemission yield combined with different orientations of plateau areas and the valley areas.

For better understanding of inhomogeneities of the sample's surface electronic structure, high-spatial-resolution images are acquired. Then, based on this image, localized EDC's of the Ga 3d core level emission are obtained by the microprobe mode from different locations on the surface. Figure 3(a) shows a $30 \times 30 \mu\text{m}^2$ image with a step size of 0.3 μm made with the Ga 3d peak emission at an electron kinetic energy of 104.6 eV. Panel (b) is the line profile across the sample surface at the arrow-marked position on the image. Localized EDC's for the Ga 3d core level are obtained from the sample at positions labeled a, b, and c on the image which are located at the meeting-fronts area; lateral overgrowth area; and vertical-growth window area, respectively. The spectra are shown in Fig. 3(c) where the three EDC's are normalized to the same peak intensity. The difference curve “c-b” is a flat featureless line, which demonstrates the uniformity in surface electronic structures for the vertical growth window areas and the lateral overgrowth areas. However, curve a, which is from a meeting-fronts area shows an energy shift of 0.15 eV. The difference curve “b-a” is also flat after curve a and b are lined up. The observations suggest no line shape changes. The observed peak shift is attributed to a change in the surface-Fermi-level position for the crystal orientation of the growth fronts compared to (0001) orientation of the flat areas. The observed uniformity of the line shape suggests the chemical environment of Ga is the same in the different regions.

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Figure 1 (a) An AFM image for a $100 \times 100 \mu\text{m}^2$ area of the ELO GaN surface (sample M287). The bright areas represent the flat growth stripes and the dark areas are the meeting fronts of the growth stripes. (b) A line profile obtained from the above image at the position marked by the horizontal line across the image.

Figure 2 (a) A photoemission spectromicroscopy image for a $100 \times 100 \mu\text{m}^2$ area of the ELO GaN surface (sample M287) formed by the signal at the peak of the Ga 3d core - level emission at a kinetic energy of 104.6 eV. The bright areas represent growth stripes and the dark areas represent the stripes where the growth fronts meet. The CMA detects the electron emission directed to the left. (b) A line profile obtained at the position of the line on the image.

Figure 3 (a) A photoemission spectromicroscopy image for a $30 \times 30 \mu\text{m}^2$ area of the ELO GaN surface (sample M287) formed by the signal at the peak position of the Ga 3d core level emission at a kinetic energy of 104.6 eV. (b) A line profile obtained at the position marked by the arrow. (c) Ga 3d core level EDC's collected with $0.1 \mu\text{m}$ beam spot at the positions a, b and c shown on the image. The curve "b-c" is the difference between curve b and c, where one is from the vertical growth in the window and the other is from the lateral overgrowth area, respectively. The "b-a" is the difference between curve b and curve a, which is from a meeting-fronts region after they are shifted by 0.15 eV to line up the peaks.

Soft X-ray Speckle and Dynamic Light Scattering Studies of Polystyrene Thin Films on BL12

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INTRODUCTION

A key goal of polymer physics is to forge a connection between microscopic fluctuations and macroscopic polymer properties. What microscopic forces conspire to determine that, at slow time scales, polymers are viscous, while at fast times scales they are elastic? Topological constraints - very likely entanglements of the polymer chains - play an important role in this problem. The important length scale is the so-called entanglement length, which measures the average separation between entanglements and is typically 4-8 nm. One way to study relatively slow fluctuations on this time scale is to apply the newly emerging techniques of dynamic x-ray or soft x-ray scattering. We have initiated a program in this area on BL12.0.1.2. Specifically, we wish to probe the thermally driven fluctuations at polymer surfaces at length scales as short as the entanglement length and to understand these in terms of other properties of the polymer.

APPARATUS

A schematic of the scattering apparatus is shown in Fig. 1. Light from the 8 cm period undulator passes through the BL12 varied line space monochromator, providing a beam with a resolving power of $E/\Delta E \sim 1000$ and a coherent fraction of a few per cent. Light exiting the monochromator is spatially filtered using a two-pinhole spatial filter that selects one transverse mode. At a wavelength of ~ 8 nm, we achieve a coherent flux as high as $2 \times 10^{10}/\text{sec}$. This light is then scattered off a sample and the scattered light is detected with a CCD camera.

Figure 1: Schematic of the scattering apparatus, including the 8 cm undulator, the BL12 VLS monochromator, the spatial filter, the sample and CCD detector.

EXPERIMENTAL RESULTS

A precursor to the dynamic scattering experiment is to measure speckle-diffraction patterns from a static surface. An example is given in Fig. 2, which shows the distribution of light scattered in the near-specular direction from a high-quality polystyrene thin film surface. The left panel shows a gray-scale image, measured with the CCD camera, of transversely-coherent 75Å light that has been scattered off a PS film at a grazing angle of 7.5°. The surface was held

Fig. 2: Diffraction patterns observed upon scattering transversely-coherent 75Å light off a high-quality polystyrene surface. left: gray-scale image; right: slice through the image showing the irregularity of the fringes caused by mixing of diffuse (speckled) light with the pinhole diffraction pattern.

at room temperature, which is well below the glass transition temperature, so that the surface was not fluctuating on the length scale probed by the experiment on the time scale required to take the image. The most obvious feature observed is the single-pinhole Airy function diffraction pattern associated with the pinhole spatial filter. The reason this appears is that the surface roughness is not sufficient to destroy the specular reflection, and the specular reflection in this case is this pinhole diffraction pattern. A closer look at this pattern indicates that the fringes are somewhat irregular. This is seen more clearly in the right panel of Fig. 2, which shows a single slice through the center of the image. The irregularity is seen to be reproducible from image to image, a notable characteristic of speckle. A slightly imperfect surface scatters most of the light specularly, with a small amount being diffusely scattered in the near-specular direction. If the incident light is transversely coherent, the diffuse light will be speckled, as approximately observed. Therefore, the image is actually a superposition of the pinhole diffraction pattern and the diffusely-scattered light - a weird sort of hologram. The former falls in intensity on a scale inversely related to the pinhole diameter (10 μm), while the latter decays in a fashion inversely related to the surface height - height correlation function (probably less than 1 μm). We are currently working to understand these patterns in detail to determine whether they can be inverted directly.

More importantly, there is sufficient diffuse signal to show that dynamic scattering experiments will in principle be possible over a useful temporal dynamic range. This would entail measuring the intensity of the scattered light at a particular scattering angle and wave vector, and measuring the temporal autocorrelation function to deduce dynamical information of the corresponding length scale. We have initiated such studies and have found sample damage (both reversible and irreversible) to be a significant problem. Other scattering geometries and spatial filter configurations are being investigated to try to overcome these problems.

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Spatial Coherence Characterization of ALS Undulator Beamline 12

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INTRODUCTION

Although coherent radiation has been readily available and utilized at visible wavelengths for many years, it has just recently come into use at shorter wavelengths due to the advent of undulator radiation available at synchrotron-radiation facilities such as the ALS. Coherent radiation is important to a variety of experiments including holography, interferometry, speckle-based metrology, and scanning microscopy. When performing these experiments using undulator radiation, extended beamlines are typically employed to re-image the undulator source and “shape” the beam-coherence properties. Proper design of these experiments requires accurate measurement of the beam-coherence properties, which depend in large part on the configuration of the beamline.

Here we present the preliminary stages of the coherence characterization of beamline 12.0.1.2 as measured at the image plane of the Kirkpatrick-Baez (KB) system used to re-image the undulator source. This and subsequent characterizations will be used to help define future experiments designed to use coherent radiation at beamline 12.0.1.2. The coherence test presented here is an implementation of the famous Thompson and Wolf experiment [1] for measuring spatial-coherence properties. Future planned coherence tests include spatial-coherence-imaging techniques [2] and grating interferometry [3], which is capable of measuring both temporal- and spatial-coherence properties.

EXPERIMENT

The Thompson and Wolf experiment is an application of Young’s classic two-pinhole interference experiment [4] where the fringe visibility is recorded as a function of pinhole separation in order to determine the spatial-coherence properties of the illuminating beam. The fringe visibility can be shown to be proportional to the complex coherence factor, μ , when the intensities of the two interfering beams are equal [5]. From the complex coherence factor as a function of pinhole separation, the coherence area or lateral coherence width can be determined.

To implement this test at beamline 12.0.1.2, a patterned mask containing multiple 300-nm-pinhole pairs with separations ranging from 1 to 9 μm was placed in the vicinity of the KB system focus. The 300-nm pinhole diameter was chosen to be much smaller than the expected coherence width while providing reasonable throughput and working distance to the detector. The masks were fabricated using electron-beam lithography and reactive-ion etching, and are made up of a 360-nm-thick Ni absorbing layer evaporated on 100-nm-thick Si_3N_4 membranes. The mask features are etched completely through the membrane prior to the Ni evaporation, leaving the pinholes completely open in the finished masks.

The experimental system is depicted in Fig. 1. The pinhole mask is mounted onto an x - y - z stage allowing the various pinhole separations to be probed and the coherence to be studied as a function of focal position. An EUV, back-thinned, back-illuminated CCD camera is placed 26 cm downstream of the mask to record the resulting interference pattern.

Fig. 1. Experimental setup for measuring beamline coherence properties.

To determine the complex coherence factor from the fringe visibility the relative intensities of the two interfering beams must be known. Alternatively, they should be guaranteed to be equal. Because it is impractical to independently measure the intensity of each beam, we attempt to guarantee the equal-intensity condition. This is done by performing a large ensemble (greater than 50) of measurements for each pinhole separation while intentionally displacing the pinhole pair relative to the incident beam by a small amount. Because any beam-intensity mismatch can only degrade the fringe visibility, we take the highest fringe visibility from the ensemble of measurements to represent the coherence-limited fringe visibility.

Figure 2 shows recorded interference patterns with 13.4-nm-wavelength illumination for two representative pinhole separations. The beamline input numerical aperture is set to 80 μ rad and the exit slit of the monochromator is set to pass a temporal bandwidth of $\Delta\lambda/\lambda = 200$. The data shown is for separations of 3 and 6 μ m. As expected, the fringe visibility, and thus the magnitude of the complex coherence factor $|\mu|$, is seen to decrease with larger pinhole separation. Extended data, including measurements in the orthogonal direction, is currently being collected as a function of various beamline parameters. Preliminary results show the lateral-coherence diameter to be on the order of 5 μ m in the horizontal (x) direction with the beamline in its nominal operational configuration.

In closing, we note that these tests also provide a simultaneous characterization of the quality of the pinholes. This is significant because pinholes similar to those used here are often used as spatial filters in experiments such as EUV interferometry, which require high-quality wavefronts. The data collected here lends itself well to determining residual transmission through the mask membrane and effective pinhole size and symmetry.

Fig. 2. Two-pinhole-interference patterns for pinhole separations of 3 and 6 μm ($\lambda = 13.4 \text{ nm}$ and $\Delta\lambda/\lambda = 200$). Also shown are normalized-intensity line-out plots taken through the center of the interference patterns. The half-angle collected by the CCD is approximately 50 mrad.

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Miscellaneous Abstracts

Theory and Computation for Synchrotron Radiation Experiments

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INTRODUCTION

This project provides "theory of the experiment", to enable the interpretation of experimental data gathered at synchrotron radiation facilities like the ALS. The focus is on modeling experimental techniques that require computational simulation in order to extract useful information such as atomic positions, distances and identities, as well as electronic and magnetic structures at surfaces and interfaces. Typical applications include photoelectron diffraction (PD) and x-ray absorption fine structure (XAFS). We welcome suggestions to help select future topics for theoretical and computational development.

COMPUTER CODES - PRESENTLY AVAILABLE

Three synchrotron-related computer codes are (as of Feb. 1999) available for free downloading from the web at <http://electron.lbl.gov/software/>:

- the MSCD package: to simulate core-level photoelectron diffraction for linear polarized light, including automated fitting of atomic coordinates to experimental data [1];
- REPS: to calculate core-level relaxation energies in photoelectron spectroscopy (using the equivalent-core approximation) [2];
- a holographic package: to reconstruct atomic structures from photoelectron and x-ray diffraction data (holograms) [3].

Further details about these packages can be found at the above mentioned web site.

In addition, the FEFF codes for XAFS are available from the FEFF web site at the University of Washington, Seattle, after obtaining a license [4].

COMPUTER CODES - IN PREPARATION

In collaboration with J.J. Rehr, the FEFF codes for XAFS [4] simulations will be installed to allow ALS users to run FEFF on ALS computers.

An expansion of the photoelectron diffraction package will introduce relativistic and magnetic spin effects, as well as circular and linear dichroism [5]. This will extend accurate studies to spin-dependent and light-polarization-dependent photoelectron diffraction.

A code to calculate valence-level photoelectron diffraction is under development [6]. It will permit the detailed study of the spatial distribution and energetics of valence electron levels at surfaces and shallow interfaces.

FURTHER INTERACTIONS

A Seamless Computing Environment is planned to integrate experiment, computation and theory at the ALS and elsewhere. Its goals include: unifying data formats; providing data analysis; interfacing with graphics and simulation; and enabling remote on-line collaborations with an electronic notebook.

Workshops with topical and tutorial emphases are planned to foster close interactions between experiment, computation and theory.

A Synchrotron Radiation Research Theory Network (SRRTNet) is being set up to interconnect related efforts world-wide: see <http://electron.lbl.gov/srrtnet/srrtnet.html> for the latest information.

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Institutions Funding User Research at the ALS

This list is compiled from the funding institutions users listed in their abstracts for work done in 1998.

U.S. Department of Energy

- National Petroleum Technology Office
- Office of Civilian Radioactive Waste Management
- Office of Energy Research (now Office of Science)
 - Office of Basic Energy Sciences
 - Chemical Sciences Division
 - Materials Sciences Division
 - Office of Biological and Environmental Research
 - Health Effects and Life Sciences Research Division (now Life Sciences Division)
 - Natural and Accelerated Bioremediation Research (NABIR) Program
 - Office of Computational and Technology Research (now Office of Advanced Scientific Computing Research)
- Office of Environmental Management
 - Office of Science and Technology

Other Institutions

- 3M Canada, Ltd.
- American Chemical Society
- Applied Research Ecology Laboratory, Russia
- Basque Government
- Bayerische Forschungsstiftung, Germany
- Burroughs Wellcome Fund
- Centre National de la Recherche Scientifique (CNRS), France
- Charles E. Culpepper Foundation
- Comisión Interministerial De Ciencia Y Tecnología (CICYT), Spain
- Commissariat a l'Energie Atomique, France
- Consejo Nacional de Ciencia y Tecnología (CONACYT), Mexico
- Daresbury Laboratory (CLRC), United Kingdom
- David and Lucile Packard Foundation
- Deutsche Forschungsgemeinschaft (DFG), Germany
- Donald E. and Delia B. Baxter Foundation
- Dow Chemical Company
- DuPont
- EJLB Foundation
- Engineering and Physical Sciences Research Council (EPSRC), United Kingdom
- Ernest Orlando Lawrence Berkeley National Laboratory
- Extreme Ultraviolet Limited Liability Corporation (EUV LLC)
- Feodor-Lynen-Fellowship
- Fond National Suisse de la Recherche Scientifique, Switzerland
- Forschungszentrum Juelich GmbH, Germany
- French Department of Environment
- Fulbright Grant Program
- Genentech, Inc.
- German Academic Exchange Service (DAAD)
- German Federal Ministry of Education, Science and Technology (BMBF)

Gesellschaft für Schwerionenforschung (GSI), Germany
 Göran Gustafsson Foundation
 Hewlett Packard Laboratories
 Hitachi
 Howard Hughes Medical Institute Research Resources Program
 Intel Corporation
 Istituto Nazionale per la Fisica della Material, Italy
 Japan Ministry of Education, Science, Sports and Culture
 Jeffress Trust Memorial Foundation
 Kearney Foundation of Soil Science
 King Fahd University of Petroleum and Minerals, Saudi Arabia
 Louisiana Educational Quality Support Fund
 Max-Kade Foundation
 Max-Planck Preis der Alexander von Humboldt-Stiftung
 Miller Institute
 Ministerio de Educacion y Cultura, Spain
 National Aeronautics and Space Administration
 National Association for Research on Schizophrenia and Depression
 National Institute of General Medical Sciences
 National Institutes of Health
 National Research Council of Italy
 National Science Foundation
 National Storage Industry Consortium (NSIC)
 NATO Linkage Grant
 Natural Sciences and Engineering Research Council (NSERC), Canada
 Nippon Telephone and Telegraph (NTT), Japan
 North Carolina State University
 Packard Foundation
 Petroleum Research Fund
 Pohang Steel Company
 Research Corporation
 Russian Science Foundation for Fundamental Research
 Russian State Program on Superconductivity
 Searle Scholars Program
 Silicon Wafer Engineering and Defect Science Consortium (SiWEDS)
 Skaggs Institute for Chemical Biology
 SRC
 State of Delaware
 State of Louisiana
 Swedish Institute
 Swedish Materials Research Consortium on Clusters and Ultrafine Particles
 Swedish National Board for Industrial and Technical Development (NUTEK)
 Swedish Natural Science Research Council (NFR)
 Swiss Federal Institute of Technology (EPFL)
 Swiss Light Source (SWS), Paul Scherrer Institut (PSI), Switzerland
 Swiss National Science Foundation (FNRS)
 U.S. Air Force, Office of Scientific Research
 U.S. Army Research Office
 U.S. Department of Agriculture
 U.S. Department of Defense
 U.S. Environmental Protection Agency
 U.S. Navy, Office of Naval Research

University of California, Berkeley
University of Lausanne, Switzerland
University of Nevada, Reno
University of Tennessee, Knoxville
University of the Basque Country, Spain
University of Washington, Seattle
Virginia Commonwealth University
Waseda University, Japan
Wyeth Research

ALS Technical Reports

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Scientific Support Group Overview

During the reorganization of the ALS at the end of 1997, two new user support groups were created: the User Services Group (discussed later in this Compendium, in the User Services section) and the Scientific Support Group. The Scientific Support Group (SSG), headed by Zahid Hussain with John Bozek as deputy, consists of a team of scientists, postdocs, students, and associate beamline scientists. The primary role of the SSG is to provide scientific and technical support to ALS users. The nature of that support ranges from technical assistance in operating the beamlines or experimental equipment to full collaboration with the users' groups. The scientific staff of the SSG are all experienced synchrotron radiation users (at the ALS as well as at other facilities) who are familiar with many of the beamlines, experimental endstations, and techniques, as well as the scientific problems that can be addressed using the capabilities of the ALS. SSG members continue to assist ALS users in developing their research programs by helping in the preparation of grant proposals for new funding and in the development of new experimental equipment. A major thrust in this area over the past year has been the development of Beamline 10.0.1 and its associated endstations for high-resolution electron spectroscopy in solids and gases, described in detail below. Also, an effort is currently underway to develop a set of user-friendly data analysis tools to provide a "seamless computing environment" for working with experimental data acquired at the ALS.

Increased User-Friendliness and Experimental Efficiency

Members of the group are fully or partially responsible for the operation and development of several of the facility's beamlines, including Beamlines 1.4, 7.0.1, 8.0.1, 9.3.1, 9.3.2, 10.0.1, 10.3.1, and 10.3.2. Increasing the "user-friendliness" of these beamlines while maintaining their efficiency and effectiveness is one of the major goals of the group. To this end, the first mirror and entrance slit of Beamline 8.0.1 were replaced with internally cooled versions similar to those installed in Beamlines 7.0.1 and 10.0.1. The new mirror and slit were required to handle the high heat load from the undulator at small gap settings. The beamline can now be used with a 14-mm gap even at the top of the fill with no degradation in performance. The slits were also modified to have electrically isolated jaws, allowing the installation of a feedback loop on the first mirror to keep the beam centered on the entrance slit. Several additional improvement projects were initiated in 1998 to make several of the beamlines more user friendly. Computer control of the entrance and exit slits of the spherical grating monochromator (SGM) beamlines (7.0.1, 8.0.1, 9.3.2, and 10.0.1) is being developed to minimize errors in setting the slits as well as to provide the capability to carry out constant-bandwidth photon energy scans. Tilt sensors are being incorporated into the SGMs as calibration constants that will reduce the photon energy calibration shift observed when changing gratings. A motor-driven horizontal-deflecting-mirror positioning system is being implemented on Beamline 10.0.1 to minimize the time required for alignment when switching between endstations. Nonbeamline improvements include the development of a Laue back-diffraction system for crystal alignment (with the gracious donation of space on the Physical Biosciences diffractometer in Building 80) and replacement of the sample manipulator on the x-ray photoelectron diffraction (XPD) chamber.

Communication and Outreach

The SSG strives to maintain and further develop communications with ALS users to build and improve the scientific program. Workshops are held occasionally to identify new areas of opportunity. Outreach is also a goal of the SSG to broaden the user base of the ALS. Group members often attend and organize meetings and conferences to publicize the capabilities of the ALS to many different scientific communities.

Beamline 1.4

Infrared (IR) spectromicroscopy research at Beamline 1.4 was led by SSG member Michael C. Martin and included a wide variety of topics. This beamline came into full operation in June 1998 and has rapidly developed a broad user community. In a collaboration with other Berkeley Lab scientists, led by H. Holman, IR absorption signals from individual human cells were observed to change as a specific gene was expressed in response to environmental toxins. This observation could lead to an exciting new method for quickly measuring exposures as well as determining risk-based standards for pollutant levels. Some of the same researchers also used the IR microscopy beamline to show that specific microbes found in a toxic waste site are able to bioremediate toxic Cr (VI) compounds by reducing them to safe Cr (III) compounds. Three more research groups focused on processes in the environment: T. Raab from the University of Colorado, Boulder, began studies of the interactions between plant roots and soils in the rhizosphere; and two groups, one from the University of Delaware, led by D. Sparks, and one from Carnegie-Mellon University, led by U. Ghosh, investigated the chemistry of soils and the kinetics and mechanisms of ion sorption to soil components. Two groups from U.C. Berkeley round out the highlighted experiments for this beamline. One, led by R. Glaeser, is using IR microscopy to monitor the photocycle of bacteriorhodopsin microcrystals with the ultimate goal of doing protein crystallography on another ALS beamline to determine the atomic structure of each conformation this protein goes through. A second, led by R. Saykally, is finding signs of deeply supercooled water using liquid microjets; they hope to probe liquid water at lower temperatures than have been possible to date.

Beamline 7.0.1

The Beamline 7.0.1 angle-resolved photoemission endstation is run by SSG member Eli Rotenberg. This endstation has been optimized for high-flux, high-resolution, angle-resolved photoemission. In addition, wide flexibility in scan types (photon energy vs. sample orientation, for example) and sample preparation techniques have been and continue to be developed to cater to user needs. Some examples of work done or published in 1998 include the following:

- **Photoemission of engineered magnetic nanostructures.** The creation of a continuum of samples on a single crystal allowed systematic studies of electron standing-wave formation as a function of quantum well structure. The most important aspects of these experiments were the small photon spot size ($\sim 50 \mu\text{m}$)¹ and an *in-situ* sample preparation facility for the creation of double-wedged nanostructures.²
- **Resonant photoemission study of α and δ plutonium.** The electronic structure of various phases of plutonium metal are of tremendous interest, not only because of applications to environmental cleanup, but also because plutonium straddles the line between having localized and delocalized f electrons. Los Alamos National Laboratory scientists, together with the ALS, developed a dedicated sputter/anneal chamber to prepare clean samples and thereby enable safe transfer to the nonradioactive sample analysis chamber. (Contacts: Jeff Terry and Roland Schulze, Los Alamos National Laboratory)
- **Valence-band photoemission of icosahedral quasicrystals.** We developed a sample preparation technique for sputter/annealing AlPdMn alloy quasicrystals. Conventional valence-band angle-resolved photoemission reveals electronic bands (similar to conventional metals) with icosahedral point-group symmetry. This experiment takes advantage of the high photon flux due to the relatively low cross section of the features ($<10\%$ of total electron density participating). (Contacts: Eli Rotenberg, Advanced Light Source, or Karsten Horn, Fritz-Haber Institute, Berlin)

¹Kawakami, R.K. et al., *Phys. Rev. Lett.* **80**, 1754 (1998).

²Kawakami, R.K. et al., *Nature* **398**, 132 (1999).

Beamline 10.0.1

Two projects supported by the Department of Energy's 1996–1998 Scientific Facilities Initiative (SFI) necessitated the creation of a new beamline at the ALS with high spectral resolution in the 20- to 350-eV photon energy range. The new beamline, Beamline 10.0.1, was built using many existing components. The spherical grating monochromator (SGM) from Beamline 9.0.1 was moved to become the heart of Beamline 10.0.1. New vacuum components and optics were constructed as required to replace parts left in the shared regions of the previous beamline. A new 4.5-m-long, 10-cm-period undulator was constructed for the beamline. Permanent magnets, a support and drive system, and even a vacuum tank were salvaged from other projects and used in the construction of the new undulator for Beamline 10.0.1. The horizontal focusing of the beamline was changed through the installation of new mirrors to provide a 100- μm focus in one of the side branches of the beamline. Construction of the beamline proceeded rapidly following the shutdown of Beamline 9.0.1 in March 1998. Beam was passed into the new beamline in June 1998, at the end of the machine shutdown for installation of the new U10 undulator. The new endstations (described below) provided by the SFI funds are permanently installed on two branches of the beamline. A third large, permanent endstation for studying the photoionization of ions is installed on the third branch with space for temporary endstations provided.

High-Energy-Resolution Spectrometer (HERS)

Highly correlated electron systems such as the d- and f-band materials offer both intellectual challenges in physics and prospects for novel materials applications. Such systems, which include high-temperature superconductors and heavy-fermion and Kondo systems, are not adequately described by either atomic physics or one-electron band theory. Photoemission is an ideal tool to study highly correlated electron systems and has the potential to have a major impact on our understanding of these materials. In this collaborative effort between the spokesperson for the project, Z.X. Shen (Stanford University), members of the SSG, and the Mechanical Engineering Group, a state-of-the-art High-Energy-Resolution-Spectrometer (HERS) for angle-resolved photoemission experiments at the ALS was developed to study highly correlated electron systems. The heart of the experimental station is a state-of-the-art angle-resolved electron-energy analyzer (Scienta SES-200) mounted on a chamber that rotates about the photon beam axis. The combination of this analyzer, a high-precision low-temperature sample goniometer, and the use of Beamline 10.0.1 allows the performance of ultrahigh-energy and -momentum-resolution photoemission experiments. Also under construction is a high-efficiency electron-spin detector that will allow the determination of all three components of electron spin with high energy resolution, comparable to kT.

High-Resolution Angle-Resolved Photoemission Study of Highly Correlated Electron Systems.

Systematic study of high-temperature superconductors using HERS is providing new insight into these fascinating materials. An ultrahigh-momentum-resolution photoemission study of a Bi2212 sample indicates that the superconducting transition is not merely the opening of a gap due to an effective attractive interaction between the well-defined quasiparticles in the normal state, but rather, these quasiparticles themselves are only formed upon lowering the temperature below T_c .

The stripe phase first proposed to explain neutron data from Nd-substituted $\text{La}_{1-x}\text{Nd}_x\text{Sr}_{0.12}\text{CuO}_4$ (Nd-LSCO) represents a new paradigm for charge carriers in a solid. Unlike in conventional metals, where the charge distribution is homogeneous, the stripe phase envisages microscopic antiferromagnetic domains separated by one-dimensional domain walls (stripes) consisting of hole carriers and frustrated spins. The implication of this charge segregation propensity on the conduction as well as the superconducting mechanism is at the heart of the current debate in high- T_c research today. So far, much of the stripe information stems from interpretation of the

incommensurate neutron scattering peaks. Very little is known about the electronic structure of these materials. Angle-resolved photoemission has been applied to directly probe the electronic structure and charge dynamics of the stripe phase. Results indicate the existence of one-dimensional charge confinement. For details, see X.J. Zhou et al. in this compendium.

High-Resolution Atomic and Molecular Electron Spectrometer (HiRAMES)

The complexities of electronic structure in atoms and molecules are often only made clear when highly differential spectra are obtained. A high-resolution atomic and molecular electron spectrometer (HiRAMES) built with funding from the Scientific Facilities Initiative was designed and constructed by N. Berrah (Western Michigan University) with the assistance of the SSG. The endstation was constructed using a state-of-the-art Scienta SES-200 electron-energy analyzer mounted on a chamber that rotates about the photon beam axis. Gaseous samples are introduced into a gas cell mounted on the end of the electron lens with differentially pumped openings for the photon beam and a slit allowing electrons to leave the cell in the direction of the analyzer. Sample pressures as high as 10^{-4} Torr are isolated from the ultrahigh vacuum requirements of the beamline by windowless differential pumping. An oven has also been developed to provide a beam of low-volatility materials (i.e., metal atoms) for photoionization studies.

Atomic and Molecular Photoelectron Spectroscopy. The valence and inner-shell electron emission spectra of atoms and simple molecules offer the opportunity to study a variety of electronic structure phenomena in ideal noninteracting systems. With the assistance of SSG member John Bozek, the atomic, molecular, and optical (AMO) physics program at the ALS is targeting the fundamental understanding of many-body phenomena in the simplest systems (atoms and molecules) where full quantum-mechanical calculations can be compared with the experimental results. For example, high-resolution C 1s photoelectron spectra of the simple hydrocarbon molecule C₂H₄ have resolved the symmetry splitting of the two carbon 1s levels ($1\sigma_g$ and $1\sigma_u$), making it possible to experimentally identify the symmetry channel of the above-edge resonance.¹ Resonant Auger electron spectra of carbon monoxide, CO, have been measured with vibrational resolution for the excitation and vibrational resolution of the subsequent deexcitation. The resulting spectra highlight the dynamics of deexcitation of the inner-shell excitation (C 1s $\rightarrow$ 2 π^*) by probing the vibrational excitation of the final-state ion.² High-resolution electron spectra of the S 2p levels of carbonyl sulphide (OCS) exhibit nine lines due to vibrational and molecular field splitting. The molecular field splitting removes the degeneracy of the S 2p_{3/2} level and provides a means of accessing the fundamental amplitudes and phase shifts associated with the transition matrix element.³

¹Thomas, T.D. *et al.*, *Phys. Rev. Lett.* **81**, 5776 (1998).

²Kukk, E., J.D. Bozek, and N. Berrah, *J. Chem. Phys.*, in press.

³Kukk, E., J.D. Bozek, N. Berrah, J.A. Sheehy, and P.W. Langhoff, *Phys. Rev. Lett.*, submitted

Beamline 10.3.1

The scientific program of the microprobe beamline, Beamline 10.3.1, has been very active thanks to the efforts of SSG member Scott McHugo. Semiconductor research is taking off both for solar cells and integrated circuit semiconductors; silicon is the major research material, with GaAs also showing potential. Groups involved include S. Martinuzzi's group in France, E.R. Weber's group from U.C. Berkeley, the National Renewable Energy Laboratory (NREL) in Colorado, Astropower in Delaware, Bayer Solar in Germany, and Mitsubishi Silicon in Oregon. T. Cahill's research group (U.C. Davis) has been investigating particulates from the upper atmosphere. D. Sayers' group (North Carolina State) has used the microprobe to study cancerous lung tissue from the Chernobyl area.

In a major revitalization effort, the data acquisition system for the microprobe is being updated using funds from the Berkeley Lab's Center for X-Ray Optics. The new system will allow greater control over the speed of the scanning (rastering the sample through the microfocused beam) and will allow multiscanning. Areas of interest can be quickly defined using the short dwell times available in the new system, saving a considerable amount of setup time. The multiscanning feature allows spectra to be accumulated until the appropriate signal-to-noise level is achieved, unlike the previous system, which required guessing at the appropriate dwell time. The dead time has also been decreased in the new software, resulting in improved throughput. Finally, the data analysis software has been improved for ease of visualization and to improve users' ability to quickly disseminate their data.

Experimental Systems Group Overview

Many of the projects outlined in this section are also described in more detail in the individual beamline sections of this compendium. The intention here is to give an overview of the range of projects carried out by the Experimental Systems Group and to highlight areas of special interest.

Beamline 1.4

Beamline 1.4 was originally designed to have a single endstation for infrared (IR) microscopy. This system uses a commercial IR spectromicroscope manufactured by Nicolet, and is connected to a bend magnet port via a plane premirror, an ellipsoidal mirror, and collimating optics. This microscope is now in routine use. A number of upgrades have been carried out during the year to reduce optical noise. The noise came from two sources: low-frequency noise induced into the optical mountings by floor vibration and high-frequency electron-beam noise. The latter problem was traced to a digital synthesizer used as the master ring oscillator, and has been largely eliminated by replacing the unit with a higher-quality unit with much lower sidebands. The problem of floor vibration has been traced to the rf water pumping system, and the noise has been reduced by replacement of the water pump with a variable-frequency type operating at reduced pressure. In addition, it was found that the premirror assembly was vibrating excessively, and this was traced to the separation of the upper and lower concrete floor slabs in the IR area. This was solved by separation of the system from the upper slab and direct bolting to the lower slab. In order to reduce vibration to a minimum, in the next year we will continue to reduce the vibrations by isolation of the rf water pump and by more rigidly mounting the external switchyard mirror system. This is planned for the June 1999 shutdown. In addition, one of the switchyard mirror mounts will be replaced with a piezo-driven system, and this will be used in an active feedback loop to further reduce the effect of low-frequency vibrations. The system is currently performing well and is in routine use by a wide range of users for research ranging from environmental science to structural biology. The beamline was modified during the year to extract two new lines, one for surface infrared reflection spectroscopy of surfaces (Ross) and the other for UV-visible spectroscopy of defects in semiconductors (Haller). These beamlines are essentially complete and are undergoing commissioning.

Martin, M.C., and W.R. McKinney, "The first synchrotron radiation infrared beamlines at the Advanced Light Source: microspectroscopy and fast timing," in *1998 Spring Meeting of the Materials Research Society*, Proceedings of Materials Research Society **524**, 11, April 12-16, 1998, San Francisco, CA, USA.

Beamline 3.3

The deep lithography LIGA system was moved from Beamline 7.3.3 in January 1998 to its new location on Beamline 3.3. It was operated for the first time just before the April 1998 shutdown. The LIGA consortium includes groups from Sandia National Laboratories, the Jet Propulsion Laboratory, and Lawrence Berkeley National Laboratory. The work centers around the manufacture of various types of high-aspect-ratio structures, from parts for micromachines to x-ray telescope collimators. The scanner itself was reengineered to allow substrate cooling, and many modifications were made to provide more reliable operation. The LIGA scanner simply oscillates the sample, a photoresist-coated wafer, in the white x-ray beam to achieve a uniform exposure. The system is controlled to give precise radiation doses and is nitrogen-flowed to exclude oxygen and minimize ozone production. The beamline is simply an evacuated tube, terminated in a cooled beryllium filter and window. The front end is of a new design and is significantly simpler and less expensive than previous versions. It gives two fans of radiation, each 7 mrad in horizontal aperture. The fan width can be tailored to a specific application with a simple modification to a cooled aperture plate, an improvement that is now the standard for ALS front ends.

Beamline 4.0.1-2

Beamline and undulator construction have been slower than expected, due to problems at the vendor with the monochromator and problems at ALS with the undulator support system. The elliptically polarizing undulator (EPU) has two sets of magnets, and the polarization is changed by phasing diagonally opposite pairs of magnets with respect to the other pair at 90 degrees. The EPU period is 5 cm, and it occupies 2 m of the straight section. The straight section is divided into two parts, with two chicane vacuum chambers separated in the horizontal plane by 2.5 mrad. The vacuum chambers and chicane magnets have been installed and commissioned. To facilitate installation, the EPU is built on a C-frame support and drive system, and when first tested, it was found to have too great a deflection at minimum gap when driving the phase adjustment. The frame was reanalyzed and, based on the results, strengthening plates were added in several places. The new frame has performed well in extensive testing. The magnetic structure uses shims to position each block, and after two cycles of shimming, the field quality was well within specification. The monochromator has passed all of its qualification tests and has been shipped. Several problems arose during the construction process related to stability, but all were successfully addressed and the system eventually passed a comprehensive set of qualification tests. The monochromator is a version of the Peterson SX-700, having a silicon internally cooled plane premirror, a Glidcop water-cooled grating, and a sagittal focusing refocus mirror. The mechanical system is complex due to the large tuning range required (20–2000 eV) to accommodate the future use of an interchangeable 8-cm-period EPU. The EPU has now been installed in the storage ring and tested at low K. Light has been extracted out of the shield wall and focused onto the entrance slit of the monochromator by a horizontally focusing toroidal mirror, designed to focus on the entrance slit in the vertical direction and at the experimental end chamber in the horizontal direction. The remaining parts of the system are in place and await arrival of the monochromator. The endstation is rotatable, with two separate air bearing tables for individual experiments. Each table can be separated and replaced by systems waiting on other air bearing tables.

Beamline 5.0.2

Beamline 5.0.2 for protein crystallography is powered by a 2.1-T, 37-pole wiggler. The beamline uses a conventional arrangement of a vertically collimating premirror, a constant-exit-height double-crystal monochromator, and a toroidal refocusing mirror. The premirror is silicon and has a double-channel cooling arrangement in which two holes were gun-drilled along the length of the mirror and sealed to waterlines at each end with O rings. The monochromator employs a minichannel finned silicon crystal with internal water cooling. The system worked well from the outset, but it was noticed that at high current the beam moved vertically in the endstation hutch. This was traced to Compton-scattered-radiation heating of the mirror support plate, and was eliminated by fitting the premirror system with a water-cooled guard plate. The beam size at the sample is around 0.5 mm in diameter, with a flux at 12 keV of around 10^{12} photons/s. Typical collection times for complete data sets on average crystals are 2–3 hours, and complete multiple-wavelength anomalous diffraction (MAD) data sets have been taken in under 5 hours. The detector is a 2×2 ADSC CCD-based system. The system is providing world-class performance in terms of throughput as well as in the range and difficulty of structures being solved, including large-unit-cell crystals and microcrystals. In the latter area, structures of crystals down to $30 \times 30 \times 10$ microns have been determined. The permanent mirrors have been designed and ordered, and it is expected that the new premirror and its bending mechanism will be installed in March 1999. This, together with a new refocus mirror, will give a flux increase of 6, and will offer improved spectral resolution over that presently obtained. A small elliptical mirror was also built and tested to see the effectiveness of demagnification for microcrystal diffraction. It was shown that a beam size of 35 μm could be produced with an overall gain in flux density of 7. This mirror does not reduce the resolution of the diffraction pattern as it simply makes the vertical convergence similar to the horizontal convergence.

Beamline 7.0.1

The scanning transmission x-ray microscope (STXM) has been in routine operation on this undulator beamline for two years. Absorption contrast imaging and bulk near-edge absorption spectroscopy (NEXAFS) can be performed in a transmission geometry on submicron regions of thin samples. The instrument development has been described in a recent paper.¹ The major advance of the year has been an improvement in resolution to 67 nm. This resulted from the use of higher-resolution zone plates and by vibration isolation of the microscope support structure. The zone plate has a diameter of 90 μm , a 45-nm outer zone width, and a 30-micron-diameter central stop. It is part of the first production run of the LBNL nanowriter, operated by Erik Anderson and Bruce Hartenek of the Center for X-Ray Optics. The focal length is 1.27 mm, giving a theoretical demagnified image size of the source pinhole of 42 nm. This, convoluted with the diffraction-limited resolution of the zone plate given by the outer zone width, gives the resolution measured. Images are typically acquired with a counting time of 1–5 ms per pixel. NEXAFS spectra are obtained by the acquisition of many images over a selected spectral range of photon energy. Coordinated undulator and monochromator moves between successive images take about 250 ms, during which time a fast mechanical shutter closes to protect radiation-sensitive samples from unnecessary exposure. Due to unwanted motion of the zone plate, the focus moves laterally during photon energy scanning. The images are shifted into registry using a correlation technique, and NEXAFS spectra are extracted from small areas, normalizing against an open area of the image.² The system will be upgraded again over the next year, and we will be focusing on replacement of the zone plate z scan stage so that motion, if any, is reduced during energy scans.

¹Warwick, T., H. Ade, S. Cerasari, J. Denlinger, K. Franek, A. Garcia, S. Hayakawa, A. P. Hitchcock, J. Kikuma, S. Klinger, J. Kortright, G. Meigs, G. Morisson, M. Moronne, S. Myneni, E. Rightor, E. Rotenberg, S. Seal, H.-J. Shin, W.F. Steele, T. Tyliczszak, and B.P. Tonner, "A scanning transmission x-ray microscope for materials science spectromicroscopy at the Advanced Light Source," *Rev. Sci. Instr.* **69**, 8 (August 1998), pp. 2964-2973.

²STACKs program; C. Jacobsen, private communication and A.P.Hitchcock, private communication.

Beamline 7.3.1.1

The photoemission electron microscope (PEEM) is now in full operation and has achieved high spatial resolution. It was developed under a DOE Cooperative Research and Development Agreement (CRADA) between the ALS and Joachim Stöhr of IBM. The microscope has electrostatic focusing, and consists of a 30-kV immersion lens objective and two projector lenses, as well as a relay lens used for positioning an image of the objective back focal plane at the position of a set of interchangeable apertures. For flat, reasonably conductive surfaces, the microscope achieves its theoretical minimum resolution of 20 nm. The data rate of the system is good, with images typically taking a few seconds to acquire. This is a result of the highly optimized optical system used to illuminate the sample. This system utilizes a spherical grating to focus at approximately 1:1 in the vertical direction and a 1.2-m-long elliptical mirror to focus in the horizontal direction. This produces a monochromatic focus size of around 30 μm in diameter, with a flux of around 10^{12} photons/s in a 1/1000 bandpass. Magnetic imaging studies have begun, and 50-nm resolution has been achieved using magnetic circular dichroism as a contrast mechanism. The scientific program is centered around studies of magnetic domain structures, antiferromagnetic surfaces, and polymer surfaces. The system is equipped with a comprehensive sample preparation facility, with *in-situ* growth capability. A fully aberration-corrected microscope, which should allow imaging at 2-nm resolution, is in design. Construction of this microscope is expected to start in mid-1999.

Beamline 7.3.3

Beamline 7.3.3 is shared between three programs: an ultrafast diffraction program led by Roger Falcone (University of California, Berkeley) and Phil Heiman, a program to develop ultrafast gating techniques led by Ernie Glover, and an in-house materials diffraction program led by Alastair MacDowell. While synchrotrons have traditionally provided information about the static properties of materials important to the physical and life sciences, they have played only a limited role in studying material dynamics: the time resolution available at synchrotrons (~30 ps) is inadequate for observing the fast (~100 fs) primary events that drive many interesting dynamical processes such as chemical reactions and phase transitions. The ability to perform x-ray spectroscopy with femtosecond time resolution represents an important scientific frontier that will have an impact a number of fields in physics, chemistry, and biology. The goal of performing femtosecond x-ray spectroscopy at the ALS is being pursued via two routes: (1) development of an ultrafast x-ray source and (2) development of ultrafast x-ray detectors. In the work led by the Falcone UCB team, a Ti:Al₂O₃-based laser system produces pulses with a duration of about 100 fs. X rays are detected by an avalanche photodiode (APD) having 5-ns time resolution or a streak camera with a time resolution 1 ps. In one study, x-ray diffraction has been applied to the laser-induced melting of a semiconductor, InSb. Experimental rocking curves are used to evaluate the depth of the melted layer, the strain profile into the crystal and relaxation processes.¹ In a second experiment, NEXAFS is used as a probe of the electronic structure of a silicon foil in transition from solid to liquid to gas.

Development of x-ray detectors faster than 0.5 ps will be extremely challenging; however, recent experiments at LBNL² have demonstrated a physical mechanism upon which a femtosecond x-ray detector can be built. In brief, an intense femtosecond laser pulse is used to modify the continuum into which an x-ray photoelectron is injected, resulting in laser-induced modifications to an x-ray photoelectron energy spectrum (XPS). Modifications to the continuum are twofold. First, the continuum is dressed with optical photons so that an x-ray photoelectron is inclined to absorb or emit these optical photons (thus changing the photoelectron energy). Second, the laser causes an ac stark shift of the continuum level, resulting in an overall shift (to lower energy) of the x-ray photoelectron spectrum. These laser-induced XPS modifications can be used to construct a femtosecond x-ray detector. An ALS x-ray pulse (30–70 ps) and a femtosecond laser pulse illuminate a sample and a photoelectron spectrum is measured. Laser modifications to the XPS result from a narrow slice in time when the femtosecond laser pulse overlaps the long synchrotron x-ray pulse; the laser pulse therefore serves to "optically gate" the x-ray pulse on a femtosecond time scale. By moving the laser pulse through the x-ray pulse in time, fine time structure on the x-ray pulse can be observed, thus permitting ultrafast x-ray spectroscopy. In this approach to developing fast x-ray detectors, time resolution is limited only by the laser pulse duration, which can be as short as 5–10 fs. Experiments are underway to demonstrate optical gating on Beamlines 7.3.3 and 6.3.2 using femtosecond laser systems synchronized to the storage ring.

The diffraction program is centered around two objectives: (1) developing and applying the techniques of x-ray microdiffraction and (2) developing new x-ray user programs in diffraction. The latter usually means that we construct apparatus for demonstration experiments, carry out sets of experiments, and using this data, work with the user group in seeking funds through proposals to funding agencies for dedicated facilities. This has centered around programs in materials chemistry powder diffraction, high-pressure diffraction, protein microcrystal diffraction, and phase contrast tomography. The microdiffraction program is in the process of transferring from Beamline 10.3.2, and a new set of microfocus mirrors and a four-crystal monochromator has been

constructed. This system will be installed in July 1999. The goniometer, detector, and computer control system is under manufacture by Bruker-Siemens and uses a Huber diffractometer.

¹Larsson, J., Z. Chang, E. Judd, R.W. Falcone, P.A. Heimann, H.A. Padmore, P.H. Bucksbaum, M. Murnane, H. Kapteyn, R.W. Lee, and J.S. Wark, *Optics Letters* **22**, 1012 (1997).

²Glover, T.E., R.W. Schoenlein, A.H. Chin, and C.V. Shank, *Phys. Rev. Lett.* **76** (1996), p. 2468.

Beamline 9.3.2

A team led by Malcolm Howells (including Scott Locklin, Eddie Moler, and Zahid Hussain) has constructed an all-reflection Fourier transform spectrometer over the past few years.¹ This system should produce ultrahigh resolution (resolving power of 10^6) and will be used for a variety of gas-phase atomic and molecular science studies over the energy range from 40–120 eV. In the past year, the first results have been obtained and a resolution of 250 μ eV has been obtained in the visible region at 1.4 eV photon energy. The theoretical resolution is around 65 μ eV. Part of the difference is due to the fact that only 1/2 of the total scan range was used (the resolving power is simply the ratio of the scan length to the wavelength) and the rest is attributed to a combination of Doppler and collisional broadening as well as misalignment. The system is coupled to Beamline 9.3.2 through a branchline after the exit slits, and experiments are now underway with synchrotron radiation to extend the operation to higher photon energies.

¹Moler, E.J., R.M. Duarte, M.R. Howells, Z. Hussain, C. Oh, and J. Spring, "First measurements using the ALS soft x-ray Fourier transform spectrometer" in *Coherent Electron-Beam X-ray Sources and Applications A*, Proc. SPIE **3154**, K. Freund, H.P. Freund, and M.R. Howells, Eds. (Bellingham, 1997).

Beamline 10.3.2

Beamline 10.3.2 was built by the Center for X-Ray Optics and over the past few years had been used as a place to operate a deep-lithography (LIGA) station. With that program now having a home on Beamline 3.3.2, this station was available for other developments.

The ESG has developed a microfocusing system capable of x-ray diffraction and x-ray absorption spectroscopy in the intermediate energy range from 5–12 keV.^{1,2} The x-ray hutch is located 31 m from the source and uses a four-crystal monochromator and a Kirkpatrick-Baez mirror pair to form a monochromatic focus with a spatial resolution of 0.8 μ m. The micro x-ray diffraction (μ -XRD) program has generated significant interest from the thin-film materials community for the quantification of strain in single grains and has spun off into a new program on Beamline 7.3.3. The activities on Beamline 10.3.2 are now centered on an environmental science program, led by Geraldine Lamble, using micro x-ray absorption spectroscopy (μ -XAS) for local chemical speciation. This has been successful in generating a new user community, and has led to the need for a more permanent, dedicated experimental system. An upgraded beamline has been designed, consisting of a 1:1 relay mirror followed by an x-y slit, a collimating mirror, a four-crystal monochromator, and Kirkpatrick-Baez microfocus optics. This system will have the ability to change resolution by altering the size of the x-y slit, so that users can trade flux for resolution. The sample stage will be replaced with a fast-scan system, and the detector will be replaced with a nine-element system with DSP-based electronics. The new system is planned for commissioning in December 1999.

¹MacDowell, A.A., C.H. Chang, H.A. Padmore, J.R. Patel, and A.C. Thompson, "Grain orientation mapping of passivated aluminum interconnect lines with x-ray micro-diffraction," in *1998 Spring Meeting of the Materials Research Society, Applications of Synchrotron Radiation Techniques to Materials Science IV*, **524** (1998), pp. 55-58.

²MacDowell, A.A., C.H. Chang, G.M. Lamble, R.S. Celestre, J.R. Patel, and H.A. Padmore, "Progress towards sub-micron hard x-ray imaging using elliptically bent mirrors and its applications," presented at SPIE conference, San Diego, July 19-24 1998. To be published in SPIE **3449** (1998).

Accelerator Physics

Reported by David Robin

In 1998 the ALS user community experienced a substantial improvement in the quality and consistency of the delivered beam. In particular, both fast and slow electron beam motions were significantly reduced. With the implementation of a “slow” global orbit feedback system, the horizontal orbit drift was reduced by a factor of 5, from ± 50 microns peak-to-peak to less than ± 10 microns peak-to-peak. By replacing the rf master oscillator with a quieter version, the orbit noise at 4 kHz was reduced by a factor of 6. These and other improvements were partly a result of close cooperation between the accelerator physics group and the users.

In addition to orbit stability, large gains were made in the understanding of lifetime and injection. One discovery was that the lifetime (which is determined primarily by intrabeam scattering) is limited by the dynamic aperture, not by the momentum acceptance defined by the rf system. By understanding this unexpected result it may be possible to improve the beam lifetime and to accurately predict it under new running conditions (such as with the superbends). Improvements were made in the understanding of injection dynamics. Using several diagnostics (streak camera, longitudinal feedback buttons) measurements were made of the phase and energy mismatch of the injected beam relative to the stored beam. These and other studies of the injection dynamics should lead to higher and more stable injection rates. This will be particularly important if the machine is to be run in a top-off mode, refilled every 12 hours instead of every 4.

During 1998 the elliptically polarized undulator (EPU) was installed in the machine. Unlike other insertion devices whose gaps only move vertically to change the photon energy, the EPU's gap also shifts longitudinally to change the polarization. It was not clear if the orbit motion generated by this extra degree of gap motion could be compensated for in the same manner as is done in the other devices—with feedforward tables. Studies showed that it was possible and practical to generate and operate with a 2-D feedforward table for orbit compensation. At this point the longitudinal motion is limited to 1/10th of its maximum speed. The challenge remains to compensate the orbit when the “speed limit” is lifted.

To increase the beam lifetime, a third-harmonic cavity system will be installed in the storage ring in the June 1999 shutdown. Construction of the third-harmonic cavities is nearly complete, and commissioning of the system will take place during summer 1999. In addition, plans are underway to install three high-field (5-T) superconducting bend magnets in the storage ring. These “superbends” will be excellent sources of x rays. The plan is to install them in 2001. Theoretical accelerator physics studies of the superbends indicate that there will be no significant detriment to the performance of the machine.

Orbit Stability in the 0-300 Hz Region

Reported by Greg Portmann

The third-generation Advanced Light Source produces extremely bright and finely focused photon beams using undulators, wigglers, and bend magnets. The dominant causes of orbit motion at the ALS are temperature variation and insertion device motion. This type of motion can be removed using slow global orbit feedback with a data rate of a few hertz. The remaining orbit motion up to 300 Hz is only 1-3 micron rms. Since slow orbit feedback does not require high computational throughput, the global orbit feedback algorithm, based on the singular valued decomposition method, is coded in MATLAB and runs on a control room workstation. Using the

MATLAB environment to develop, test, and run the storage ring control algorithms has proved to be a fast and efficient way to operate the ALS.

Orbit Stability and Feedback

Maintaining the proper electron beam orbit is an important operational issue for all light sources. The most commonly used figure of merit for orbit stability is that the beam should be stable to one-tenth of the beam size. Expressed another way, the optics for most light source experiments can tolerate a ten percent fluctuation in the beam's position and angular divergence without adverse effects. As shown in Table 1, this implies a very tight tolerance for orbit motion at the ALS source points (table calculated assuming 1.8% coupling).¹

Table 1. Beam position stability requirements.

Beam Location	Horizontal	Vertical
Straight Section	24.6 μm	2.0 μm
Bend Magnet #1	5.3 μm	4.4 μm
Bend Magnet #2	10.3 μm	1.2 μm

Local and global orbit feedback algorithms can potentially regulate the beam position to the accuracy of the beam position monitor (BPM) system; however, building a BPM system that is accurate to the micron level is quite difficult. Many third-generation light sources have BPM systems capable of submicron accuracy over relatively short time intervals. At the ALS, the electron beam can be accurately measured to 0.6 μm horizontally and 0.8 μm vertically over a 0.1–300 Hz frequency range. The problem for measuring beam motion at the ALS is over longer time intervals. The two major sources of error are the current dependence of the BPM electronics and physical motion of the vacuum chamber. (Harmonic correction algorithms can be used to mitigate these effects.) Due to these problems, we have taken a very conservative approach to adding orbit feedback to the ALS storage ring.

In addition to the original 96 BPMs in the ALS storage ring, a pair of high-sensitivity BPMs have been installed in each insertion device straight section (20 BPMs total).² By rigidly mounting these BPMs to each insertion device structure that is installed in a temperature controlled housing, the positional stability of the BPM is ensured. The relative motion between the BPM and the storage ring floor is a few microns per week.³ With the addition of these new monitors, global orbit feedback in the horizontal plane has been added to the standard operation of the ALS.

Without orbit feedback, but with temperature stabilization of the tunnel-air and low-conductivity water, we have achieved the positional stability shown in Table 2.

¹ D. Robin, private communication (1998).

² J. Hinkson, private communication (1999).

³ G. Krebs, "Measurement of Storage Ring Motion at the ALS," *Proceedings of the 1997 IEEE Particle Accelerator Conf.*

Table 2. Beam stability without orbit feedback.

Frequency	Magnitude	Dominant Cause
Two weeks (A typical experimental run)	Horizontally $\pm 200\ \mu\text{m}$ Vertically $\pm 100\ \mu\text{m}$	Magnet hysteresis Temperature fluctuations Component heating between 1.5 GeV and 1.9 GeV
1 Day	Horizontally $\pm 125\ \mu\text{m}$ Vertically $\pm 75\ \mu\text{m}$	Temperature fluctuations
4 Hour Fill	Horizontally $\pm 50\ \mu\text{m}$ Vertically $\pm 20\ \mu\text{m}$	Temperature fluctuations Feed forward errors
Minutes	5 to 10 μm	Feed forward errors
0.1 to 300 Hz	1 to 3 μm	Ground vibration

Slow Orbit Drift

The dominant source of orbit motion at the ALS is slow drift due to temperature variations. There are three basic causes of thermal variations: (1) change in ambient air temperature of the storage ring tunnel; (2) change in the low conductivity cooling water (LCW) temperature; and (3) change in the photon beam power as the electron beam decays. The regulation specifications are ± 0.2 and $\pm 0.1^\circ\text{C}$ for the air and LCW temperatures, respectively. However, temperature regulation to this level is difficult to achieve day-to-day.

Insertion device motion is the next largest source of slow orbit distortion. The ALS experimenters can freely adjust the insertion device gap at any time. Feedforward tables are empirically generated to compensate for this motion. The table accuracy is 5-10 μm rms.

Figures 1 and 2 show the electron beam orbit in the insertion device straight sections for a typical day before the orbit feedback system was operational. The horizontal orbit is more sensitive to temperature variation.

Figure 1. Horizontal orbit stability without feedback, August 15, 1998.

Figure 2. Vertical orbit stability without feedback, August 15, 1998.

A slow global orbit feedback system in the horizontal plane has been in operation at the ALS since September 1998. Before that time, orbit correction was only done at the beginning of an experiment run. Besides the feedforward correction to compensate for insertion device motion, the storage ring magnet control would be static for the length of the run—typically two weeks. As shown in Table 2, the ALS is surprisingly quite stable without orbit correction. However, in order to meet the tolerances in Table 1, a slow global orbit feedback system was developed. Figure 3 shows the results of applying the correction.

One could correct the orbit to the micron level, but the orbit correction algorithm is presently over-constrained. This is a conservative way of running, done so that the feedback system does not particularly track vacuum chamber motion.

“Fast” Orbit Motion

The dominant cause of “fast” orbit motion (up to about 300 Hz) at the ALS is vibration. Power supply regulation is a common cause of orbit stability problems in this frequency range; however, it thankfully has not been an issue at the ALS. Figure 4 shows the power spectrum for the orbit motion in the horizontal plane from 0.3–50 Hz. The rms motion from 0.1–300 Hz is typically 3.0 μm horizontally and 1.2 μm vertically. These numbers have not changed very much over the last five years, which implies that the ALS can inherently meet the stability goals (Table 1) in this frequency range without orbit feedback.

Future Work

Improving the orbit stability at the ALS will be a continual process. The immediate goal is to include vertical orbit correction with the slow orbit feedback and add faster orbit correction during insertion device gap motion. Once this is accomplished, the orbit stability goal given in Table 1 will be reliably achieved. Presently we achieve the stability goal by temperature regulation and maintaining accurate insertion device feed forward tables. This will continue to be important; however, with additional feedback, the reliability of orbit stability at the ALS will improve even further.

Presently, our knowledge of electron beam motion comes mainly from 20 electron beam position monitors (BPMs). Increasing the number of monitors and adding photon beam position monitors with adequate stability and bandwidth will be very helpful in diagnosing beam stability problems.

Figure 3. Horizontal orbit stability with feedback on, February 6, 1999.

Figure 4. Power spectral density of the horizontal orbit.

Orbit Stability in the >300 Hz Region

Reported by John Byrd

Fast beam motion has several deleterious effects on photon beam quality. Synchrotron (longitudinal) electron beam motion results in increased average energy spread, which widens undulator harmonics, as well as increased horizontal beam size at dispersive lattice points, thereby reducing the beam brightness at these locations. Longitudinal motion can also result in erratic variation of centroid position and angle at dispersive lattice locations. Betatron, or transverse, motion can cause an average increase in the transverse beam size, also reducing the brightness. It also can result in erratic centroid motion or angle, leading to motion on the user's sample or intensity modulation through an aperture. Another possible result is erratic change in beam size, leading to intensity modulation through an aperture such as a slit.

There are several potential sources of fast beam motion at the ALS that either excite the beam directly or make possible self-excited beam motions (i.e., instabilities.) Sources driving the beam include random amplitude or phase noise in the rf system, exciting synchrotron oscillations; klystron power supply noise; and noise in the multibunch feedback systems. The sources of multibunch self-excited motion include rf cavity higher-order modes, resistive wall impedance (longitudinal and transverse), and vertical coupled bunch instabilities driven by ion trapping. In high-current single-bunch mode (i.e., above 4–5 mA/bunch), there are longitudinal microwave instabilities and a vertical mode-coupling instability, both driven by the broadband impedance of the vacuum aperture.

We have made several improvements in the area of fast beam motion over the past year. The main efforts have been in increasing the reliability of the multibunch feedback systems, both through hardware upgrades and operational adjustment. These efforts have been extremely successful, such that these systems operate almost without fail. Another area in which we made an improvement was in the understanding of how phase noise in the rf master oscillator excites synchrotron oscillations. This is described in more detail below.

Beam Motion Driven by RF Phase Noise

In the spring of 1998, scientists using the ALS infrared synchrotron light beamline (Beamline 1.4) reported observations of beam motion in the frequency range of 4 to 10 kHz, variable with total beam current. Our investigations linked the beam motion to energy oscillations of the beam at a point of dispersion in the lattice. These oscillations were found to be driven by phase noise in the rf master oscillator (MO) through the Robinson effect.

This effect, first explained by Robinson in 1964, describes the dynamics of the interaction between synchrotron oscillations of the beam and the fundamental mode of the rf cavity. Under normal cavity conditions, this interaction causes a damping of the beam's synchrotron oscillations as well as a downward shift in the oscillation frequency, illustrated in Figure 5, which shows the transfer function for beam energy oscillations excited by rf cavity phase modulation.

Although the beam-cavity interaction is inherently stable, beam oscillations can still be driven by modulations in the rf cavity amplitude or phase. One of the sources of excitation is phase noise on the rf master oscillator. The characteristic spectrum of phase noise decreases exponentially with distance from the carrier, as shown by the two spectra shown in Figure 5. The main problem is that the overlap of the beam response and the phase noise increases as the beam frequency is shifted to lower values at higher currents. Shown in Figure 6 are measured beam spectra at various beam currents along with a calculation of the expected beam motion using the known phase noise in the master oscillator. The agreement is good, enabling us to predict the beam motion for any noise source.

Figure 5. Beam energy transfer function as a function of beam current showing the Robinson frequency shift. The phase noise of two master oscillator (MO) sources is also shown.

Figure 6. Measured and calculated spectrum of beam phase oscillations as a function of current.

To improve the situation at the ALS, we simply replaced the existing MO with a cleaner source. The result is shown in Figure 7: an overall improvement in the beam noise by a factor of six. This improvement was clearly visible on the infrared beamline. With the cleaner MO, harmonics of the klystron power supply are now visible in the beam spectrum. Improvements being planned include an additional phase feedback loop using a separate beam phase detector.

Figure 7. Comparison of beam motion for two MO sources.

Longitudinal Beam Dynamics at Injection

Reported by John Byrd and Stefano De Santis

Optimizing beam injection into electron rings is important for increasing the filling rate and reducing radiation background. Understanding the injection process has become increasingly important for the continuous-top-up injection that maintains a constant beam current. We have begun a study of beam dynamics at injection in the ALS with an initial emphasis on longitudinal beam dynamics. Some of the questions we hope to resolve include the following: What is the proper adjustment of the injected energy and phase for maximum capture in the storage ring? What are the loss mechanisms during injection? How do we minimally disturb the stored beam?

Some Possible Outcomes of Injection

Consider the injection of a bunch into a storage ring bucket as shown in Figure 8. If the bunch is injected away from the center of the bucket, either in phase or energy, as shown in Figure 8a, it will rotate in the bucket until it eventually damps to the stored beam. There may also be a mismatch of the injected bunch shape to the rf bucket, as shown in Figure 8 b, resulting in a quadrupole oscillation.

In these measurements we looked at the beam intensity following injection using a photomultiplier tube observing the intensity of synchrotron light. The photomultiplier is gated at the revolution frequency (1.5 MHz) synchronously with the passage of the injected bunch. It is then possible to have a measure of the bunch current from turn to turn proportional to the intensity of the synchrotron light emitted. Figure 9 shows a typical signal obtained injecting into an empty bucket; the time scale of the current decay is several milliseconds, indicating that the energy-phase acceptance is the limiting factor.

Figure 8. Beam phase space mismatch to the RF bucket at injection in two cases: (a) for phase offset and shape mismatch, resulting in dipole and quadrupole oscillations, and (b) for only a shape mismatch, resulting in quadrupole oscillations.

We can also look at the offset in the phase of the center-of-charge by detecting the phase of the signal induced in a beam position monitor. Shown in Figure 10 is an oscilloscope trace of this signal following injection with and without an energy offset to the injected beam.

Figure 9. Photomultiplier tube data on BL 3.1, showing injection transient.

Figure 10. Longitudinal feedback pickups signal. Off-energy (dark) and on-energy (light) injection.

After increasing the energy of the injected beam by almost 1%, setting a new delay on the extraction trigger control, and re-tuning the transfer line from the booster to the storage ring, the injection rate went up from around 1 mA/shot to above 1.5 mA/shot.

We can make a detailed study of the longitudinal dynamics using a dual-scan synchroscan streak camera, with which we observe the time evolution of the longitudinal beam distribution following injection. When an electron bunch is injected into the storage ring, its length and energy spread will either grow or damp to the natural bunch length and energy spread of the storage ring; in the latter case the damping occurs over several radiation damping times. In the ALS, the injected bunch length is about five times the natural bunch length, and the injected energy spread is close to the natural energy spread. If this mismatched bunch is injected into the center of an rf bucket, it rotates in the bucket at the synchrotron frequency, modulating the bunch length as shown schematically in Figure 8b. However, the nonlinearity of the rf voltage creates a

dependence of synchrotron frequency on amplitude, causing the bunch head and tail to advance slower in phase than the center, resulting in filamentation of the bunch distribution.

Shown in Figure 11a is a synchroscan camera image of the beam 0.3 ms after injection into an empty storage ring. The vertical axis represents the longitudinal bunch length in units of time, and the horizontal axis is time. The bunch length is modulated at half the synchrotron period of $87\text{ }\mu\text{s}$ due to the rotation of the mismatched bunch shape as shown in Figure 8. Figure 11b shows the synchroscan camera image 2.4 msec later. The bunch filamentation is evidenced by the tails forming on the bunch distribution. This compares very well with a simulated synchroscan camera image as shown in Figure 11c, where each vertical slice is the projection of the phase space distribution.

Figure 11. (a) Measured SC image 0.3 msec following injection showing modulation of the bunch length. (b) SC image 2.4 msec later showing filamentation of the large amplitude particles. (c) A computer simulated image found from tracking.

Lifetime and Momentum Acceptance

Reported by David Robin

Beam lifetime in a storage ring is limited by different effects: quantum lifetime, elastic gas scattering, inelastic gas scattering, and intrabeam scattering. The relative contributions of these various mechanisms have been measured for the ALS and are displayed in Table 3. As seen in the table, the lifetime limit is dominated by intrabeam (Touschek) scattering. In fact, Touschek scattering is the main lifetime limitation for most third-generation synchrotron radiation sources.

Table 3. Contributions of the lifetime limiting effects to the total lifetime at 400 mA in 1.5 GeV operation 1% emittance coupling.

	400 mA
quantum lifetime τ_q	>250 hours
elastic scattering lifetime τ_{el}	>18 hours
inelastic lifetime τ_{inel}	>55 hours
Touschek lifetime τ_{tou}	2.2 hours
total lifetime τ_t	>1.9 hours

Factors Affecting Touschek Lifetime

Touschek lifetime, τ_{tou} , is a function of the beam energy, E , the bunch current, I_b , the bunch volume, V_b , the bunch divergence, σ'_x , and the momentum acceptance, ϵ :

$$\frac{1}{\tau_{tou}(s)} \propto \frac{1}{E^3} \frac{I_b}{V_b(s)\sigma'_x(s)\epsilon(s)^2} f\left(\frac{\epsilon(s)^2}{\sigma'_x(s)E^2}\right)$$

The momentum acceptance, ϵ , is the maximum relative momentum deviation from the design momentum a particle can experience without being lost. τ_{tou} is strongly dependent upon the momentum acceptance (roughly proportional to the square of the momentum acceptance). The bunch volume, bunch divergence, and momentum acceptance all depend upon the longitudinal position, s , in the ring. Therefore, τ_{tou} needs to be averaged over s .

The momentum acceptance is limited by either the rf aperture or the dynamic aperture. The rf aperture is determined by the size of the rf bucket, which is proportional to the square root of the rf cavity voltage, and can be increased by adding rf power. The dynamic aperture limits the aperture through synchrotron coupling, which causes particles with large energy offsets to begin large transverse oscillations, resulting in the particle colliding with a transverse aperture in the ring. The momentum acceptance is determined by the smaller of the rf aperture or dynamic aperture. Both of these apertures are displayed in Figure 12.

In Figure 12 the blue lines represent the induced amplitudes—one for the arc section and the other for the straight section. In the straight section, where there is no dispersion, the induced transverse amplitude is nearly zero. In the arc section, with finite dispersion, the induced amplitude is much larger. The momentum acceptance is shown by the intersection of these blue lines with the aperture, and is limited by the dynamic aperture in the arc and the rf aperture in the straight.

Great effort is spent during the design of the storage rings to insure that the dynamic aperture is greater than the rf aperture and thus does not limit the momentum acceptance. In the past year we have made many measurements of the momentum acceptance and found that, in many cases, the dynamic aperture, not the rf, aperture limits the momentum acceptance.

Figure 12. Contributions of the different aperture effects to the total momentum aperture. The thin lines are the invariant induced amplitudes at different positions in the ring.

Measurements of the Momentum Acceptance

We infer the acceptance primarily from measurements of the lifetime. Measurements of the lifetime as a function of the rf voltage were conducted under different storage ring conditions. The synchrotron tune was measured simultaneously, from which one can calculate the bunch length and the rf-bucket height. To enhance the effect of the Touschek scattering over other lifetime effects, a high current per bunch was filled in a few equidistant-spaced bunches. The low number of bunches avoids multibunch instabilities. The beam conditions were 1mA/bunch and 8 bunches (out of 328) filled. Results can be seen in Figure 13.

Figure 13. Beam lifetime as a function of the rf aperture with three different working points (left) and two different values of the chromaticities (right).

The data are fitted by applying the equation given earlier with the following fit parameters: assuming an initial 1% coupling the bunch volume is corrected by a constant factor that takes into account any volume changes such as variation of the coupling, instabilities, etc. The bunch volume is also adjusted according to the changing rf voltage (the bunch length is proportional to the inverse of the square root of the rf voltage). The other parameters are the momentum acceptances, ϵ , in the straight section and in the arc. Thus the data can be fitted with just three parameters.

The dynamic momentum aperture in the arcs can be seen in Figure 13 as the position where the data points start deviating from the quadratic line. In all cases this happens at values less than 3%. For the left plot, the dynamic momentum aperture of the arcs decreased as we moved to lower tunes. The aperture was measured to be 2.7% at the “high” tunes, 2.4% at the “middle” tunes, and 2.0% at the “low” tunes. In Figure 13 (*right*), we see that the dynamic momentum aperture decreased as we increased the chromaticity. When the horizontal and vertical chromaticities were adjusted to 6, the momentum acceptance in the arcs reduced to 1.4%.

Simulations of the Momentum Acceptance

Tracking calculations have been performed to understand the experimental results and test the accuracy of the model. Particles were tracked through the ALS lattice with a six-dimensional symplectic integrator. The following errors and constraints were included in the model to simulate the realistic machine:

- Physical aperture borders were included in the tracking to prevent particle oscillations outside the realistic vacuum chamber. This is important because large-amplitude particles may perform large, but stable, oscillations that would be outside the physical aperture but not lead to a loss of the particle in the tracking.
- Linear field errors are simulated according to the optics measurements done at the ALS with the response-matrix fitting method. These errors lead to a break in the lattice periodicity and excitation of resonances.
- Random skew quadrupole errors were distributed in all quadrupoles of the lattice and adjusted to obtain a 1% coupling.
- The wiggler was simulated as a chain of “hard-edged” bending magnets obtaining the correct linear focusing and longitudinal dynamics properties.

Particles were launched off-energy and off-axis with respect to their off-energy orbit and tracked for 512 turns or until lost. Results for three different tunes and three different chromaticities are shown in Figure 14. The thick symbols represent the measured momentum apertures, distributed along the curve showing the amplitude induced by Touschek scattering in the arc. In the case of the simulations, the aperture was calculated to be 2.8% at the “high” tunes, 2.4% at the “middle” tunes, and 1.9% at the “low” tunes. For the case of the chromaticity set to 6 the aperture was calculated to be 1.3%. The agreement between measurement and tracking is excellent.

Figure 14. Maximum stable transverse emittance as a function of momentum deviation. The left side is a case with three different working points, while the right side shows two different chromaticities.

In addition to these measurements, the momentum acceptance was measured under various different conditions, including high coupling and with the wiggler magnet turned on. The results of all measurements are summarized in Table 4. The agreement between simulation and measurement is better than 15%.

Table 4. Measured and calculated momentum aperture in the straight and in the arc section for different machine conditions.

Coupling	Chromaticity	Horizontal Tune	Vertical Tune	Measured ϵ (straight)	Measured ϵ (arc)	Calculated ϵ (straight)	Calculated ϵ (arc)
Wiggler off							
0.01	1.0	0.31	0.22	>3.2%	2.7%	3.9%	2.8%
0.01	1.0	0.27	0.18	>3.3%	2.4%	3.3%	2.4%
0.01	1.0	0.22	0.13	2.6%	2.0%	2.8%	1.9%
0.01	1.0	0.27	0.18	>2.8%	2.8%	-	-
0.01	6.0	0.27	0.18	1.7%	1.4%	1.6%	1.3%
0.10	1.0	0.27	0.18	2.8%	2.3%	3.0%	1.8%
Wiggler on							
0.01	1.0	0.27	0.18	>3.3%	2.1%	3.0%	2.1%
0.10	1.0	0.27	0.18	>2.8%	1.6%	2.8%	1.6%
0.10	0.0	0.27	0.18	>2.8%	1.7%	-	-
0.10	6.0	0.27	0.18	1.8%	1.3%	-	-
0.10	1.0	0.31	0.22	>3.2%	1.9%	3.5%	2.0%

At this time we feel that we can draw several conclusions:

- The dynamic aperture limits the momentum acceptance in the ALS.
- Particles tend to get lost when they collide with the narrow vertical aperture in the ring. The mechanism for particle loss appears to be nonlinear synchrotron coupling that causes the motion of particles to reach the vertical aperture.
- By knowing the location of these dangerous synchrotron resonances, as well as the knowledge of the tune shifts with energy and with amplitude, one can accurately estimate the aperture.

Understanding these dynamic limits is important in order to improve the lifetime in the ALS and accurately predict the lifetime (and dynamic aperture) in future machines.

Orbit Compensation of the Elliptically Polarized Undulator (EPU)

Reported by Greg Portmann

By changing the insertion device gap, the photon beam energy can be varied. Unfortunately, the electron beam orbit is perturbed when the gap is changed. However, the resulting orbit perturbation can be removed by adjusting the corrector magnets on either side of the insertion device. Without compensation, the electron beam would move by 200 to 400 microns (depending on the device) during a full open-to-closed transition of the gap. Using a simple feedforward lookup table, the orbit accuracy can be maintained to ± 10 microns. Due to the effectiveness of the feedforward system, ALS users can freely adjust the gaps at any time.

The elliptically polarized undulator (EPU) adds a new dimension to the problem. The EPU has not only a vertical gap drive system, but a longitudinal drive as well. The vertical gap is varied to control the energy of the radiation. At a given vertical gap, the longitudinal gap is changed in

order to control the helicity of the radiation. Unfortunately, this motion produces gap-dependent error fields. We have shown that, despite this added degree of complexity, we can compensate for these error fields using lookup tables, just as is done with the less complicated insertion devices. Figure 15 shows the vertical feedforward. A one gauss-centimeter dipole error will cause a 1–1.5 micron distortion in the storage ring orbit.

Figure 15. Vertical feedforward table for the EPU.

If the longitudinal motion of the EPU were left uncompensated, the maximum orbit distortion would be ± 50 microns horizontally and ± 200 microns vertically. Figures 16 and 17 show the 2-dimensional feedforward tables for each plane. It takes about 2 hours of machine time to generate a 2-dimensional table, compared to 10 minutes for the 1-dimensional vertical table. The sensitivity of these tables to the electron beam position in the insertion device is quite small: 10–20 microns over 1 mm of orbit change through the insertion device. Since the electron beam orbit should be stable to 0.05 mm or less, the 2-dimensional table should not need to be generated very often.

Figure 16. Longitudinal feedforward table in the horizontal orbit direction.

Figure 17. Longitudinal feed forward table in the vertical orbit direction.

Increasing Beam Lifetime Without Losing Brightness

Reported by John Byrd

The beam lifetime is one of the most important parameters to the ALS users. As described earlier in this chapter, it is dominated by large-angle intrabeam (Touschek) scattering, which occurs when electrons within the bunch scatter and transfer enough momentum that they are knocked outside the momentum acceptance of the storage ring. For a given beam energy, we can improve the lifetime by either increasing the momentum acceptance of the ring or by reducing the charge density of the electron bunch. We expect only marginal improvements in the momentum acceptance as either the rf voltage is slowly increased or as the momentum acceptance of the lattice is better understood.

A Lifetime Improvement Idea

We currently increase the lifetime by increasing the vertical beam size through excitation of the betatron coupling resonance, effectively reducing the transverse beam brightness. An alternative has been proposed where the bunch is lengthened using a third-harmonic voltage of the 500 MHz main accelerating cavities as illustrated in Figure 18.

The harmonic voltage is adjusted to cancel the slope of the main rf voltage at the bunch center, effectively lengthening the bunch. The effect on the bunch shape at optimum lengthening is shown in Figure 19. We expect an increase of lifetime of a factor of 3 at optimum.

To produce the required harmonic voltage, a team of LBNL physicists and engineers have designed a 1.5 GHz (3 x 500 MHz) rf cavity to be installed at the ALS. The cavities (Figure 20) were fabricated at Lawrence Livermore National Laboratory by the same team that made the main rf cavities for the PEP-II B Factory. Five such cavities will be installed in the downstream half of straight section 2 in June 1999. The cavities will be operated in a passive mode, i.e., the cavity voltage will be generated by the beam. The design is upgradeable to an active system, should the need arise.

Figure 18. Third-harmonic bunch lengthening scheme.

Figure 19. Effect of third-harmonic cavity upon bunch shape, at optimum lengthening.

Figure 20. Third-harmonic cavity (1.5 GHz).

Superbends at the ALS

Reported by David Robin

There is an increasing demand for more high-energy, high-brightness x-ray ports at the Advanced Light Source (ALS). To satisfy this demand, a plan is being implemented to replace three 1.3-T normal-conducting bend magnets with three 5-T superconducting bend magnets. In principle, one could create high-energy sources by placing wigglers or wavelength shifters in the long straight sections. However, of the 12 straight sections, only 2.5 are empty at present. By replacing the existing bends with high-field bends, we can obtain additional high-energy sources without using the straight sections. Figure 21 compares the flux and brightness of the superbends with other sources of high-energy photons. Compared to a normal ALS bend, a superbend provides an order of magnitude more flux and brightness at 10 keV—two orders of magnitude at 20 keV.

Figure 21. The flux (*left*) and brightness (*right*) of several high energy sources: the normal ALS bend, a superbend, the W16 wiggler, and APS bend and APS undulator A.

Planned Configuration with Superbends

The plan is to modify three of the twelve ALS sectors to include superbends. A typical sector can be seen in Figure 22 (top). The sector has three dipole magnets, each bending the beam by 10° . The dipoles are combined function magnets having both dipole and quadrupole field components. The superbends, unlike the normal dipoles, do not have a large quadrupole (focusing component); therefore additional quadrupoles are placed on both sides. Figure 22 shows the lattice of a sector in its original configuration (upper) and as modified to include a superbend and two additional quadrupoles.

In Table 5, the parameters of the ALS are given without the superbends and matched to zero dispersion in the straights (column 1); with 3 superbends and matched to zero dispersion in the straights (column 2); and finally with 3 superbends matched to 6 cm dispersion

Figure 22. Magnet layout of a normal (*top*) and modified (*bottom*) sector.

in the straights (column 3). Due to increased quantum fluctuation with the superbends, the horizontal emittance, ϵ_x , increases. However, by operating with finite dispersion in the straight section, it is possible to reduce ϵ_x .

Table 5. Storage ring parameters without superbends, with three ($\eta_x=0$), and with three ($\eta_x=6\text{cm}$).

	No Superbends ($\eta_x = 0$)	Three Superbends ($\eta_x = 0$)	Three Superbends ($\eta_x = 6 \text{ cm}$)
Energy	1.9 GeV	1.9 GeV	1.9 GeV
ϵ_x	5.5 [nm rad]	13 [nm rad]	7.5 [nm rad]
σ_E	0.08%	0.10%	0.10%
$\Delta E/\text{turn}$	232 keV	281 keV	281 keV

Impact on Machine Performance

It is important that there be no major impact on normal operation; therefore it is necessary to check that the stability of the beam motion remains sufficient for good injection and lifetime. We know that the superbends will perturb the ring's 12-fold periodicity, as well as introducing some nonlinear fields, which may excite low-order resonances that affect the beam dynamics.

A useful way to visualize the impact of periodicity breaking is through tune scans. We use simple 4x4 matrix code to do the tracking where the sextupoles are modeled as thin kicks. The superbends are modeled as isomagnetic sector bends with linear hard-edged fringe fields. The strength of the magnetic field, B , and length, L , is adjusted such that the longitudinal integral of B and B^2 is the same as for the true superbend fields. The chromaticity is set to zero in both planes and the dispersion fitted to zero in the straight sections. Attached to the tracking code is a frequency analysis post processor that numerically computes the fundamental frequencies of an orbit.

First the betatron tunes are set. Then a particle is launched with an initial offset of 10 mm horizontally and 1 mm vertically and tracked for 1024 turns or until lost. If the particle survives 1024 turns, the frequency post processor computes the fundamental frequencies for that particle. The procedure is then repeated for many different tunes. In total the machine is adjusted to 900 tunes (on an evenly spaced grid of 31×31 tunes between $\nu_x = 14.1$ to 14.4 and $\nu_y = 8.1$ to 8.4). The results are plotted in Figure 23.

Figure 23. Tunes scans: A comparison of 0 and 3 superbends.

On the left in Figure 23 is the lattice with no superbends. On the right is a lattice with three superbends, evenly spaced. Superimposed lines plot all allowed resonances of up to the 5th order. The dots correspond to the numerically calculated frequencies. Excitation of resonances can be observed either from missing points or distortion in the point spacing.

In the case of no superbends (*left*), one only sees the influence of the $2\nu_x - 2\nu_y = 12$ resonance. In the case of three evenly spaced superbends (*right*), one sees that there are more resonances excited. In particular, one sees a 4th-order resonance, $4\nu_x = 57$, that is strongly excited and also several coupled resonances that cross at $\nu_x = 14.25$ and $\nu_y = 8.25$. In these regions, the motion of large-amplitude particles is chaotic. However, there still seem to be large regions in tune space where it is possible to operate. This is not true in the case of three superbends located asymmetrically around the ring. In that case, the tunes scans were greatly distorted, with many missing points. Based upon the tunes scans for the three evenly spaced superbends, a working point was chosen ($\nu_x = 14.25$ and $\nu_y = 8.2$) for more detailed tracking studies.

For more quantitative particle tracking studies, we use a 6-D symplectic integrator. We include a ± 25 mm horizontal and ± 4 mm vertical physical aperture. Quadrupole gradient errors are included that match the existing machine producing a 5% horizontal and vertical β -beat and 1% coupling. For the superbends we included an integrated sextupole (-5.6 m^{-2}) and decapole (-4.1 m^{-4}), which are the values measured for a prototype magnet.⁴

At the ALS, injection is done off axis in the horizontal plane. It is necessary to have at least a 7-mm horizontal aperture to capture the beam. So for injection studies, the particles were launched with different horizontal offsets and no energy offset and tracked for 512 turns or until lost. The results can be seen in Figure 24. Without superbends, the smallest aperture with errors was calculated to be 14 mm. With superbends, it reduced to 11 mm, but there still exists a sufficiently large region for injection.

Figure 24. Injection simulations for a lattice without superbends (left) and one with superbends (right). The blue circles are the results with no errors and no physical aperture. The red crosses are the results with field errors and realistic physical apertures.

⁴ C. E. Taylor et al., "Test of a High-Field Bend Magnet for the ALS," *Proceedings of the 1998 Applied Superconductivity Conference*.

As previously mentioned, the lifetime is determined by intrabeam scattering. Therefore it is important to ensure that the momentum acceptance is acceptably large. At the ALS, the dynamic momentum acceptance is smallest in the arcs and largest in the straight section. We were particularly concerned that a reduction in the momentum acceptance in the arcs would make it less than the rf acceptance and reduce the lifetime. To determine the dynamic momentum acceptance, the particles are launched with an initial horizontal offset and an energy offset and tracked with synchrotron oscillations.

The results of the tracking that can be seen in Figure 25 showed that the dynamic momentum acceptance (in the arcs) decreased from 2.8% to 2.4% with superbends. However, this is still larger than the rf acceptance, which is 2% at 1.9 GeV. Therefore there should be no impact on the lifetime.

Figure 25. Off energy tracking with no superbends (*left*) and 3 superbends (*right*). Three error seeds are presented. The black line shows the induced betatron amplitude in the arcs. The momentum acceptance (marked with a blue dot) is given by the intersection of the tracking data with the induced amplitude.

If all goes as planned, the ALS will be operating successfully with 3 superbends in 2001.

Operations

Reported by Robert M. Miller

ALS operations continued on a 3-shift-per-day, 7-day-per-week schedule, with 14 to 20 user shifts per week. Operational efficiency (beam delivered versus beam scheduled) was about 94 percent. We continued using the schedule put in place last year, which reduced scheduled maintenance time and increased the number of day shifts available for user operations during the work week.

Long-term scheduling is done at least six months in advance by the Users' Executive Committee and ALS management representatives. Weekly scheduling meetings coordinate the short-term needs of user operations and maintenance and installation activities. A well-attended weekly ALS Users Forum brings ALS users and staff together for informal discussions and information exchange.

The Beamlines Operations Section, part of the Scientific Support Group, has continued to expand, adding associate beamline scientists and operations coordinator support. Mechanical technician support is now on available on the evening shift. Two accelerator operators were hired to fill openings created by a retirement and a reassignment to an associate beamline scientist position. Training of operations staff and documentation of procedures in compliance with DOE Conduct of Operations standards was a significant ongoing activity.

About 3/4 of the user operation time was at 1.9 GeV (up from about 2/3 last year), the rest being at 1.5 GeV, and we provided two weeks of 1.9-GeV two-bunch operation. (The femtosecond x-ray experiments, which use the linac beam rather than the storage ring beam, are among those carried out during 1.5 GeV operation.) A "camshaft" high-current single-bunch mode, which allows time-resolved and time-of-flight measurements, was available on request. In 1999, this mode will need to be requested at least a week in advance to prevent conflicts with other user operations. There were no major outages during 1998.

Improvement of both short- and long-term beam stability is always a major area of interest. Stability from fill to fill continued to be improved; a highlight was refinement of the "one button fill routine" using MATLAB to carry out a set of predetermined routines at each fill. A machine setup period precedes each energy change, to correct the orbit and to set up the beam feedforward and feedback systems. Accelerator Physics staff began training the operators to carry out these setup tasks.

A new 450-ton chiller unit was commissioned in Fall 1998 to supply all the chilled water needs for the ALS complex. This improved the temperature stability of the storage ring by eliminating the need to switch on an additional chiller during warm weather. The storage ring rf water system was identified as a source of vibration, affecting Beamline 1.4, the infrared beamline. This situation was improved by reducing the diameter of the water pump impellers and installing variable-frequency drives to allow the pumps to be operated at a lower speed. A team of ALS physicists, users, and mechanical and operations staff continue to identify and characterize vibration and noise sources and develop plans for mitigation. This will be an ongoing activity.

A variety of improvements to the storage ring and its experimental facilities and procedures were implemented. An elliptically polarized undulator was commissioned in 1998, and we began to allow changes in its vertical gap during user operations. Orbit correction for the polarization mode has been tested and will be implemented in Spring 1999. Finally, third-harmonic cavities will be installed and commissioned in June 1999. This will increase beam lifetime by lengthening the beam bunches, with the goal of being able to refill the storage ring every 12 hours instead of every four hours.

Publications and Preprints Based on Work Done at the ALS

If a publication is associated with a particular beamline, the beamline number appears to the left of the reference.

Refereed Journal Articles

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User Services

The User Services Group, led by Gary Krebs, is a multifaceted group. Its main function is to provide an interface between the user community and the ALS facility. To better serve ALS users, the group was reorganized this year into three sections: the User Services Office, Beamline Coordination, and Technical Information.

The User Services Office, led by Ruth Pepe and located on the ALS mezzanine, assists users in a variety of ways. The User Services Office administrators coordinate all requests for independent-investigator beam time, help users find lodging in the new ALS user apartments, and provide new-user orientation, which includes the dispensing of building access key-cards. The User Services Office provides users with assistance throughout their visits to the ALS.

The Beamline Coordination section, led by Donna Hamamoto, assists users with shipping and receiving and various other on-the-floor needs. Section members help set up experiments and make sure that users' equipment meets ALS safety standards. The Beamline Coordination section serves as a liaison between users and available ALS and Berkeley Lab resources.

The Technical Information section, led by Art Robinson, is responsible for the document you are reading and many others, such as the annual ALS Activity Report. These publications are available as hard copies and on our World Wide Web site. The Technical Information section also publishes special reports, creates illustrations and graphic designs, maintains the ALS Web site, writes and edits the electronic ALSNews, and manages a multifaceted outreach program to the local community. One of the priorities for the User Services Group this year has been to make full use of the capabilities of the World Wide Web to make information available to users and to permit electronic submittal of forms. We now have a suite of interactive pages, which can be reached through the main ALS Web site.

Home page	http://www-als.lbl.gov/
Activity Report 1996–97	http://www-als.lbl.gov/als/actrep/
1997 Compendium of User Abstracts and Technical Reports	http://alspubs.lbl.gov/compendium/
ALSNews	http://www-als.lbl.gov/als/als_news/als_news.html
Beam time proposal submission	http://www-als.lbl.gov/als/quickguide/becomealsuser.html
New user registration	http://wwwals.lbl.gov/als/quickguide/comingtoals.html

Becoming an ALS User

The ALS, a Department of Energy national user facility, welcomes researchers from universities, industry, and government laboratories. Qualified users have access either as members of participating research teams (PRTs) or as independent investigators. PRTs (groups of researchers with related interests from one or more institutions) construct and operate beamlines and have primary responsibility for experiment endstation equipment. Each PRT is entitled to a certain percentage of its beamline's operating time according to the resources contributed by the PRT. The obligations of the PRT and the ALS are recorded in a Memorandum of Understanding. Through a peer-review process, the remaining beam time is granted to independent investigators who submit proposals.

Anyone wishing to explore the potential of synchrotron radiation in their research should review the beamline tables in the next section to gain some familiarity with the photon energy ranges and other individual capabilities of the beamlines. To inquire more specifically about a particular beamline, use the contact information given in the beamline tables.

The ALS Quick Guide for Users on the Internet (<http://www-als.lbl.gov/als/quickguide/>) provides the most up-to-date information on beamlines and the process of becoming an ALS user.

Independent Investigator Program

Independent investigators may propose experimental programs or single experiments to be performed on existing beamlines. Proposals may involve bringing experiment chambers to the ALS from other locations, or they may involve the use of chambers provided by the ALS facility or by a PRT. Independent investigators may also establish collaborations with PRT members.

In the physical sciences, the ALS has two semesters per year for independent investigator research: June–November and December–May. The deadlines for receipt of the beam time proposals for these two running periods are December 1 and June 1, respectively. Protein crystallography proposals have their own proposal submission deadlines. Those deadlines are March 15 and September 15 for the crystallography running periods of July–December and January–June, respectively. After the proposals are submitted, they are reviewed by ALS personnel for technical feasibility and safety, and PRT members from the appropriate beamline check the proposal for conformance to the beamline's capabilities. If a particular beamline is specified in the proposal, it is strongly recommended that the independent investigator contact the appropriate PRT spokesperson before submitting the proposal. Contact information for the PRT spokespersons and local contacts for each beamline are given in the beamline tables. For information on beamlines available to independent investigators, contact the ALS User Services Office; for information on the submission process and deadlines, contact the ALS User Services Administrator (see inside back cover for contact information) or check the Web at <http://www-als.lbl.gov/als/quickguide/independinvest.html>.

After the ALS and PRT review, the proposals undergo peer review by a Proposal Study Panel, which rates the proposals and makes recommendations for the beam time to be granted. Highly rated proposals are allocated beam time by the User Services Office in consultation with the PRT members and the beamline scientists.

Non-Proprietary Research

The ALS does not charge users for beam time if their research is non-proprietary. However, they must sign a user agreement which, among other things, requires the experimenter to send the ALS copies of all publications resulting from data collected at the ALS. For research to be considered non-proprietary, the research results must be published in the open literature. All users are responsible for the day-to-day costs of research (e.g., supplies, phone calls, and technical support).

Proprietary Research

Proprietary research can also be performed at the ALS. Users performing proprietary research will be charged a fee based on cost recovery for the beam time provided. In return, the user may choose to take title to any inventions made during the proprietary research program and treat as proprietary all technical data generated during the program. Contact the ALS User Services Administrator for information on proprietary research proposals (see inside back cover for contact information).

Table of Beamlines at the ALS

Beamline	Source*	Areas of Research	Energy Range	Avail.	Pages**
1.4.1	Bend	Ultraviolet photoluminescence	1.6–6.2 eV	Now	1/669
1.4.2	Bend	Visible and infrared Fourier transform spectroscopy	0.006–3 eV	Now	1/670
1.4.3	Bend	Infrared spectromicroscopy	0.05–1 eV	Now	1/671
3.1	Bend	Diagnostic beamline	200–280 eV	Now	–/–
3.3.2	Bend	Deep-etch x-ray lithography (LIGA)	3–12 keV	Now	31/672
4.0.1-2	EPU5	Magnetic spectroscopy	20–1800 eV	Now	41/673
5.0.1	W16	Monochromatic protein crystallography	7–14 keV	1999	–/674
5.0.2	W16	Multiple-wavelength (MAD) and monochromatic protein crystallography	3.5–14 keV	Now	45/675
5.3.2	Bend	Polymer STXM	150–650 eV	2000	–/676
6.1.2	Bend	High-resolution zone-plate microscopy	500–800 eV	Now	87/677
6.3.1	Bend	Calibration and standards, EUV/soft x-ray optics testing, solid-state chemistry	500–2000 eV	Now	–/678
6.3.2	Bend	Calibration and standards; EUV optics testing; atomic, molecular, and materials science	50–1300 eV	Now	117/679
7.0.1	U5	Surface and materials science, spectromicroscopy, spin resolution, photon-polarization dichroism	60–1000 eV	Now	163/680
7.3.1.1	Bend	Magnetic microscopy, spectromicroscopy	175–1500 eV	Now	295/684
7.3.1.2	Bend	Surface and materials science, micro x-ray photoelectron spectroscopy	260–1500 eV	Now	–/685
7.3.3	Bend	Micro x-ray diffraction, micro x-ray absorption spectroscopy	0.1–12 keV	Now	307/686
8.0.1	U5	Surface and materials science, spectromicroscopy, imaging photoelectron spectroscopy, soft x-ray fluorescence	65–1400 eV	Now	329/688
9.0.1	U10	Coherent optics experiments	200–650 eV	Now	–/690
9.0.2.1	U10	Chemical reaction dynamics, photochemistry	5–30 eV	Now	415/691
9.0.2.2	U10	High-resolution photoelectron and photoionization spectroscopy	5–30 eV	Now	415/692
9.0.2.3	U10	Photoelectron and photoionization imaging and spectroscopy	5–30 eV	Now	415/693
9.3.1	Bend	Atomic, molecular, and materials science	2.2–6 keV	Now	455/694
9.3.2	Bend	Chemical and materials science, circular dichroism, spin resolution	30–1500 eV	Now	467/697
10.0.1	U10	High-resolution atomic, molecular, and optical physics; photoemission of highly correlated materials	17–340 eV	Now	495/699
10.3.1	Bend	X-ray fluorescence microprobe	3–20 keV	Now	527/702
10.3.2	Bend	X-ray optics development, materials science	3–20 keV	Now	551/703
11.3.2	Bend	Inspection of EUV lithography masks	50–1000 eV	Now	587/704
12.0.1.1	U8	Surface and materials science, spectromicroscopy	95–130 eV	Now	593/705
12.0.1.2	U8	EUV lithography optics testing, interferometry	60–320 eV	Now	593/706
BTF	ALS linac	Beam Test Facility	50 MeV electrons	Now	–/707

* Bend = bend magnet; EPU5 = 5-cm-period elliptical polarization undulator; W16 = 16-cm-period wiggler; Ux = x-cm-period undulator

**Abstracts/Technical Information

Beamline 1.4.1

Ultraviolet Photoluminescence (Abstracts begin on page 1)

Operational	Now
Source characteristics	Bend magnet
Energy range	1.6–6.2 eV
Frequency range	750–200 nm
Spectrometer resolution	Depends on slit size
Endstation	Optical table
Spatial resolution	Diffraction limited
Detector	Photomultiplier tube
Spot size at sample	Diffraction limited
Samples	
Preparation	ALS user wet lab available
Sample environment	Air, cryostat, high pressure
Scientific applications	UV-visible photoluminescence
Local contact	Name: Joel W. Ager Phone: (510) 486-6715 Fax: (510) 486-4114 Email: jwager@lbl.gov
Spokesperson	Name: Eugene E. Haller Affiliation: Materials Science Division, Berkeley Lab; MSME Department, U. California Berkeley Phone: (510) 486-5294 Fax: (510) 486-5530 Email: eehaller@lbl.gov

Beamline 1.4.2

Visible and Infrared Fourier Transform Spectroscopy (FTIR) (Abstracts begin on page 1)

Operational	Now
Source characteristics	Bend magnet
Energy range	0.006–3 eV
Frequency range	50 cm ⁻¹ to 25,000 cm ⁻¹
Interferometer resolution	0.125 cm ⁻¹
Endstations	Bruker IFS66v/S FTIR (vacuum), surface science UHV chamber
Characteristics	Rapid- and Step-Scan FTIR, up to 5 nsec time resolution, transmission and reflection modes
Spatial resolution	Diffraction limited ($\approx$ wavelength)
Detectors	Silicon bolometer (LHe cooled) Wide-range MCT (mercury cadmium telluride) Gap diode Silicon diode Fast silicon diode DTGS mid-IR DTGS far-IR
Spot size at sample	1 mm (varies with coupling optics)
Samples Preparation	Stereo microscope and table available UHV surface science chamber
Sample environment	10 ⁻² Torr vacuum in main FTIR bench or 10 ⁻⁹ Torr vacuum in surface science chamber
Scientific applications	Sub-monolayers on surfaces, polymers, semiconductors, superconductors, environmental samples, forensic studies, etc.
Local contact	Name: Michael C. Martin Phone: (510) 495-2231 Fax: (510) 486-7696 Email: mcmartin@lbl.gov
Spokesperson	Name: Wayne R. McKinney Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-4395 Fax: (510) 486-7696 Email: wrmckinney@lbl.gov

Beamline 1.4.3

Infrared Spectromicroscopy (Abstracts begin on page 1)

Operational	Now
Source characteristics	Bend magnet
Energy range	0.05–1 eV
Frequency range	450 cm ⁻¹ to 10,000 cm ⁻¹
Interferometer resolution	0.125 cm ⁻¹
Endstations	Nicolet 760 FTIR, Nic-Plan IR microscope (N ₂ purged)
Characteristics	Motorized sample stage, micron resolution, transmission and reflection modes
Spatial resolution	Diffraction limited ($\approx$ wavelength)
Detectors	Extended-range MCT (mercury cadmium telluride)
Spot size at sample	10 μ m (diffraction limited)
Samples	
Preparation	Stereo microscope and table available
Sample environment	N ₂ purged, minimal clean area (no particle specification)
Scientific applications	Particulate contamination, biological samples, forensic studies, laminates, polymers, fibers, environmental samples
Local contact	Name: Michael C. Martin Phone: (510) 495-2231 Fax: (510) 486-7696 Email: mcmartin@lbl.gov
Spokesperson	Name: Wayne R. McKinney Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-4395 Fax: (510) 486-7696 Email: wrmckinney@lbl.gov

Beamline 3.3.2

Deep-Etch X-Ray Lithography (LIGA) (Abstracts begin on page 31)

Operational	Now
Source characteristics	Bend magnet (7 horizontal mrad at 17 m from bend magnet)
Energy range	3–12 keV
Monochromator	None
Calculated flux (1.9 GeV, 400 mA)	2.7×10^{13} photons/sec/0.1%BW
Endstation	Deep-etch x-ray lithography
Characteristics	Hutchless, self-contained scanner and shutter endstation
Spot size at sample	10 cm $\times$ 1.3 mm
Scientific applications	Research and development on deep-etch x-ray lithography such as LIGA (micromachining of high-aspect-ratio microstructures)
Local contact	Name: Cheryl Hauck Phone: (510) 486-7885 Fax: (510) 486-4102 Email: cahauck@lbl.gov
Spokesperson	Name: Jill Hruby Affiliation: Sandia National Laboratories Phone: (925) 294-2596 Fax: (925) 294-3410 Email: jmhruby@sandia.gov

Beamline 4.0.1-2

Magnetic Spectroscopy (Abstracts begin on page 41)

Operational	Now
Source characteristics	5.0-cm-period elliptical polarization undulator (EPU5.0), EPU7.5 (planned)
Energy range	20–1800 eV
Monochromator	Variable included angle PGM
Calculated flux (1.9 GeV, 400 mA)	1×10^{13} photons/sec/0.1%BW at 800 eV
Resolving power ($E/\Delta E$)	5,000–10,000
Endstations	Total yield, XPS, and fluorescence detectors in UHV chambers with magnets generating fields up to 6 T
Local contact	Name: Anthony T. Young Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-7746 Fax: (510) 486-7696 Email: atyoung@lbl.gov

¹ Polarization is user selectable, from horizontal to vertical and left and right elliptical (or circular) polarization. Value reported is the merit function flux = total flux $\times$ (degree of circular polarization)².

Beamline 5.0.1

Monochromatic Protein Crystallography

Operational	1999
Source characteristics	16-cm-period wiggler (W16)
Energy range	7–14 keV
Monochromator	Single crystal, cylindrically bent
Calculated flux (1.9 GeV, 400 mA)	8.5×10^{13} photons/sec/0.1%BW at 12 keV (energy dependent)
Resolving power (E/ Δ E)	≈ 6000 with Si(111) at 10° asymmetry angle
Endstation	Macromolecular crystallography facility
Detectors	CCD (planned)
Spot size at sample (FWHM)	0.7 mm (h) $\times$ 0.3 mm (v)
Samples	
Format	Single crystals of biological molecules
Preparation	Support labs available
Sample environment	Ambient or $\approx 100^\circ\text{K}$
Special notes	Computers for data processing and analysis are available
Scientific applications	Biological crystallography; monochromatic
Local contact/spokesperson	Name: Thomas Earnest Affiliation: Physical Biosciences Division, Berkeley Lab Phone: (510) 486-4603 Fax: (510) 486-5664 Email: tearnest@lbl.gov

Beamline 5.0.2

Multiple-Wavelength Anomalous Diffraction (MAD) and Monochromatic Protein Crystallography (Abstracts begin on page 45)

Operational	Now
Source characteristics	16-cm-period wiggler (W16)
Energy range	3.5–14 keV
Monochromator	Double crystal
Calculated flux (1.9 GeV, 400 mA)	2.3×10^{13} photons/sec/0.1%BW into 1.5 mrad at 12.4 keV
Resolving power (E/ΔE)	15,000 for Si(111)
Endstation	Macromolecular crystallography facility
Characteristics	Kappa-geometry camera, CCD detector, low-temperature system
Detectors	2 × 2 array CCD detector
Spot size at sample (FWHM)	0.4 mm (h) × 0.4 mm (v)
Samples	
Format	Single crystals of biological molecules
Preparation	Support labs available
Sample environment	Ambient or ≈100°K
Special notes	Computers for data processing and analysis are available
Scientific applications	Biological crystallography; multiple-wavelength anomalous diffraction (MAD); monochromatic
Local contact/spokesperson	Name: Thomas Earnest Affiliation: Physical Biosciences Division, Berkeley Lab Phone: (510) 486-4603 Fax: (510) 486-5664 Email: tearnest@lbl.gov

Beamline 5.3.2

Polymer STXM

Operational	2000
Source characteristics	Bend magnet
Energy range	150–650 eV
Monochromator	Low-dispersion, spherical-grating monochromator, one grating
Calculated flux (1.9 GeV, 400 mA)	1×10^6 photons/s at sample
Resolving power ($E/\Delta E$)	3000
Endstation	Scanning transmission x-ray microscope (STXM)
Characteristics	Servo-stabilized collecting mirror
Spot size at sample (FWHM)	50 nm
Scientific applications	Serves user group and independent investigators using dedicated polymer STXM for NEXAFS spectromicroscopy at the C, N, and O K edges.
Local contact	Name: Tony Warwick Phone: (510) 486-5819 Fax: (510) 486-7696 Email: t_warwick@lbl.gov
Spokesperson	Name: Harald W. Ade Affiliation: North Carolina State University Phone: (510) 486-5738 Fax: (510) 486-7588 Email: harald_ade@ncsu.edu

Beamline 6.1.2

High-Resolution Zone-Plate Microscopy (Abstracts begin on page 87)

Operational	Now
Source characteristics	Bend magnet
Energy range	500–800 eV (extended range 250–950 eV)
Monochromator	Zone plate linear
Calculated flux (1.9 GeV, 400 mA)	Images with 1000×1000 pixels, 1000 photons/pixel are recorded in 0.2 sec at 517 eV/0.3%BW
Resolving power ($E/\Delta E$)	200–750 (with 20–5 μm field of view)
Endstation	X-ray microscope (XM-1)
Characteristics	Conventional-type (full-field) soft x-ray microscope
Spatial resolution	40 nm
Detectors	Back-thinned CCD camera
Field of view	5 to 20 μm single field; larger areas can be tiled together like a mosaic
Samples	Thin samples (up to 10 μm thick) on silicon nitride or other foils, wet chamber provided Sample dependent
Format	
Preparation	
Sample environment	Helium at atmospheric pressure, wet or dry, low temperature (cryo) (in preparation)
Special notes	Mutual indexing system with visible-light microscopy provided to position and focus sample
Scientific applications	Biology, environmental sciences, material sciences, polymers
Local contact/spokesperson	Name: David T. Attwood Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-4463 Fax: (510) 486-4955 Email: dtattwood@lbl.gov

Beamline 6.3.1

Calibration and Standards, EUV/Soft X-Ray Optics Testing, Solid State Chemistry

Operational	Now
Source characteristics	Bend magnet
Energy range	500–2000 eV
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power ($E/\Delta E$)	Double crystal 10^{11} photons/sec/0.01%BW at 1000 eV 5000
Endstation	Reflectometer
Characteristics	VLS-PGM monochromator with fixed exit slit and refocusing mirror; 2-circle goniometer with x, y, z, θ sample mirror
Spatial resolution	Can position to 1 μm
Detectors	Si diode, CEM, MCP, total yield
Spot size at sample	$5 \times 200 \mu\text{m}$
Samples Format	Solid-state, gas phase Foils, powders, etc.
Sample environment	High vacuum or UHV
Scientific applications	Solid-state chemistry to the Al and Si K edges, atomic physics reflectometry, scattering
Local contact/spokesperson	Name: Jim H. Underwood Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-4958 Fax: (510) 486-4550 Email: jhunderwood@lbl.gov

Beamline 6.3.2

Calibration and Standards; EUV Optics Testing; Atomic, Molecular, and Materials Science (Abstracts begin on page 117)

Operational	Now
Source characteristics	Bend magnet
Energy range	50–1300 eV
Monochromator	VLS-PGM
Calculated flux (1.9 GeV, 400 mA)	10^{11} photons/sec/0.01%BW at 100 eV
Resolving power ($E/\Delta E$)	7000
Endstation	Reflectometer
Characteristics	2-circle goniometer with x, y, z, θ movement of sample
Spatial resolution	Can position to 1 μm
Detectors	Si diode, CEM, MCP, total yield
Spot size at sample	5 μm (v) $\times$ 300 μm (h)
Samples	Solid state, gas phase
Format	Foils, powders, films
Sample environment	High vacuum or UHV
Scientific applications	Solid-state chemistry, gas phase, atomic physics, reflectometry, scattering
Local contact/spokesperson	Name: Eric Gullikson Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-6646 Fax: (510) 486-4550 Email: emgullikson@lbl.gov

Beamline 7.0.1

Surface and Materials Science, Spectromicroscopy, Spin Resolution,
Photon-Polarization Dichroism (Abstracts begin on page 163)

Operational	Now
Source characteristics	5-cm-period undulator (U5) (first, third, and fifth harmonics)
Energy range	60–1000 eV
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power (E/ΔE)	SGM (gratings: 150, 380, 925 l/mm) ≈10 ¹² photons/sec/0.01%BW (resolution dependent) 3000 typical, 8000 optimized
Endstations	UltraESCA Scanning transmission x-ray microscope (STXM) Scanning photoemission microscope (SPEM) Fluorescence spectrometer

Endstation identifier	UltraESCA
Characteristics	High-resolution, angle-resolved XPS spectroscopy; capable of making images by rastering the sample through a fixed spot; sample is rotated for angle- resolved measurements
Spatial resolution	50 μm
Detectors	Hemispherical electron energy analyzer; total electron yield detector
Spot size at sample	50 μm
Samples Format Preparation	Solid samples, 1" (2.54 cm) maximum diameter Preparation chamber with sputtering is provided
Sample environment	UHV
Special notes	LEED and in-situ sample heating and cooling available
Scientific applications	XPS, XPD, NEXAFS of solids and surfaces
Local contact	Name: Eli Rotenberg Phone: (510) 486-5975 Fax: (510) 495-2930 Email: erotenberg@lbl.gov
Spokesperson	Name: James Tobin Affiliation: Lawrence Livermore National Laboratory Phone: (925) 422-7247 Fax: (925) 423-7040 Email: tobin1@llnl.gov

Beamline 7.0.1, cont.

Endstation identifier	Scanning transmission x-ray microscope (STXM)
Characteristics	Used to make x-ray images and NEXAFS spectra of thin samples in transmission in the photon energy range 180–900 eV
Spatial resolution	Scanning microscope with focusing by means of Fresnel zone plates; resolution determined by spot size, which is 150 nm with current zone plates but will improve with new zone plates
Detectors	Gas proportional counter, silicon photodiode
Spot size at sample	150 nm with current zone plates
Samples	Solids
Format	Thin sections or thin films (100 nm thick) typically 3 × 3 mm in area
Preparation	No preparation chamber available
Sample environment	Helium at 1 atm
Special notes	Samples may be wet or dirty; thin films may be deposited on silicon nitride widows; optical alignment is provided by looking at the back side of the sample to locate regions of interest from optical micrographs
Scientific applications	Imaging, NEXAFS in small spots
Local contact	Name: Tony Warwick Phone: (510) 486-5819 Fax: (510) 486-7696 Email: t_warwick@lbl.gov
Spokesperson	Name: James Tobin Affiliation: Lawrence Livermore National Laboratory Phone: (925) 422-7247 Fax: (925) 423-7040 Email: tobin1@llnl.gov

Beamline 7.0.1, cont.

Endstation identifier	Scanning photoemission microscope (SPEM)
Characteristics	Designed for sub-micron XPS in the photon energy range 200–800 eV
Spatial resolution	Scanning microscope with focusing by means of Fresnel zone plates; resolution determined by spot size, which is 150 nm with current zone plates but will improve with new zone plates
Detectors	Hemispherical electron energy analyzer; total electron yield detector
Spot size at sample	150 nm with current zone plates
Samples	Solids
Format	1" (2.54 cm) maximum diameter
Preparation	Preparation chamber with sputtering and annealing provided
Sample environment	UHV
Special notes	Optical alignment equipment provided so that visible marks on the sample surface can be used to find an area of interest prior to x-ray measurements; in-situ heating and cooling.
Scientific applications	Imaging, XPS and NEXAFS in small spots
Local contact	Name: Tony Warwick Phone: (510) 486-5819 Fax: (510) 486-7696 Email: t_warwick@lbl.gov
Spokesperson	Name: James Tobin Affiliation: Lawrence Livermore National Laboratory Phone: (925) 422-7247 Fax: (925) 423-7040 Email: tobin1@llnl.gov

Beamline 7.0.1, cont.

Endstation identifier	Fluorescence spectrometer
Characteristics	Grating spectrometer for high-resolution (1:3000) photon-in/photon-out spectroscopy in the 50–1200 eV range
Detectors	Channel-plate photon counter in spectrometer focal plane
Spot size at sample	50 μm
Samples	
Format	Solids or gases in windowed cell
Preparation	No preparation chamber provided
Sample environment	UHV
Special notes	This spectrometer is installed by the group from the University of Uppsala, Sweden. Potential users are asked to contact Professor Nordgren to explore possible collaborations.
Scientific applications	Photon-in/photon-out spectroscopy
Local contact	Name: Tony Warwick Phone: (510) 486-5819 Fax: (510) 486-7696 Email: t_warwick@lbl.gov
Spokesperson	Name: Professor Joseph Nordgren Affiliation: Uppsala University, Sweden Phone: 46-18-471-3554 Fax: 46-1851-2227 Email: joseph@fysik.uu.se

Beamline 7.3.1.1

Magnetic Microscopy, Spectromicroscopy (Abstracts begin on page 295)

Operational	Now
Source characteristics	Bend magnet
Energy range	175–1500 eV
Monochromator	SGM
Calculated flux (1.9 GeV, 400 mA) (linearly polarized)	3×10^{12} photons/sec/0.1%BW at 800 eV
Resolving power ($E/\Delta E$)	1800 at 800 eV
Endstation	Photoemission electron microscope (PEEM2)
Characteristics	Imaging of electron emission
Spatial resolution	$200 \times 200 \text{ \AA}$
Detectors	Slow scan CCD
Spot size at sample	$\leq 30 \times 30 \text{ }\mu\text{m}$
Samples	Conductive solids up to 1 cm^2 in area
Format	Solid
Preparation	Sputtering, heating, evaporation, LEED, transfer capability
Sample environment	UHV
Special notes	Choice of linearly or circularly polarized radiation (flux of circularly polarized radiation is reduced)
Scientific applications	Real-time study of magnetic, elemental, chemical, and topological properties of materials
Local contact	Name: Simone Anders Phone: (510) 486-5928 Fax: (510) 486-7696 Email: sanders@lbl.gov
Spokesperson	Name: Joachim Stöhr Affiliation: IBM Almaden Research Center Phone: (408) 927-2461 Fax: (408) 927-2100 Email: stohr@almaden.ibm.com

Beamline 7.3.1.2

Surface and Materials Science, Micro X-Ray Photoelectron Spectroscopy

Operational	Now
Source characteristics	Bend magnet
Energy range	260–1500 eV
Monochromator	SGM
Calculated flux (1.9 GeV, 400 mA)	1×10^{10} photons/sec/0.1%BW at 800 eV
Resolving power ($E/\Delta E$)	1800 at 800 eV
Endstation	Micro-XPS
Characteristics	X-ray photoelectron spectroscopy study of 50×50 mm sample with $1\text{-}\mu\text{m}^2$ spot size
Spatial resolution	$1 \times 1 \mu\text{m}$ (designed)
Spot size at sample	$1.5 \times 1.5 \mu\text{m}$ (now)
Detectors	Electron energy analyzer detector
Samples	Up to 50×50 mm
Format	Solid
Preparation	Heating, sputtering
Sample environment	UHV
Special notes	In-vacuum fiducialization of sample using optical visible-light microscope; high-precision $2'' \times 4.5''$ x-y stage; laser interferometer encoding
Experimental techniques	Micro-XPS, NEXAFS, MCD
Scientific applications	Study of microstructures and interfaces in integrated circuits
Local contact	Name: Zahid Hussain Phone: (510) 486-7591 Fax: (510) 486-7696 Email: zhussain@lbl.gov
Spokesperson	Name: Baylor Triplett Affiliation: Intel Corporation Phone : (408) 765-2069 Fax: (408) 765-2949 Email: baylor_b_triplett@ccm.sc.intel.com

Beamline 7.3.3

Micro X-Ray Diffraction, Micro X-Ray Absorption Spectroscopy
(Abstracts begin on page 307)

Operational	Now
Source characteristics	Bend magnet
Energy range	See endstation tables
Monochromator	See endstation tables
Endstations	Micro x-ray diffraction/micro x-ray absorption Femtosecond laser-driven x-ray diffraction and absorption

Endstation identifier	Micro x-ray diffraction/micro x-ray absorption
Characteristics	Designed for microprobe, white light, and monochromatic experiments
Energy range	4–12 keV
Monochromator	White light and monochromatic [Four-crystal Ge(111)]
Calculated flux (1.9 GeV, 400 mA)	Monochromatic (8.5 keV): 1×10^9 photons/sec/ $\mu\text{m}^2/3 \times 10^4$ BW ($1 \times 1 \mu\text{m}$ spot) 1×10^{12} photons/sec/ 3×10^4 BW ($100 \times 300 \mu\text{m}$ spot)
Resolving power ($E/\Delta E$)	3500 at 8.5 keV (monochromatic)
Spot size at sample	$100 \times 300 \mu\text{m}$ down to $1 \times 1 \mu\text{m}$
Detectors	X-ray CCD, fluorescence SiLi detector
Samples	
Format	Typically $< 1 \text{ cm}^2 \times 1 \text{ mm}$ thick
Sample environment	Typically air
Scientific applications	Measurement of strain, micro-XAS, environmental science
Local contact/spokesperson	Name: A.A. MacDowell Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-4276 Fax: (510) 486-7696 Email: aamacdowell@lbl.gov

Endstation identifier	Femtosecond laser-driven x-ray diffraction
Characteristics	Designed for time-resolved x-ray diffraction and absorption
Energy range	0.1–12 keV
Monochromator	White light and monochromatic, with various monochromatizing elements
Flux (1.9 GeV, 400 mA)	$\sim 1 \times 10^{12}$ photons/sec/ 3×10^{-4} BW
Resolving power (E/ ΔE)	Dependent on monochromatizing element
Spot size at sample	$50 \times 300 \mu\text{m}$
Detectors	Femtosecond streak camera
Samples	
Format	Typically $< 1 \text{ cm}^3 \times 1 \text{ mm}$ thick
Sample environment	Typically 10^{-5} Torr vacuum
Scientific applications	Sub-picosecond diffraction/absorption
Local contact/spokesperson	Name: Phil Heimann Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-7628 Fax: (510) 486-7696 Email: paheimann@lbl.gov

Beamline 8.0.1

Surface and Materials Science, Spectromicroscopy,
Imaging Photoelectron Spectroscopy, Soft X-Ray Fluorescence
(Abstracts begin on page 329)

Operational	Now
Source characteristics	5-cm-period undulator (U5) (first, third, and fifth harmonics)
Energy range	65–1400 eV (1.5 GeV); ~80–1400 eV (1.9 GeV)
Monochromator Flux (1.9 GeV, 400 mA) Resolving power (E/ΔE)	SGM (gratings: 150, 380, 925 l/mm) 10^{11} – 6×10^{15} photons/sec (resolution and energy dependent) < 8000
Endstations	Ellipsoidal-mirror electron energy analyzer Soft x-ray fluorescence spectrometer

Endstation identifier	Ellipsoidal-mirror electron energy analyzer (EMA)
Characteristics	Measures 84° of electron emission angles from solid samples with 80 meV resolution
Spot size at sample	100 μm
Samples Format Preparation	Solids < 1 × 1 cm <i>In-situ</i> resistive heating; <i>in-situ</i> evaporation
Sample environment	UHV
Special notes	Sample transfer capabilities; preparation chamber
Scientific applications	XPS, ARPES, NEXAFS of solids and surfaces
Local contact	Name: Nicolas Franco Cerame Phone: (510) 486-7448 Fax: (510) 495-2111 Email: nfranco@lbl.gov
Spokesperson	Name: Franz Himpsel Affiliation: University of Wisconsin, Madison Phone: (608) 263-5590 Fax: (608) 263-2334 Email: himpsel@comb.physics.wisc.edu

Beamline 8.0.1, cont.

Endstation identifier	Soft x-ray fluorescence spectrometer
Characteristics	Measures the soft x-ray emission from solid samples with a dispersive grating spectrometer
Spot size at sample	100 μm (h) $\times$ 50 μm –3 mm (v)
Samples	Solids
Format	Samples up to 2 cm in diameter; 5 mm diameter optimal
Sample environment	UHV
Special notes	Sample transfer capabilities
Scientific applications	SXF, fluorescence-yield XAS of solids
Local contact	Name: Melissa Grush Phone: (510) 486-6645 Fax: (510) 495-2111 Email: mmgrush@lbl.gov
Spokesperson	Name: Thomas Callcott Affiliation: University of Tennessee Phone: (423) 974-6765 Fax: (423) 974-3949 Email: tcallcott@utk.edu

Beamline 9.0.1

Coherent Optics Experiments

(Beamline 7.0.2 was moved to Sector 9 in 1998 and became Beamline 9.0.1.)

Operational	Now
Source characteristics	10-cm-period undulator (U10)
Energy range	200–650 eV
Monochromator	None
Calculated flux (1.9 GeV, 400 mA)	2.8×10^{15} photons/sec/1%BW/central cone at 457 eV
Resolving power ($E/\Delta E$)	70
Endstations	General purpose
Detectors	Resist and CCD
Samples	Any
Format	Mount on thin membrane
Preparation	Can be cryo
Sample environment	Clean high vacuum
Special notes	Endstation separated from beamline by cooled window
Scientific applications	Coherent scattering, holography, diffraction, correlation spectroscopy
Local contact/spokesperson	Name: Malcolm Howells Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-4949 Fax: (510) 486-7696 Email: mrhowells@lbl.gov

Beamline 9.0.2.1

Chemical Reaction Dynamics, Photochemistry (Abstracts begin on page 415)

Operational	Now
Source characteristics	10-cm-period undulator (U10) (fundamental)
Energy range	5–30 eV
Monochromator	None
Calculated flux (1.9 GeV, 400 mA)	$\approx 10^{16}$ photons/sec/2.5% BW
Resolving power (E/ ΔE)	40
Endstation	Crossed molecular beam
Characteristics	Designed for photofragmentation spectroscopy and reactive scattering; two rotatable molecular-beam sources
Detectors	Time-of-flight spectroscopy by quadrupole mass analyzer
Spot size at sample (calculated)	170 μm (h) $\times$ 50 μm (v)
Samples	
Format	Gas sample
Preparation	Molecular beam, seeded in rare gas
Sample environment	Vacuum $\approx 10^{-6}$ Torr
Scientific applications	Photofragmentation spectroscopy, reactive scattering
Local contact/spokesperson	Name: Arthur Suits Affiliation: Chemical Sciences Division, Berkeley Lab Phone: (510) 486-4754 Fax: (510) 486-5311 Email: agsuits@lbl.gov

Beamline 9.0.2.2

High-Resolution Photoelectron and Photoionization Spectroscopy (Abstracts begin on page 415)

Operational	Now
Source characteristics	10-cm-period undulator (U10) (fundamental)
Energy range	5–30 eV
Monochromator	Off-plane Eagle
Calculated flux (1.9 GeV, 400 mA)	$\approx 10^{11}$ photons/sec/0.01% BW
Resolving power ($E/\Delta E$)	70,000
Endstation	Molecular-beam photoelectron/photoion spectroscopy
Characteristics	Multipurpose design for high-resolution photoelectron spectroscopy and photoelectron/photoion coincidence experiments
Detectors	Time-of-flight and quadrupole ion and pulse field ionization electron detector
Spot size at sample (calculated)	360 μm (h) $\times$ 240 μm (v)
Samples	
Format	Gas sample
Preparation	Molecular beam, seeded in rare gas
Sample environment	Vacuum $\approx 10^{-6}$ Torr
Scientific applications	Pulse field ionization photoelectron spectroscopy, threshold photoelectron/photoion coincidence
Local contact	Name: Arthur Suits Phone: (510) 486-4754 Fax: (510) 486-5311 Email: agsuits@lbl.gov
Spokesperson	Name: Cheuk Ng Affiliation: Iowa State University Phone: (515) 294-4225 Fax: (515) 294-5825 Email: cyng@ameslab.gov

Beamline 9.0.2.3

Photoelectron and Photoionization Imaging and Spectroscopy (Abstracts begin on page 415)

Operational	Now
Source characteristics	10-cm-period undulator (U10) (fundamental)
Energy range	5–30 eV
Monochromator	Off-plane Eagle
Calculated flux (1.9 GeV, 400 mA)	$\approx 10^{14}$ photons/sec/0.1%BW
Resolving power ($E/\Delta E$)	1,000
Endstation	Molecular-beam photoelectron/photoion imaging and spectroscopy
Characteristics	Multipurpose design for photoion and photoelectron imaging and photoelectron/photoion coincidence experiments
Detectors	Time-of-flight 2-D position sensitive detectors
Spot size at sample (calculated)	300 μm (h) $\times$ 1000 μm (v)
Samples	Gas sample Molecular beam, seeded in rare gas Laser ablation source Laser photolysis source Plasma discharge
Format	
Preparation	
Sample environment	Vacuum $\approx 10^{-5}$ Torr
Scientific applications	Spectroscopy and dynamics of radicals, metastable, and other novel species
Local contact	Name: Darcy Peterka Phone: (510) 495-2207 Fax: (510) 486-5311 Email: dspeterka@lbl.gov
Spokesperson	Name: Arthur Suits Affiliation: Chemical Sciences Division, Berkeley Lab Phone: (510)-486-4754 Fax: (510)-486-5311 Email: agsuits@lbl.gov

Beamline 9.3.1

Atomic, Molecular, and Materials Science (Abstracts begin on page 455)

Operational	Now
Source characteristics	Bend magnet
Energy range	2200–6000 eV with Si(111) crystals
Monochromator	Double crystal
Measured flux (1.9 GeV, 300 mA)	$> 10^{11}$ photons/sec/2200–5000 eV
Resolving power ($E/\Delta E$)	3000–8000
Endstations	X-ray absorption cell Ion time-of-flight spectrometer Angle-resolved time-of-flight electron spectrometer Angle-resolved hemispherical electron analyzer Polarized-x-ray emission spectrometer
Local contacts	Name: Fred Schlachter Phone: (510) 486-4892 Fax: (510) 495-2111 Email: fsschachter@lbl.gov Name: Wayne Stolte Phone: (510) 486-5538 Fax: (510) 495-2111 Email: wcostolte@lbl.gov

Endstation identifier	X-ray absorption cell
Detectors	Photodiode
Spot size at sample	< 0.5 mm
Samples	Powder, 1/2" diameter; gases
Sample environment	UHV, gas cell
Scientific applications	NEXAFS
Spokesperson	Name: Dennis Lindle Affiliation: University of Nevada, Las Vegas Phone: (702) 895-4426 Fax: (702) 895-4072 Email: lindle@nevada.edu

Beamline 9.3.1, cont.

Endstation identifier	Ion time-of-flight spectrometer
Characteristics	Timing resolution ≈ 200 ps; capable of coincidence measurement (ion–ion, ion–ion–ion, electron–ion, electron–ion–ion, etc.)
Detectors	Microchannel plates for ions, channeltron for electrons
Spot size at sample	< 0.5 mm
Samples	Gases
Sample environment	Gas-phase flow system
Scientific applications	Ion spectroscopy, total and partial ion yields, PIPICO, PEPICO, PEPIICO, etc.
Spokesperson	Name: Dennis Lindle Affiliation: University of Nevada, Las Vegas Phone: (702) 895-4426 Fax: (702) 895-4072 Email: lindle@nevada.edu

Endstation identifier	Angle-resolved time-of-flight electron spectrometer
Characteristics	Timing resolution ≈ 200 ps; chamber rotates about x-ray beam ($\pm 100^\circ$)
Detectors	4 time-of-flight electron analyzers (0.5 m long)
Spot size at sample	< 0.5 mm
Samples	Gases
Sample environment	Gas-phase flow system
Scientific applications	Photoelectron and Auger spectroscopy, electron–electron coincidence
Spokesperson	Name: Dennis Lindle Affiliation: University of Nevada, Las Vegas Phone: (702) 895-4426 Fax: (702) 895-4072 Email: lindle@nevada.edu

Beamline 9.3.1, cont.

Endstation identifier	Angle-resolved hemispherical electron analyzer
Characteristics	High energy resolution ($E/\Delta E \leq 5000$) and high electron kinetic energies (≤ 5 keV); chamber rotates about x-ray beam and analyzer rotates about a perpendicular axis, allowing coverage of $\approx 1\pi$ steradians
Detectors	2-D position-sensitive detector (microchannel plates plus resistive anode)
Spot size at sample	< 0.5 mm
Samples	Gases
Sample environment	Gas-phase flow system
Scientific applications	Photoelectron and Auger spectroscopy
Spokesperson	Name: Dennis Lindle Affiliation: University of Nevada, Las Vegas Phone: (702) 895-4426 Fax: (702) 895-4072 Email: lindle@nevada.edu

Endstation identifier	Polarized-x-ray emission spectrometer (available in 1999)
Characteristics	High x-ray energy resolution ($E/\Delta E \approx 3000$). Curved-crystal Rowland-circle spectrometer
Detectors	2-D position-sensitive detector (microchannel plates plus resistive anode)
Spot size at sample	< 0.5 mm
Samples	Gases
Sample environment	Static gas cell with windows
Scientific applications	X-ray emission
Spokesperson	Name: Dennis Lindle Affiliation: University of Nevada, Las Vegas Phone: (702) 895-4426 Fax: (702) 895-4072 Email: lindle@nevada.edu

Beamline 9.3.2

Chemical and Materials Science, Circular Dichroism, Spin Resolution
(Abstracts begin on page 467)

Operational	Now
Source characteristics	Bend magnet
Energy range	30–1500 eV
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power (E/ΔE)	SGM (gratings: 100, 600, 1200 l/mm) ≈10 ¹¹ photons/sec/0.1%BW at 400 eV 3000 typical, 8000 max (with 10-μm slits) Capability for circularly polarized radiation
Endstations	Advanced materials chamber (AMC) Advanced photoelectron spectrometer/diffractometer (APSD) Users may bring their own endstation

Endstation identifier	Advanced materials chamber (AMC)
Characteristics	PHI analyzer, sample preparation with LEED, XPS, evaporation, sputtering, precision manipulator
Spatial resolution	0.5 × 1 mm ²
Detectors	16-element multichannel detector, partial electron yield detector
Spot size at sample	0.5 × 1 mm ²
Samples Format Preparation	Solid Up to 10 mm diameter Sputtering, evaporation, XPS, LEED, heating up to 2000 C; cooling down to 100 K
Sample environment	UHV
Special notes	Sample transfer capability
Experimental techniques	Photoelectron diffraction, XPS, NEXAFS, MCD
Scientific applications	Studies of atomic and electronic structure of surfaces
Local contact/Spokesperson	Name: Zahid Hussain Affiliation: Advanced Light Source, Berkeley Lab Phone: (510) 486-7591 Fax: (510) 486-7696 Email: zhussain@lbl.gov

Beamline 9.3.2, cont.

Endstation identifier	Advanced photoelectron spectrometer/diffractometer (APSD)
Characteristics	High-resolution rotatable Scienta analyzer, sample preparation with LEED, evaporator, high-precision sample manipulator, sputtering
Spatial resolution	5 μ m with pre-lens
Detectors	Multichannel detector and spin-resolved mini Mott
Spot size at sample	0.5 $\times$ 1.0 mm
Samples Format Preparation	Solid 5–10 mm diameter, 1–2 mm thick Sputtering, evaporation, LEED, XPS, heating up to 2000 C; cooling down to 150 K
Sample environment	UHV
Special notes	Capability of using either a multichannel detector or a spin detector; analyzer rotatable in horizontal plane
Experimental techniques	Photoelectron diffraction, high-resolution XPS, UPS, MCD
Scientific applications	Studies of the atomic, electronic, and magnetic structure of surfaces, interfaces, and nanostructures
Local contact	Name: Zahid Hussain Phone: (510) 486-7591 Fax: (510) 486-7696 Email: zhussain@lbl.gov
Spokesperson	Name: Professor C. S. Fadley Affiliation: Material Sciences Division, Berkeley Lab and U. California, Davis Phone: (510) 486-5774; (916) 752-8788 Fax: (510) 486-5530 Email: csfadley@lbl.gov

Beamline 10.0.1

**High-Resolution Atomic, Molecular, and Optical Physics;
Photoemission of Highly Correlated Materials**

(Abstracts begin on page 495)

Operational	Now
Source characteristics	10-cm-period undulator (U10) (first and third harmonics)
Energy range	17–340 eV
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power ($E/\Delta E$)	SGM (gratings: 380, 925, 2100 l/mm) $\approx 10^{13}$ photons/sec/0.01%BW (resolution dependent) $\approx 10,000$ (selectable by slit width)
Endstations	High-energy-resolution spectrometer (HERS) Ion-beam endstation High-resolution atomic and molecular electron spectrometer (HiRAMES)

Endstation identifier	High-energy-resolution spectrometer (HERS)
Scientific applications	Studies of highly correlated electron systems using angle-resolved photoemission of solids
Characteristics	Designed for very high energy and angular resolution photoelectron spectroscopy of solids. The electron energy analyzer rotates 120° about the polarization vector of the incoming beam. The sample manipulator has five degrees of freedom, three translational and two angular, and a temperature range of 10 K to 450 K. Additionally, the endstation has the standard surface science preparation and characterization equipment.
Detectors	Scienta SES-200 hemispherical electron energy analyzer with angular mode LEED Partial-yield detector
Spot size at sample	$100\text{ }\mu\text{m}$ (h) $\times$ $<100\text{ }\mu\text{m}$ (v) depending on exit slit setting
Samples	Solids in UHV
Local contact	Name: Scot Kellar Phone: (510) 486-4989 Fax: (510) 486-4299 Email: sakellar@lbl.gov
Spokesperson	Name: Prof. Z.X. Shen Affiliation: Stanford University Phone: (650) 725-8254 Fax: (650) 725-5457 Email: shen@ee.stanford.edu

Beamline 10.0.1, cont.

Endstation identifier	Ion-beam endstation
Scientific applications	Photoionization of ions
Characteristics	The charged ion beam from the ion accelerator is merged with the photon beam (counter propagating) for approximately 0.5 m. An analyzing magnet disperses the ion beam based on charge state following the interaction region.
Spot size at sample	1.5 mm (h) $\times$ 1.5 mm (v)
Samples	Beam of positively charged ions
Sample environment	Differential pumping permits gas pressures of up to 10^{-5} Torr
Local contact	Name: Aaron Covington Phone: (510) 495-2090 Fax: (510) 495-2930 Email: amcovington@lbl.gov
Spokespersons	Name: Nora Berrah Affiliation: Western Michigan University Phone: (616) 387-4955 Fax: (616) 387-4939 Email: berrah@wmich.edu Name: Prof. Ronald A. Phaneuf Affiliation: University of Nevada–Reno Phone: (775) 784-6816 Fax: (775) 784-1398 Email: phaneuf@physics.unr.edu

Beamline 10.0.1, cont.

Endstation identifier	High-resolution atomic and molecular electron spectrometer (HiRAMES)
Scientific applications	High-resolution atomic and molecular electron spectroscopy
Characteristics	The electron spectrometer uses a gas cell on the beam axis to form the interaction region between the sample and the photon beam. The analyzer rotates from 0° to 90° relative to the polarization vector of the photon beam, permitting angle-resolved measurements.
Detector	Scienta electron spectrometer
Spot size at sample	0.4 mm (h) × 0.1–0.5 mm (v) depending on exit slit setting
Samples	Gas cell
Sample environment	Differential pumping permits gas pressures of up to 10 ⁻⁵ Torr
Special notes	Vented gas cabinets are available for hazardous samples
Local contact	Name: John D. Bozek Phone: (510) 486-4967 Fax: (510) 486-7696 Email: jdbozek@lbl.gov
Spokesperson	Name: Nora Berrah Affiliation: Western Michigan University Phone: (616) 387-4955 Fax: (616) 387-4939 Email: berrah@wmich.edu

Beamline 10.3.1

X-Ray Fluorescence Microprobe (Abstracts begin on page 527)

Operational	Now
Source characteristics	Bend magnet
Energy range	3–20 keV (without multilayer mirrors) 6–15 keV (with multilayer mirrors)
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power ($E/\Delta E$)	Multilayer mirrors in Kirkpatrick-Baez configuration 3×10^{10} photons/sec 25 at 12.5 keV
Endstation	Large hutch with optical table
Characteristics	X-ray fluorescence analysis of samples with high elemental sensitivity and high spatial resolution
Spatial resolution	$1.0 \times 1.2 \mu\text{m}$
Detectors	Si (Li)
Spot size at sample	$1.0 \times 1.2 \mu\text{m}$
Samples Format Preparation	Samples are usually mounted between two layers of super-clean polypropylene. Standard sample holders are available for samples less than 2 cm in diameter. Almost any sample can be measured since samples are measured in air.
Sample environment	Air
Special notes	By special arrangement, the focusing mirrors can be removed and then the white-light beam can be used for experiments that require white radiation (e.g., testing capillary optics or evaluating x-ray collimators)
Scientific applications	Trace element analysis with high spatial resolution, for example silicon solar cells, GaN, environmental soil samples, and biological samples; testing of x-ray capillary optics and new x-ray detectors
Local contact/spokesperson	Name: Al Thompson Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-5590 Fax: (510) 486-4550 Email: acthompson@lbl.gov

Beamline 10.3.2

X-Ray Optics Development, Materials Science (Abstracts begin on page 551)

Operational	Now
Source characteristics	Bend magnet (2 horizontal mrad at 32 m from bend magnet)
Energy range	3–20 keV
Monochromator Calculated flux (1.9 GeV, 400 mA)	None 2.7×10^{13} photons/sec/0.1%BW A Si(111) 4-bounce monochromator is also available for high-energy-resolution experiments.
Endstation	Large hutch with optical table for experimental equipment
Characteristics	A large 10 cm $\times$ 1 cm white radiation beam is available. At present a silicon monochromator and a pair of grazing-incidence focusing mirrors are installed to produce a 1.5×2 - μ m spot that can be either white radiation or monochromatic ($E/\Delta E = 10^4$).
Scientific applications	Many different experiments have been done which use x-ray energies above 3 keV: past experiments include x-ray microdiffraction, micro-XAFS, LIGA, TXRF of silicon wafers, femtosecond timing, and testing of x-ray optical elements
Local contact/spokesperson	Name: Al Thompson Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-5590 Fax: (510) 486-4550 Email: athompson@lbl.gov

Beamline 11.3.2

Inspection of EUV Lithography Masks (Abstracts begin on page 587)

Operational	Now
Source characteristics	Bend magnet
Energy range	50–1000 eV
Monochromator	VLS-PGM
Calculated flux (1.9 GeV, 400 mA)	10^{11} photons/sec/0.01%BW at 100 eV
Resolving power ($E/\Delta E$)	7000
Endstation system	Scanning bright field and dark field mask inspection
Spot size at sample	$4 \times 6 \mu\text{m}$
Local contact/spokesperson	Name: Jim H. Underwood Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-4958 Fax: (510) 486-4550 Email: jhunderwood@lbl.gov

Beamline 12.0.1.1

Surface and Materials Science, Spectromicroscopy
(Abstracts begin on page 593)

Operational	Now
Source characteristics	8-cm-period undulator (U8)
Energy range	95–130 eV
Monochromator	VLG-PGM
Calculated flux (1.9 GeV, 400 mA)	$\approx 6 \times 10^{11}$ photons/sec/1%BW after 1- μ m pinhole
Resolving power (E/ Δ E)	200–1000
Endstation	MAXIMUM
Characteristics	Scanning photoelectron microscope with multilayer optics at 95 eV or 130 eV
Spatial resolution	0.1 μ m
Detectors	CMA-MCP
Spot size at sample	0.1 μ m
Samples	
Format	15 $\times$ 15 mm maximum sample size
Preparation	Deposition, cleaving, ion beam sputtering, annealing
Sample environment	UHV; in-situ heating and electrical testing
Scientific applications	Semiconductor surfaces and interfaces, microelectronics, metallization, silicides
Local contact	Name: Gian Franco Lorusso Phone: (510) 486-6853 Fax: (510) 486-4550 Email: glorusso@grace.lbl.gov
Spokesperson	Name: Jim H. Underwood Affiliation: Center for X-Ray Optics, Berkeley Lab Phone: (510) 486-4958 Fax: (510) 486-4550 Email: jhunderwood@lbl.gov

Beamline 12.0.1.2

EUV Lithography Optics Testing, Interferometry (Abstracts begin on page 593)

Operational	Now
Source characteristics	8-cm-period undulator (U8)
Energy range	60–320 eV
Monochromator Calculated flux (1.9 GeV, 400 mA) Resolving power ($E/\Delta E$)	VLG-PGM $\approx 5 \times 10^{13}$ photons/sec/1%BW at 134 eV 200–1000
Endstation	EUV interferometer
Detectors	GaAsP flux monitor, silicon 1000×1000 CCD array
Samples Format	All-reflective, multilayer-coated EUV optics
Sample environment	10^{-7} Torr or 10^{-4} Torr of O_2
Scientific applications	Interferometric wavefront measurement of optics designed for EUV lithography
Local contact	Name: Kenneth A. Goldberg Phone: (510) 486-2261 Fax: (510) 486-4550 Email: kagoldberg@lbl.gov
Spokesperson	Name: Jeffrey Bokor Affiliation: U.C. Berkeley; Center for X-Ray Optics, Berkeley Lab Phone: (510) 642-4134 Fax: (510) 642-2739 Email: jbokor@eecs.berkeley.edu

Beam Test Facility

Operational	Now
Electron beam energy	50 MeV
Charge/bunch	1–1.5 nC
Bunch length	25–35 ps
Emittance	0.2–0.5 mm-mrad
Number of bunches/macropulse	1–8
Repetition rate	1, 2 Hz
Minimum spot size	35 μm
Lasers	<p>Nd:YAG</p> <p>$\lambda = 1.064 \mu\text{m}, 0.532 \mu\text{m}, 0.266 \mu\text{m}$</p> <p>$\epsilon = 1 \text{ J}, 0.5 \text{ J}, 0.1 \text{ J}$</p> <p>$\tau = 9 \text{ ns}, 7 \text{ ns}, 4\text{--}5 \text{ ns}$</p> <p>Rep. rate: 10 Hz</p>
Local contact/spokesperson	<p>Name: Wim Leemans</p> <p>Affiliation: Center for Beam Physics, Berkeley Lab</p> <p>Phone: (510) 486-7788</p> <p>Fax: (510) 486-7981</p> <p>Email: wpleemans@lbl.gov</p>