Surface Reactions Studied by Synchrotron Based
Photoelectron Spectroscopy

RECEIVED
JAN 28 1999
OSTI

J. Hrbek

Chemistry Department 555
Brookhaven National Laboratory
Upton, NY 11973-5000, USA

Abstract

The goal of this article is to illustrate the use of synchrotron radiation for investigating surface chemical reactions by photoelectron spectroscopy. A brief introduction and background information is followed by examples of layer resolved spectroscopy, oxidation and sulfidation of metallic, semiconducting and oxide surfaces.

Table of Content

- I. Introduction
- II. Background
- III. Layer resolved spectroscopy
- IV. CO adsorption
- V. Oxidation
- VI. Sulfidation
- VII. SO₂ reactions
- VIII. Etching and Passivation
- IX. Outlook

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. Introduction

Chemical transformations of surfaces affect the usefulness of products in many industries. The microelectronic industry depends heavily on understanding the interface chemistry of semiconductors; the controlled growth of oxide layers and the deposition of metallic films are two typical examples. The studies of corrosion and its inhibition are another examples of the utility of surface science and chemistry in practical industrial circumstances. So is catalysis: heterogeneous catalysts used by the chemical industry and in environmental control, are easily poisoned, e.g., by sulfur and nitrogen containing compounds. The prevention of the loss of catalytic activity and selectivity requires understanding of surface processes that lead to deactivation.

The interaction of atoms or molecules on solid surfaces is a complex multi-step phenomenon. First, gas phase species impinging on the surface are trapped in a two-dimensional layer at a phase boundary. This event is then followed by diffusion of adatoms or admolecules and by possible surface reconstruction. Lastly, reactions among the adsorbates or between the adsorbate and the adsorbent

can lead to a formation of new chemical compounds that may desorb or stay on the surface. Strongly adsorbed, i.e. chemisorbed species, form a chemical bond with a solid surface, with characteristic chemisorption bond energies ranging from 40 to 400 kJ/mol⁻¹. This bond energy range is also typical for most chemical compounds, making the distinction between a chemisorb species and surface chemical compound difficult.

II. Background

Photoelectron spectroscopy is one of several surface sensitive analytical techniques that provide chemical information about the surface. In fact, X-ray Photoelectron Spectroscopy (XPS) is used quite extensively for this purpose by chemists, physicists and material scientists¹. The analytical information is extracted from the measured kinetic energy, E_K , of the outgoing electrons excited by photons, $h\nu$, from the core levels of individual atoms. Since the electron binding energies, BE , of the core levels (given by $BE = h\nu - E_K - \phi$, where ϕ is the work function) are well known, the unambiguous identification of all elements of the periodic table but hydrogen is possible.

The core level binding energies are not only unique to the individual elements, they are also sensitive to the charge distribution of the valence electrons, and therefore to the chemical bonding of the element. The core level chemical shifts can be as big as 5 eV and are easily detected with conventional laboratory $MgK\alpha$ and $AlK\alpha$ X-ray sources of photons of fixed energy.

What makes the photoelectron spectroscopy surface sensitive is the very short distance a photoelectron can travel in a solid without losing energy. The mean free path, λ , of the excited electrons is strongly energy dependent, and more or less independent of the solid composition. The λ parameter plays an important role in photoelectron spectroscopy since it determines the sampling or escape depth of photoelectrons. λ values are usually less than 10 Å for energies E_K between 20 and 300 eV. Because electrons with $E_K \sim 50$ eV have mean free path limited to ~ 4 Å, they carry information exclusively about the atoms present in the first few surface layers of the sample.

Beryllium metal represents a very interesting and unique example where the high-resolution photoemission spectrum of the Be 1s core level shows four well-resolved peaks². The intensity of the individual peaks varies as a

function of photon energy, figure 1. This dependence can be used to assign their origin, and to determine the mean free path from the measured surface to bulk ratios³. As the surface layer attenuates the signal from layers below, the surface I_{S1} to the bulk I_B intensity ratio can be expressed as

$$I_{S1}/I_B = e^{(3d_0/\lambda)} (1 - e^{(-d_0/\lambda)})$$

for a (0001) surface with interlayer spacing d_0 , where the surface contribution comes from the first layer and the bulk contribution from the fourth and deeper layers. The mean free path has a lowest value of $\sim 1.8 \text{ \AA}$ at the electron kinetic energy of $\sim 25 \text{ eV}$.

Atoms at the surface of a solid differ from those in the bulk. Their lower coordination in the surface layer leads not only to a structural relaxation, but also to changes in the electronic structure, and to modification of chemical properties. Consequently, the core levels of atoms at surfaces are shifted with respect to the core levels of bulk atoms. We define the surface core-level shift (SCLS) as the difference in the energy needed to remove a core electron from a surface and from a bulk atom, respectively. The surface core-level shifts are usually a few tenths of an electron volt, much smaller than the core level chemical shifts.

Using figure 1 as an example, a spectrum has four components labeled S1, S2, S3 and B, that originate from the three outermost atomic layers of the (0001) surface and the bulk (the fourth and deeper layers). Surface shifts determined for S1, S2 and S3 are -825, -570 and -265 meV, respectively^{2,3}.

Conventional X-ray photoelectron spectroscopy does not have the sufficient energy resolution and surface sensitivity to allow precise measurements of SCLS. Figure 2 illustrates the point: the S $2p_{3/2,1/2}$ core level doublet with the spin-orbit splitting of 1.18 eV is difficult to discern in the XPS data, while the well-resolved doublets are clearly observed in the synchrotron excited soft X-ray photoemission data. Synchrotron radiation offers many advantages over traditional laboratory photon sources. For photoemission experiments, the high flux of polarized monochromatic photons with tunable energy are the most important characteristics.

The very first report of SCLS on a clean surface of Au was based on XPS data measured at glancing emission angles at which the escape depth decreases and surface sensitivity is enhanced⁴. An early synchrotron photoemission experiment demonstrated the SCLS of the Al $2p$ level after oxygen interaction with the Al(111) surface⁵. The synchrotron

experiment on the clean W(100)⁶ showed that a small SCLS, in this instance -0.28 eV, can be measured with confidence. These were the first experiments that clearly manifested the advantages of synchrotron radiation in surface photoemission studies, and showed a great potential for exploration of surface chemistry in two dimensions.

An important consideration in carrying out the SCLS measurements is the intrinsic width of the core levels of the element in question, and an access to monochromatic photons with an energy that will photoexcite electrons with kinetic energy around 50 eV to minimize the sampling depth. Most elements in the periodic table can be excited with photons having energy below 1 keV⁷. The limits imposed by the requirement for using the sharpest core level are becoming less restraining with the recent development of instrumentation, data analysis and advances in understanding of physics of surface core level spectra.

I outlined above several basic requirements needed for successful SCLS experimental measurements. Tunable source of monochromatic soft X-rays and high resolution electron energy analyzer together with a carefully selected and well defined sample, usually a single crystal, prepared under UHV condition, may provide experimental data of high quality. The fundamental physical processes governing the

photoemission lead to core level spectra with a complex line shape, so an accurate measurement of the SCLS requires the use of a curve fitting.

The commonly used fitting procedure for metallic core levels starts with a proper background subtraction followed by the nonlinear least-squares fits of Doniach-Šunjić line profiles⁸ convoluted with Gaussian functions. Each core-level component is defined by five parameters: three of them are related to the line shape, and the remaining two are intensity and BE. A Lorentzian width is inversely proportional to the lifetime of the core level. A singularity index, related to the screening of the core hole by the conduction electron charge density, defines the asymmetric high BE tail of the peak. A Gaussian width relates to phonon, inhomogeneous and instrumental broadening. Details about the physics of the core-level broadening mechanisms and curve fitting can be found elsewhere⁹.

Johansson and Martensson¹⁰ proposed the theoretical interpretation of binding energy shifts in a metallic system. The basic assumption is a completely screened final state. The SCLS is defined as an energy difference between the final and initial states, i.e. between the final excited Z^* impurity atom within the bulk of the Z metal

host and the initial nonexcited Z metal, and the excited Z^* surface impurity and the nonexcited Z metal in the bulk. Within the $(Z+1)$ equivalent core approximation, one assumes that the core-ionized initial state atom with atomic number Z can be replaced by a valence ionized final state impurity with atomic number $(Z+1)$. From a point of view of valence electrons, a core hole mimics the properties of an additional proton in the nucleus. It is then possible to extract thermochemical properties from core-level binding energy measurements and *vice versa*.

The SCLS in transition metal series are large positive on the left side of the periodic table and large negative on the right. A surface atom has fewer neighbors than a bulk atom and the local density of states in the surface layer therefore narrows. To maintain a common Fermi level, and layerwise charge neutrality of the surface layer, the density of states must shift. This change in the amount of charge produces a difference between an electrostatic potential at a surface and a bulk atom. Consequently, the deeper core levels of the surface atoms shift down or up with respect to their bulk counterparts, if the bulk density of states is less or more than half-filled¹¹. The SCLS of a particular core level is the difference in total energy between a sample where the core hole is in a bulk

atom and in a surface atom. These differences in total energy have been calculated accurately, using *ab initio* methods based on density functional theory, as shown for a number of 4d metals¹². The calculations reproduced well the trends of the experimental SCLS within the 4d metals and with the crystal plane, and demonstrated the importance of inclusion of final state effects.

III. Layer Resolved Spectroscopy

The SCLS measurements on clean single crystal surfaces stimulated a lot of photoemission studies in surface science. Of particular interest to surface chemistry are studies of alkali metal adsorption on well-defined surfaces of single crystals. These experimental systems represent useful models of industrial catalysts, many of which use alkali metals as promoters in large-scale industrial processes.

In the mid eighties several research groups reported the coverage dependence of the K 2p and Cs 5p core levels of alkali metals adsorbed on close packed Ru and Pt surfaces¹³⁻¹⁵ using conventional XPS/UPS instruments. Synchrotron experiments followed shortly¹⁶⁻¹⁸. Some of the core levels of alkali metals fulfill the requirements for

successful measurements of the SCLS outlined above and are accessible for high-resolution synchrotron radiation photoemission experiments. The lifetime widths and phonon-induced broadening of the Na $2p$, K $2p$, K $3p$, Cs $5p$ and Cs $4d$ levels are small enough allowing the observation of energy shifts down to 100 meV.

Figure 3 shows the K $3p$ core level photoelectron spectra of 2.5 ML of potassium adsorbed on Ru(001) with 40 eV photon energy at normal and 70° off-normal emission¹⁹. Even in the raw data, several peaks whose relative intensities vary with changing electron emission exit angle, can be readily seen. The electron escape depth scales with the cosine of exit angle, so the surface contribution shows more prominently in the off-normal spectrum. The assignment based on the escape depth considerations was confirmed by the coverage dependence of spectral features²⁰. A complex envelope of overlapping peaks was fitted into three sets of the K $3p$ spin-orbit doublets and individual contributions were identified as interface (i), immediate bulk (b) and surface (s), following notation used by Martensson et al.²¹ in their study of Yb adsorption on a Mo(110) surface. The 0.23 eV spin-orbit splitting of the K $3p$ level, measured for the first time by

photoemission, was found to be in good agreement with values (0.26-0.27 eV) deduced by other techniques.

The experimental value of SCLS $\Delta E = BE_S^F - BE_B^F$ (subscripts B and S denote bulk and surface, respectively, and superscript F reminds us that the Fermi level is used as a reference in measuring BE's) is +0.25 eV. It is useful to show how the thermodynamic model, which is a variation of a familiar Born-Haber cycle, can be constructed for a general photoemission experiment with metal Z.

Following figure 4, a single atom is removed from metal Z, a step that needs the cohesive energy $E_{coh}(Z)$. The Z atom is core ionized, requiring the free electron binding energy $BE^V(Z)$ in a process. Within the (Z+1) core level approximation a valence-ionized (Z+1) atom replaces the core-ionized atom. By its neutralization, an energy equal to the first ionization potential, $I(Z+1)$, of atom (Z+1) is obtained. The condensation of the (Z+1) atom the cohesive energy $E_{coh}(Z+1)$ provides additional gain, and in the final step the (Z+1) impurity is dissolved in a Z metal matrix with an expenditure of the energy of solution $E_{sol}((Z+1)/Z)$. The core level binding energy $BE^F(Z)$ of atom Z in the bulk, that represents the last link of the cycle, is then the sum of individual terms:

$$BE^F(Z) = E_{coh}(Z) + BE^V(Z) - I(Z+1) - E_{coh}(Z+1) + E_{sol}((Z+1)/Z).$$

Application of this equation to the specific example of the K SCLS gives

$$\Delta E = BE_S - BE_B = 0.2[E_{\text{coh}}(\text{K}) - E_{\text{coh}}(\text{Ca}) + E_{\text{sol}}(\text{Ca/K})],$$

when using an approximation $E_{\text{coh}}(\text{surf}) = 0.2E_{\text{coh}}(\text{bulk})$. This yields +0.11 eV, in reasonable agreement with the experimental value of +0.25 eV quoted above.

The thermodynamic cycle was also applied to monolayer, bilayer and multilayer data of K adsorbed on Ru(001)²⁰. Not all data needed for the calculations are available, but when a proper approximation is made, an agreement between the measured and calculated values is quite good. In fact one can use the experimental core-level shifts to obtain the thermodynamic parameters such as the adhesion energy and surface segregation energy that are either difficult or impossible to measure using thermochemical methods⁷.

IV. CO Adsorption

Carbon monoxide is a prototypical molecule for surface science and a vast number of core-level photoelectron studies of molecular adsorbates deal with CO. Because CO adsorption is one of better understood systems in surface science, carbon monoxide is often used as a probe molecules for more complex surfaces.

A recent example is a high-resolution core-level photoemission study of CO adsorption on Pd/Rh(111) bimetallic surface²². CO forms several ordered structures on the Rh(111), and corresponding C 1s spectra are shown in figure 5 A. For CO coverages smaller than 0.33 ML only the on-top sites are populated, and a single core level peak has BE of 286.07 eV. The three-fold hollow sites are filled at higher coverages and their BE is seen at ~285.35 eV.

Pd grows in a layer-by-layer mode on Rh(111)²³ and core level spectra of CO adsorbed on a full Pd monolayer (1 ML Pd/Rh(111)) show only one peak shifting towards higher BE from 285.7 to 285.85 eV with increasing Θ_{CO} while its linewidth remains the same (figure 5B)²². At submonolayer coverages Pd forms two-dimensional islands; figure 5C shows the C 1s spectra for CO adsorption on 0.5 ML Pd/Rh(111). At low CO exposures only a single peak spectrum with BE corresponding to CO adsorbed in on-top on Rh(111) is seen. With increasing exposure the three fold hollows on Rh(111) are populated next, the Pd islands being the last to adsorb CO.

The C 1s spectra provide information about the adsorption on both Pd islands and on a bare Rh(111) surface, while the Pd $3d_{3/2}$ spectra are affected only by adsorption on Pd islands. The Pd core-level spectra

corroborate the above CO adsorption sequence. The exclusive population of the Rh domains at low CO exposures implies efficient diffusion of CO from the Pd islands to the Rh patches.

Rh metal is one component in exhaust gas converters that catalyzes CO oxidation. The reaction proceeds by the Langmuir-Hinshelwood mechanism between coadsorbed O and CO. Titration of adsorbed oxygen by CO can provide information about factors controlling the reaction rate. The O 1s spectra were monitored in real-time during CO titration at three temperatures and for two oxygen superstructures²⁴. The intensity of the O 1s spectral components reflected the changes in the oxygen and carbon monoxide coverages during titration. A loss of the O 1s intensity at BE of < 530.5 eV was taken as a measure of CO oxidation rate, while a growth of a second O 1s component at BE of > 531.0 eV represented CO uptake. Oxygen decay plots obtained from the O 1s core level spectra showed that the initial oxidation rate depends mainly on differences in reactivity of oxygen adsorbed in different domains.

V. Oxidation

Oxide formation at the surface of Al was the first surface chemical reaction studied with synchrotron radiation⁵. Results of the recent high-resolution study²⁵ are shown in figure 6. The spectrum of oxygen exposed Al(111) surface shows several peaks that were interpreted as two metallic Al doublets, three chemisorption states shifted by 0.37, 0.84 and 1.37 eV, and the broad oxide peak with a chemical shift of ~2.6 eV relative to the bulk metallic state. The states are regarded as a chemisorption precursor to three-dimensional oxidation and attributed to Al atoms bonded to one, two or three oxygen atoms.

Many high-resolution studies were devoted to oxygen interaction with Si because the ubiquity of SiO₂/Si structures in most semiconducting devices. Recent Si 2p core level data are shown in figure 7²⁶. The line shape consists of five 2p_{3/2,1/2} doublets, assigned to bulk Si and the four oxidation states, Si¹⁺ to Si⁴⁺. As the structure of the individual chemical components at the interface controls the physics the understanding of the structure is very important. By applying extended fine structure analysis to high-resolution photoemission data collected at a wide range of photon energies, the local atomic bond

lengths were measured for individual oxidation states of Si. The results showed evidence for a chemically abrupt interface, with Si^{2+} and Si^{3+} confined between Si and SiO_2 .

Alkali metal promoters of catalysts exist in ionized form in oxidizing environment, so their oxidation is of technological interest. It is also of fundamental importance to understand the details of oxidation of simple metals such as alkali. Use of high-resolution photoemission for this particular system offers clear advantages. As discussed above, the individual layers of adsorbed alkali can be resolved and thus a possibility to study the reactivity of individual layers exists. Upon oxygen adsorption on a layer of alkali, in addition to chemisorbed atomic oxygen, oxide ion, O^{2-} , and dioxygen ion species such as peroxide, O_2^{2-} , and superoxide, O_2^- , were shown to exist at alkali metal interfaces^{27,28}. In addition to the O 1s core level and valence band data, the assignments of individual species were based on the results of several surface sensitive techniques²⁹.

A set of electron distribution curves shown in figure 8 was recorded for the initial K coverage $\Theta_K = 2.5$ ML and for cumulative oxygen exposures as indicated³⁰. A clean K layer had a well-defined Fermi edge, a featureless valence band, a resolved emission from the K 3p core levels at the

interface, bulk and surface, and unresolved plasmon peaks overlapping with the $M_{23}VV$ Auger transition. After exposure of 0.1 L O_2 , oxygen related peaks appeared in the valence band, the intensity of the K 3p (s+b) decreased together with plasmons, while the K 3p (i) increased. The K 3p (s) shoulder at 18.6 eV was discernable after 0.25 L O_2 and additional peaks appeared in the valence band. In the early oxidation stage the metallic state of the alkali surface was preserved as the K 3p surface and plasmons were still observed. A strong valence band peak at 2.7 eV was assigned to the presence of the octahedrally coordinated O^{2-} ions in K layer below the surface layer of potassium. Additional peaks in the valence band suggested the presence of peroxide ions.

Qualitative changes were observed after 1 L O_2 exposure. The K 3p core level grew in intensity and shifted to a lower binding energy. Visible peak narrowing indicated more homogeneous sample within the probing depth. In the valence band, the O 2p related multiplets suggested the presence of oxide and superoxide ions. The O 1s core level spectra measured with 600 eV photons are shown in fig 9. A well defined peak at 531.5 eV binding energy seen after 8 L O_2 exposures is typical of peroxide ion, while a peak at 535.6 eV after higher oxygen exposures corresponds to

superoxide. With the excitation energy of 600 eV, the kinetic energy of photoelectrons was ~ 65 eV and the probing depth was limited to the two topmost layers of adsorbate.

A rather detailed description of potassium oxidation emerged from the high-resolution photoemission studies: in the early stage of oxidation, the O^{2-} ion forms under the surface layer of metallic potassium. The intermediate stage is dominated by peroxide ions while at higher and saturation exposures of dioxygen, superoxide species are also present.

The W $4f_{7/2}$ core level photoemission spectra from the close-packed W(110) surface as a function of oxygen exposure were measured with a total resolution of 83 meV at a photon energy of 70 eV and are shown in figure 10³¹. The data provided unprecedented details about the early stages of oxidation of W(110). The clean surface spectrum displayed two well-defined peaks. The 31.1 eV peak was assigned to the first layer (surface) atoms while the 31.4 eV peak originated from atoms in the second and deeper layers (bulk). The bulk peak remained at the same binding energy throughout the room temperature oxidation process, suggesting that reaction was limited to the surface layer of W atoms. The surface peak lost intensity gradually and

shifted closer to the bulk feature, while at a higher O₂ exposure a new peak developed at a larger BE of 31.75 eV. A rigorous application of nonlinear least-squares curve fitting showed that in addition to the three components needed for data description from a visual inspection of figure 10, three more peaks were required for physically and chemically meaningful results. Assignment of the components in the W 4f_{7/2} spectra was related to the oxygen adsorption site and to the local arrangement of oxygen adatoms at a given coverage. At low coverages lattice gas O atom in a three-fold site creates two distinct singly coordinated W atoms with the SCLS of -160 and +78 meV. A doubly coordinated W atom appeared at higher oxygen coverages in the [001]-oriented structures with SCLS of 275 meV. At even higher coverages oxygen formed the p(2x2) and p(1x1) domains with the W surface atom with three oxygen nearest neighbors and SCLS of ~650 meV. The core level binding energy correlated with a degree of formal oxidation similarly to Al and Si oxidation described above. The triply-coordinated W atom had the largest BE, the doubly-coordinated W atom the intermediate BE and singly-coordinated W atom the smallest BE.

Alkali promoted oxidation of semiconductors and metals attracted a lot of attention recently. Because oxygen has a

high sticking probability on alkali metals, and alkali metal oxides have relatively low thermal stability, oxidation of surfaces, where dissociative chemisorption of dioxygen is a slow process, can be achieved in an UVH environment³²⁻³⁴. Once again high-resolution photoemission provided unique information about the enhanced oxidation process^{31,35}.

VI. Sulfidation

Elemental sulfur and S-containing molecules are regarded today as a liability. Poisoning by sulfur is one of the major problems facing catalyst development, and some sulfur containing compounds are global air pollutants. Cobalt promoted molybdenum sulfide-based catalysts are used in oil refineries to reduce or completely remove S from the hydrocarbon feed in a hydrodesulfurization process thereby allowing the use of expensive Pt-based catalysts for conversion of the S-free hydrocarbons to desirable products.

Sulfur adsorbed on Pt(111) lowers the density of the Pt 5d states that are lying just under the Fermi level³⁶, and are mainly responsible for the catalytic activity of the metal. Figure 11 of valence band spectra of a clean and

S covered Pt(111) surface shows clearly depletion in the d population of Pt. Figure 12 displays the S 2p spectra as a function of S coverage on Pt(111). At Θ_s below 0.3 ML only a three-fold hollow adsorption site is occupied. At higher coverages sulfur atoms occupy the bridge sites, and corresponding core level shifts to lower BE by 0.94 eV. Sulfur behaves as an electron acceptor when bonded to Pt(111), in agreement with the large difference in the electronegativities of S and Pt. The calculation showed that the negative charge on S is mainly a consequence of a Pt 5d $\rightarrow$ S 3p electron transfer and the charge on the S adatom adsorbed in the hollow site is smaller than that on the bridge site. The Pt 4f spectra of S covered Pt showed no evidence for the platinum sulfide, PtS₂, formation.

A Sn/Pt(111) surface alloy is a model for commercially used Pt-Sn bimetallic catalysts that show much better performance in hydrocarbon reforming and dehydrogenation reactions than pure Pt³⁷. The S 2p spectra acquired after the reaction of H₂S with a well-defined ($\sqrt{3} \times \sqrt{3}$)R30°-Sn/Pt(111) surface alloy is shown in fig 13. For small exposures of H₂S the molecule completely decomposed, and the S 2p BE (~162.4 eV) suggested that the S atoms were bonded predominantly to Pt atoms, probably on hollow sites formed

by one Sn and two Pt atoms. With additional exposure two new S 2p doublets appeared at higher BE, and were assigned to H₂S and HS. The H₂S doublet that dominated the spectra at a low temperature disappeared after annealing to 500K, and the sulfur interacted mainly with Pt on this S-saturated surface. The amount of atomic sulfur deposited on Sn/Pt(111) surface after H₂S exposure is smaller than that on either Sn(thin film) or Pt(111) surfaces. Although pure tin is much more reactive than Pt(111), bimetallic bonding substantially reduced the Sn reactivity and also lowered the reactivity of Pt. The redistribution of electrons induced by metal-metal bonding lowers the reactivity of both metals towards H₂S. Neither Sn nor Pt sulfide formation was observed on Sn/Pt(111) surface in contrast to Cu/Pt and Ag/Pt bimetallic systems^{38,39}.

When Cu, Ag and Sn are added to Pt catalysts to improve their selectivity for hydrocarbon reforming, the admetal functions as a site blocker. The large ensembles of Pt atoms that are very effective in C-C hydrogenolysis are broken down while small Pt ensembles on which the isomerization of hydrocarbons takes place remain intact. On Pt(111) silver reacts with sulfur to form silver sulfides and promotes the synthesis of platinum sulfides. Figure 14 shows the Pt 4f spectra from clean and Ag covered surfaces

measured after S adsorption at two temperatures. Large chemical shifts of the Pt 4f core levels ranging from 0.6 to 1.1 eV are immediately obvious and indicate the formation of platinum sulfides. The comparison of S/Pt(111) and S/Ag/Pt(111) results lead to the conclusion that Ag promotes the sulfidation of platinum.

Promotional effect of second metal on sulfidation of Mo(110) surface was also found and it was shown that Co and Ni were most active for this process⁴⁰. This finding correlates with the HDS activity of commercial catalysts that are based on supported MoS₂/Al₂O₃ with CoS_x or NiS_y modifiers.

Recently, the S₂ molecule was also used to probe the reactivity of oxide surfaces⁴¹. It was shown that the reactivity of oxides scales inversely with the band gap size. Figure 15 illustrates the results of photoemission measurements for ZnO and Al₂O₃. The uptake of sulfur on ZnO is 5 times bigger than that on alumina for comparable sulfur exposures. The energy position and the line shape of the S 2p spectrum for S/Al₂O₃ surface indicate that sulfur is bonded to the Al³⁺ centers of the oxide surface and more that one type of adsorption sites is involved. The S 2p spectra of the S/ZnO system are more complex displaying two intense doublets in the 161-165 eV region and weaker

features in the 166-169 region. The doublets were attributed to atomic S and S_n species adsorbed on Zn^{2+} sites of ZnO. The S 2p features at higher BE (166-169 eV) were assigned to sulfur bound to O^{2-} sites, i.e. to SO_x species. As shown in the following chapter the SO_x species are formed on surfaces after adsorption of SO_2 .

VII. SO_2 Reaction

SO_2 , generated in enormous quantities by both natural processes and human activity, is a major air pollutant. Its oxidation and reaction with water leads to the formation of sulfuric acid and to corrosion of metals and other materials. Though many transition metal catalysts are poisoned by SO_2 , the catalytic oxidation of SO_2 to SO_3 uses a Pt catalyst in one of the largest chemical industrial process.

A casual look at figure 16 suggests a very rich SO_2 chemistry occurring on a Ru(001) surface even at low temperatures⁴². Up to six distinct S-species can be seen, and results of fitting provided the following S $2p_{3/2}$ BEs: 168.2, 166.1, 165.4, 164.9, 162.4 and 161.8 eV. The highest BE was assigned to SO_2 multilayers, while the two lowest values correspond to atomic S adsorbed on clean Ru and in

the vicinity of coadsorbed oxygen. Remaining peaks were assigned following reported values in the literature and theoretical calculations that predicted the following order based on changes in the S electron density:

$BE(SO_4) > BE(SO_3) > BE(SO_2) > BE(S+O) > BE(S)$. A general trend is that the BE increases with increasing number of oxygen in a sulfur oxide species. We have already seen similar trends in the Al, Si and W interactions with oxygen, where the interpretation of the SCLS was based on different local metal-oxygen coordination. Annealing to 160 K leads to desorption of SO_2 multilayer, and decomposition or disproportionation of SO_2 that results in formation of SO_4 , SO_3 and atomic S and O. After annealing to 260 K, the SO_4 and S are the dominant species on the surface. A final annealing step induces decomposition of sulfur oxides into atomic S and O.

The SO_2 chemistry on the Cu(100) surface is less complex as can be seen in figure 17⁴³. The data show, however, new kinetic aspects of surface species conversion. Every single spectrum displayed is collected in 10 s intervals, while temperature is ramped $\sim 0.1K/s$. A total of three different S species with BE at 165.3, 164.3 and 160.2 eV were identified and assigned to SO_2 , SO and S, respectively. The O 1s spectra together with X-ray

absorption also used in the study, suggested the following reaction pathway for SO₂ decomposition on the Cu(100) surface:

VIII. Etching and Passivation

The ability to control the structure of solid surfaces with atomic precision depends among other things on our abilities to analyze them. Here once again high-resolution core level spectroscopy plays quite a unique role. A perfect example is the reactivity study of InAs(001) surface with iodine⁴⁴. III-V semiconductors have alternating layers of group III and group V atoms along the [001] direction, so it is expected that surfaces with different termination will display different reactivity. Halogens are often used to etch these surfaces in device fabrication and understanding of underlying processes is of crucial importance. In some cases halogen passivates the surface instead of etching it. High-resolution core level spectra of iodine reaction with the In- and As-terminated InAs(001) surfaces are shown in figure 18. The chemically shifted components of the In 4d due to InI and InI₂ species are at BE's 0.6 and 1.3 eV higher than the bulk component, and are

seen for both In- and As- surface terminations. The As 3d core level shifts by 0.7 and 1.6 eV after AsI and AsI₂ are formed by the reaction on As-terminated surface. On the In-terminated surface InI is the main reaction product, and no As iodides are formed.

The reaction of iodide is therefore limited to the outermost In atoms and LEED measurement confirms that an ordered overlayer forms. In contrast, on the As-terminated surface both In and As iodides form, which indicates that In-As bond are broken during reaction. Bond breaking precedes etching, and leads to surface disordering, also confirmed by LEED. The understanding of chemistry at binary compound surfaces can form the basis for processing materials with atomic precision.

Sulfur has found its use in some beneficial application. The surfaces of the III-V semiconductors are quite reactive and sulfur is used for their passivation. High-resolution photoemission data were used to study the reaction of S with InP(001) surface recently ⁴⁵.

IX. Outlook

In this brief overview, I have tried to demonstrate the uniqueness of photomission data obtained with synchrotron radiation. Although I drew mainly on the results of our Brookhaven group, many teams are very active in the field, both in exploring new systems and in developing new techniques. Equally important is the development of new generation of the synchrotron radiation sources. In several examples discussed below the third generation synchrotron Elettra in Trieste was used to perform experiments that would not be possible with the previous generations of synchrotrons. I see four main areas where the progress already being made will enhance our understanding of surface chemistry.

Time-resolved data:

As already demonstrated by the Elettra synchrotron group^{24,43}, both time-resolved and high-resolution data acquisition can be accomplished. A recent work of the group from Japan⁴⁶ is very promising. The authors measured the Ga 3d and Sb 4d core level spectra with a total energy resolution 0.3 eV and data acquisition time of 100 ms per spectrum. Many physical and chemical phenomena occur on

this time scale and real-time studies of surface kinetics should be possible.

Spatially-resolved data:

In contrast to many microscopic techniques, photoelectron spectromicroscopy offers elemental and chemical imaging of surfaces, i.e. the ability to distinguish between the different oxidation states of elements⁴⁷. The X-ray beam is focused to a micron-sized spot of the surface, and by scanning the sample with respect to the photon beam with the electron energy analyzer tuned to a selected energy, two-dimensional elemental images can be obtained.

Very high-resolution data:

With the overall resolution of 50 and 30 meV at 700 and 320 eV photon energy the authors⁴⁸ have resolved core-level vibrational fine structure in adsorbed CO on Ni(100), with electronic and vibrational contributions separated in both O 1s and C 1s spectra. The adsorption of CO in different chemical states modifies the vibrational fine structure in the core level (figure 19), and provides therefore additional details about the electronic and geometric structure of adsorbates.

Photoemission in combination with other synchrotron-based techniques:

As discussed in part II the surface of beryllium (0001) has three unusually large SCLS. The (1010) surface has also three surface components but their initial assignment is now challenged⁴⁹. Theory predicted that the origin of the S1 peak with the greatest shift is Be atom in the second layer. It is known from photoelectron diffraction theory that in the so-called forward scattering geometry the second layer core level component is enhanced versus the first layer one for electrons with kinetic energies > 400 eV. The authors used 500 eV photons to perform an azimuthal scan at a polar emission of 75° off the surface normal. Three spectra in figure 20 taken at different azimuthal directions show a very clear increase in the intensity on the low binding energy side. The measured diffracted intensity S1 of photoelectrons emitted from the second layer has pronounced maximum at the expected angle 57.5° , whereas the S2 intensity does not change, in full agreement with a multiple-scattering calculation. The combined photoemission, photoelectron diffraction and theoretical calculation thus provided a new insight into the origin of the surface core level shifts, the crucial parameter for our understanding of chemical reactions on surface.

Acknowledgement

I would like to thank my colleagues, research associates and collaborators who over the years participated on many projects described in this account. This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-98CH10886 with the U.S. Department of Energy, Office of Basic ^{Energy} Sciences, Chemical Science Division. Part of the review was written during the sabbatical at Sandia National Laboratories, Livermore, CA, whose hospitality I greatly appreciate.

Figure Captions

Figure 1: Be $1s$ photoemission spectra from Be(0001) recorded (dots) using photon energies from 123 to 160 eV and at a sample temperature of 100 K. The results of a curve fitting procedure are shown by solid curves. The four curves labeled S1, S2, S3 and B show the four components fitted to the 123 eV spectrum (from Ref.³).

Figure 2: S $2p$ core-level spectra of S adsorbed on Ru surface at room temperature measured using a conventional XPS and synchrotron based soft XPS.

Figure 3: K $3p$ photoemission spectrum of 2.5 monolayer of potassium adsorbed on Ru(001) measured with 40 eV photon energy at two emission angles: bottom - normal emission, top - 70° off normal. The experimental data (triangles) are curve fitted with three doublets (lines). The inset illustrates the morphology of K overlayer (s - surface, i - interface, b - bulk) (from Ref.¹⁹).

Figure 4: (Z+1) Equivalent Core Approximation (Born-Haber cycle). The energy scale is only approximately valid for potassium. See text for the explanation of terms.

Figure 5: C $1s$ spectra and their curve fitted components at different CO coverages/exposures on (A) Rh(111), (B) 1 ML Pd/Rh(111), and (C) 0.5 ML Pd/Rh(111).

The intensities have been normalized to the background at around 284 eV (from Ref.²²).

Figure 6: Al 2p spectrum after 40 L O₂ exposure to clean Al(111) at room temperature. A curve fitting was done using two metallic (a,b), oxide (f) and three chemisorption (c,d,e) states, each of them a spin-orbit split doublet (from Ref.²⁵).

Figure 7: A representative Si 2p core level photoemission spectrum for SiO₂/Si(111). The circles are data points, and the curves show a fit and the decomposition into bulk and four surface components (from Ref.²⁶).

Figure 8: (top) K 3p and valence band photoemission spectra of 2.5 ML K on Ru(001) with 40 eV photon energy as function of oxygen exposure. (bottom) Detail view of changes in the K 3p level during early stages of oxidation (from Ref.³⁰).

Figure 9: Changes in the O 1s photoemission spectra during oxidation of 1ML K on Ru(001) measured with photon energy of 600 eV. Experimental points (circles) are plotted after the background subtraction and solid lines represent a fit by a Lorentzian folded with a Gaussian (from Ref.³⁰).

Figure 10: (A) W(110) 4 $f_{7/2}$ core level photoemission spectra for room temperature adsorption of O₂. The bulk

component BE at 31.4 eV is indicated as well as the BE of the clean surface peak at ~31.1 eV and an oxygen induced feature at 31.75 eV. (B) W(110) $4f_{7/2}$ core level photoemission spectrum with 0.34 ML of adsorbed O. Also shown is a nonlinear least squares fit of the data (from Ref.³¹).

Figure 11: Valence band photoemission spectra acquired after dosing S₂ to Pt(111) at 500 K. The electron were excited with photons having energies of 70 (left panel) and 45 eV (right panel) (from Ref.³⁶).

Figure 12: S 2p spectra acquired after dosing S₂ to Pt(111) at 300 K. For surfaces with $\Theta_s < 0.8$ ML, the sample was briefly annealed to 500 K before taking the photoemission spectra. The S 2p electrons are excited using a photon energy of 250 eV. Shown in the right panel is a curve fit to high coverage spectrum with two spin-orbit split components, baseline and residuals (from Ref.³⁶).

Figure 13: S 2p spectra for adsorption of H₂S on a $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Pt(111) alloy. H₂S was dosed at 100 K and then the surface was annealed to temperatures indicated. All spectra were taken using a photon energy of 260 eV. The third spectrum from the bottom was curve fitted (from Ref.³⁷).

Figure 14: Pt 4f photemission spectra acquired after exposing $\text{Ag}_{1.16}/\text{Pt}(111)$ and $\text{Ag}_{3.28}/\text{Pt}(111)$ to S_2 at 325 (top) and 550 K (bottom). A photon energy of 250 eV was used in these experiments (from Ref.³⁹).

Figure 15: S 2p spectra for adsorption of S_2 on Al_2O_3 (top) and ZnO (bottom) at 300 K. The spectrum in the top panel ($\text{S}_2/\text{Al}_2\text{O}_3$, $\Theta_s \sim 0.1$ ML) and the top spectrum in the bottom panel (S_2/ZnO , $\Theta_s \sim 0.7$ ML) were measured after dosing the same amount of S_2 to both oxide surfaces. The electrons were excited using a photon energy of 240 eV (from Ref.⁴¹).

Figure 16: S 2p photoemission spectra of SO_2 adsorbed on clean Ru at 100 K as a function of exposure. A photon energy used for electron excitation was 260 eV (from Ref.⁴²).

Figure 17: S 2p (top left) and O 1s (top right) core level photoemission spectra for $\text{SO}_2/\text{Cu}(100)$ with the sample temperature as parameter during continuous heating (~ 0.1 K/s). Curve fits of the S 2p (bottom left) and O 1s (bottom right) for four distinct temperatures (from Ref.⁴³).

Figure 18: Representative high-resolution SXPS spectra of In 4d and As 3d collected from In- and As-terminated InAs(001) after I_2 exposure. The raw data after background subtraction are shown as dots. The individual components of

the numerical fits are shown as dashed lines. The solid lines are the sum of the fit components (from Ref.⁴⁴).

Figure 19: C *1s* and O *1s* photoemission spectra of c(2x2) CO/Ni(100). Vibrational fine structure due to intramolecular stretch; C *1s* 217.8 ± 2.2 meV, O *1s* 173 ± 8 meV. Adiabatic transitions at 285.8 ± 0.1 eV (C *1s*) and 531.4 ± 0.2 eV (O *1s*) (from Ref.⁴⁸).

Figure 20: Three Be *1s* core level spectra taken with 500 eV photons at a polar emission angle of 75° off normal and azimuthal emission directions of (1) [1210], (2) [0001] and (3) 57.5° off [1210]. A clear enhancement of the intensity on the low BE side is seen and a fit show that this is due to the intensity increase of S1 component at 111.08 eV. The inset shows a sketch of the measurement geometry (from Ref.⁴⁹).

References

- 1 N. H. Turner and J. A. Schreifels, *Anal. Chem.* **70**, R 229 (1998).
- 2 L. I. Johansson, H. I. P. Johansson, J. N. Andersen, E. Lundgren, and R. Nyholm, *Phys. Rev. Lett.* **71**, 2453 (1993).
- 3 L. I. Johansson and B. E. Sernelius, *Phys. Rev. B* **50**, 16817 (1994).
- 4 P. H. Citrin, G. K. Wertheim, and Y. Baer, *Phys. Rev. Lett.* **41**, 1425 (1978).
- 5 S. A. Flodstrom, C. W. B. Martinsson, R. Z. Bachrach, S. B. M. Hagstrom, and R. S. Bauer, *Phys. Rev. Lett.* **40**, 907 (1978).
- 6 T. M. Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vedrine, *Phys. Rev. Lett.* **43**, 789 (1979).
- 7 A. Flodstrom, R. Nyholm, and B. Johanson, in *Synchrotron Radiation Reserch: Advances in Surface and Interface Science. Techniques.*, Vol. 1, edited by R. Z. Bachrach (Plenum Press, New York, 1992), pp. 199-251.
- 8 S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).
- 9 S. Hufner, *Phoelectron Spectroscopy* (Springer-Verlag, Berlin, 1995).

- 10 B. Johansson and N. Martensson, *Phys. Rev. B* **21**, 4427 (1980).
- 11 P. H. Citrin and G. K. Wertheim, *Phys. Rev. B* **27**, 3176 (1983).
- 12 J. N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm, and M. Scheffler, *Phys. Rev. B* **50**, 17525 (1994).
- 13 J. J. Weimer, E. Umbach, and D. Menzel, *Surf. Sci.* **155**, 132 (1985).
- 14 G. Pirug, A. Winkler, and H. P. Bonzel, *Surf. Sci.* **163** (1985).
- 15 J. Hrbek, *Surf. Sci.* **164**, 139 (1985).
- 16 M. Domke, T. Mandel, L. Lauschbach, M. Prietch, and G. Kaindl, *Surf. Sci.* **189/190**, 268 (1987).
- 17 A. Hohlfeld, M. Sunjic, and K. Horn, *J. Vac. Sci. Technol. A* **5**, 1987 (1987).
- 18 T. K. Sham and J. Hrbek, *J. Chem. Phys.* **89**, 1188-1194 (1988).
- 19 T. K. Sham, G.-Q. Xu, J. Hrbek, and M.-L. Shek, *Surf. Sci.* **210**, L185 (1989).
- 20 J. Hrbek, M.-L. Shek, T. K. Sham, and G.-Q. Xu, *J. Chem. Phys.* **91**, 5786 (1989).
- 21 N. Martensson, A. Stenborg, O. Bjorneholm, A. Nilsson, and J. N. Andersen, *Phys. Rev. Lett.* **60**, 1731 (1988).

- 22 A. Beutler, F. Strisland, A. Snadell, A. J. Jaworski, R. Nyholm, M. Wiklund, and J. N. Andersen, *Surf. Sci.* **411**, 111 (1998).
- 23 J. A. Rodriguez and M. Kuhn, *Surf. Sci.* **365**, L669 (1996).
- 24 A. Baraldi, S. Lizzit, D. Cocco, G. Comelli, G. Paolucci, R. Rosei, and M. Kiskinova, *Surf. Sci.* **385**, 376 (1997).
- 25 C. Berg, S. Raaen, A. Borg, J. N. Andersen, E. Lundgren, and R. Nyholm, *Phys. Rev. B* **47**, 13063 (1993).
- 26 M. T. Sieger, D. A. Luh, T. Miller, and T. C. Chiang, *Phys. Rev. Lett.* **77**, 2758 (1996).
- 27 B. Woratschek, W. Sesselman, J. Kupperts, G. Ertl, and H. Haberland, *J. Chem. Phys.* **86**, 523 (1987).
- 28 S. L. Qiu, C. L. Lin, J. Chen, and M. Strongin, *Phys. Rev. B* **39**, 6194 (1989).
- 29 J. Jupille, P. Dolle, and M. Besancon, *Surf. Sci.* **260**, 271 (1992).
- 30 J. Hrbek, T. K. Sham, M. L. Shek, and G. Q. Xu, *Langmuir* **8**, 2461 (1992).
- 31 D. M. Riffe and G. K. Wertheim, *Surf. Sci.* **399**, 248 (1998).

- 32 J. A. Rodriguez and J. Hrbek, *Catal. Lett.* **26**, 393 (1994).
- 33 Y. Huttel, E. Bourdie, P. Soukiassian, P. S. Mangat, and Z. Hurych, *J. Vac. Sci. Technol. A* **11**, 2168 (1992).
- 34 F. M. Hoffmann, K. C. Lin, R. G. Tobin, C. J. Hirschmugl, G. P. Williams, and P. Dumas, *Surf. Sci.* **275**, L675 (1992).
- 35 S. M. Driver, J. Ludecke, R. J. Dixon, P. B. J. Thompson, G. Scragg, D. P. Woodruff, and B. C. C. Cowie, *Surf. Sci.* **391**, 300 (1997).
- 36 J. A. Rodriguez, M. Kuhn, and J. Hrbek, *Chem. Phys. Lett.* **251**, 13 (1996).
- 37 J. A. Rodriguez, S. Chaturvedi, T. Jirsak, and J. Hrbek, *J. Chem. Phys.* **109**, 4052 (1998).
- 38 M. Kuhn and J. A. Rodriguez, *J. Catal.* **154**, 355 (1995).
- 39 J. A. Rodriguez, M. Kuhn, and J. Hrbek, *J. Phys. Chem.* **100**, 15494 (1996).
- 40 M. Kuhn, J. A. Rodriguez, and J. Hrbek, *Surf. Sci.* **365**, 53 (1996).
- 41 J. A. Rodriguez, S. Chaturvedi, M. Kuhn, and J. Hrbek, *J. Phys. Chem.* **102**, 5511 (1998).

- 42 T. Jirsak, J. A. Rodriguez, S. Chaturvedi, and J. Hrbek, *Surf. Sci.* (1998).
- 43 M. Polcik, L. Wilde, J. Haase, B. Brenna, D. Cocco, G. Comelli, and G. Paolucci, *Phys. Rev. B* **53**, 13720 (1996).
- 44 W. K. Wang, W. C. Simpson, and J. A. Yarmoff, *Phys. Rev. Lett.* **81**, 1465 (1998).
- 45 Z. Tian, M. W. C. Dharma-wardana, Z. H. Lu, R. Cao, and L. J. Lewis, *Phys. Rev. B* **55**, 5376 (1997).
- 46 F. Maeda, Y. Watanabe, and M. Oshima, *Phys. Rev. Lett.* **78**, 4233 (1997).
- 47 M. Kiskinova and G. Paolucci, *Surf. Sci.* **377**, 735 (1997).
- 48 A. Fohlish, N. Wassdahl, J. Hasselstrom, O. Karis, D. Menzel, N. Martensson, and A. Nilsson, *Phys. Rev. Lett.* **81**, 1730 (1998).
- 49 S. Lizzit, K. Pohl, A. Baraldi, G. Comelli, V. Fritzsche, E. W. Plummer, R. Stumpf, and P. Hofmann, *Phys. Rev. Lett.* **81**, 3271 (1998).

Figure 1

Figure 2

Figure 3

(Z+1) EQUIVALENT CORE APPROXIMATION

Figure 4

A

B

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Figure 19

Figure 20