10/125/95 JS(1)

SAND--94-2257

Physical and Chemical Sciences Center

F. L. Vook, Director

Research Briefs

**Sandia National Laboratories
Albuquerque, New Mexico 87185**

A Department of Energy Multiprogram Laboratory

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, makes 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.

Volume 9-94

Integrated Materials Research Laboratory - 1994

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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

Physical and Chemical Sciences at Sandia National Laboratories

"Exceptional Service in the National Interest"

Message from the Director

As Sandia National Laboratories and the Physical and Chemical Sciences Center develop an increasingly diverse set of customers, research partners, and Cooperative Research and Development Agreements (CRADA's) with industry, there is a need for providing more concise information describing our technical achievements and capabilities. This publication, *Research Briefs*, is designed to inform our present and potential partners in research and technology advancement.

Our research emphasizes semiconductor physics, electronic materials, surface physics and chemistry, plasma and chemical processing sciences, lasers and optics, vision science, ion-solid interactions and defect physics, and advanced materials physics. The specific programs we pursue are driven by our research goals which are greatly influenced by interactions with our government and industrial customers.

People are our most important asset and their creative research is fundamental to our accomplishments. Leadership, teamwork, and individual innovation are the strengths we use to help Sandia respond to the present and future needs of our country.

Frederick L. Vook

Frederick L. Vook
Director

Research Briefs for the Physical and Chemical Sciences Center is published by Sandia National Laboratories. Additional complimentary copies are available by contacting:

J. Alan Nichelason
Physical and Chemical Sciences Center, 1101
Sandia National Laboratories
Albuquerque, New Mexico 87185-0336

Phone: (505) 844-2379
FAX: (505) 844-6098
E-mail: janiche@somnet.sandia.gov

Research Briefs

Editors

F. L. Vook
G. A. Samara

Production

L. G. Martinez

Physical and Chemical Sciences Center

Research Briefs

Table of Contents

Advanced Materials & Technology	4
<u>Shock Waves</u>	
<i>Recent Measurements Define the Dispersion of Shock-Waves in Highly Porous Solids</i>	<i>4</i>
<u>Ion Beams</u>	
<i>Roughening Instability and Surface Evolution During Ion Sputtering of Ge(001) Have Been</i>	
<i>Measured and Explained by a New Model</i>	<i>6</i>
<i>A New Single Event Upset (SEU) Mechanism has been Discovered by Combining SEU-Imaging with</i>	
<i>Ion Beam Induced Charge Collection (IBICC) Microscopy of ICs</i>	<i>8</i>
<i>Ion Beam Induced Radiation can be used for Medical Applications</i>	<i>10</i>
<i>Heavy Ion Backscattering Spectrometry is Setting Record Sensitivities because of a</i>	
<i>New Time-of-Flight Detector</i>	<i>12</i>
<i>Ion Irradiation Strongly Enhances the Vortex Pinning Potential of High-Temperature</i>	
<i>Superconducting YBa₂Cu₃O₇ Thin Films</i>	<i>14</i>
<i>Ion Beam Analysis has found many important uses in Magnetic Fusion Energy Technology</i>	<i>16</i>
<i>Hydrogen Retention at Radiation Damage in Graphite Depends on Both</i>	
<i>Composition and Microstructure</i>	<i>18</i>
<u>Superconductors</u>	
<i>High-Temperature Phase Equilibria Established for Tl-Ca-Ba-Cu-O Superconductors</i>	<i>20</i>
<i>Improved Single Crystal Growth of Tl-containing Superconductors has been Achieved</i>	<i>22</i>
<i>Pressure Tuning Determines the Orientational Order and Phase Transitions in Solid C₆₀ and C₇₀</i>	<i>24</i>
<i>Gas Separation is Possible with C₆₀ "Lattice Sieves"</i>	<i>26</i>
<i>Phonon-Mediated Attraction Between Large Bipolarons Can Lead to</i>	
<i>Formation of Charged Bose Liquid</i>	<i>28</i>
<u>Semiconductors</u>	
<i>Photoluminescence from Porous Silicon has been Related to</i>	
<i>Particle Size Measured in K-Map X-Ray Diffraction</i>	<i>30</i>
<i>Strong Quantum-Size Effects Observed in a Layered Semiconductor: MoS₂ Nanoclusters</i>	<i>32</i>
<i>Midwave (4 μm) Infrared Emitters have been Demonstrated with</i>	
<i>Biaxially Compressed InAsSb Active Regions</i>	<i>34</i>
<i>A New Capability for MBE Growth has been Applied to</i>	
<i>Bandgap-Engineered Group IV SiGeC Alloys</i>	<i>36</i>
<i>Pulsed-Laser Deposition has been used to Deposit Diamond-Like Carbon Thin Films</i>	<i>38</i>
<i>KMAP Reciprocal Space Analysis has been Used to Nondestructively Observe the</i>	
<i>Ordering of III-V Compound Semiconductors</i>	<i>40</i>
<i>The Strength of the Ge-H Surface Bond on Germanium was Determined</i>	
<i>Through Studies of Internal Microvoids</i>	<i>42</i>
<i>Theoretical Calculation of the Direct to Indirect Transition in InAlGaP</i>	<i>44</i>
<i>SiGeC Alloys Stability Shown to be Sufficient for Device Processing</i>	<i>46</i>
<i>One Nonlinear Electrical Phenomenon in RF-Excited Plasmas has been Explained and Controlled</i>	<i>48</i>
Applied Physics & Chemistry	50
<u>CVD</u>	
<i>Diamond CVD Growth Models have been Developed</i>	<i>50</i>
<i>Infrared Spectroscopy of Adsorbates on GaAs Surfaces has been Developed</i>	<i>52</i>

Physical and Chemical Sciences Center
Research Briefs

Table of Contents

<i>Laser Measurements of Si Atoms Lead to an Improved Reaction Mechanism for Silane CVD</i>	<i>54</i>
<i>Stimulated Chemistry of Ammonia (NH₃) on Surfaces</i>	<i>56</i>
Surface Physics-Chemistry	
<i>Direct Observation of Substitutional-Atom Trapping on a Metal Surface</i>	<i>58</i>
<i>Direct Patterned Deposition of Adherent Copper on Teflon</i>	<i>60</i>
<i>Interfacial-Force Microscopy Probes The Mechanical Properties Of Single, Nanometer-Size Grains On Various Substrates</i>	<i>62</i>
<i>The First Direct Observation of Boron-Hydroxyls Enhancing TEOS Chemisorption in Boron-Doped SiO₂ CVD has been Made</i>	<i>64</i>
Semiconductors	
<i>Rapid Methods for Calculating Reflectance Spectra of Growing Semiconductor Films are Being Developed for Applications in Process Control</i>	<i>66</i>
<i>Determination of the Direct to Indirect Band-to-Band Transitions in In_x(Al_yGa_{1-y})_{1-x}P Alloys by Pressure Dependent Photoluminescence Measurements</i>	<i>68</i>
<i>Real Time Control of MBE by Optical-based Flux Monitoring (OFM)</i>	<i>70</i>
<i>Inter-Quantum-Well Tunneling in a Double-Well Structure with In-Plane Magnetic Fields</i>	<i>72</i>
<i>Thermal Stability Studies Demonstrate Usefulness of Diamond-like Carbon as a Coating Material up to 250° C</i>	<i>74</i>
<i>New Technique Developed for High-Accuracy Measurement of Two-Dimensional Electron Density in Pseudomorphic HEMT Structures With Highly Doped Contact Layers</i>	<i>76</i>
<i>Gate-Controllable "Artificial Impurity" Fabricated By Use of a Nanostructure Air-Bridge Technique</i>	<i>78</i>
<i>A Localized Vibrational Mode for Nitrogen has been identified in ZnSe using Ion Implantation and Infrared Absorption</i>	<i>80</i>
<i>Measurements have been Made of the Electrical Properties of Implantation-Induced Nanocavities in Silicon</i>	<i>82</i>
Computing	
<i>Development of a Massively Parallel Unstructured Finite Element Reacting Flow Code for Multiple Instruction Multiple Data Computers</i>	<i>84</i>
Lasers, Optics, and Vision.....	86
<i>2-Dimensional Photonic Lattices Demonstrate Lateral Control of Photon Propagation</i>	<i>86</i>
<i>Binary Optics Have Been Used To Make Optical Phase Sensors With Extremely Large Dynamic Range, High Bandwidth And Sensitivity For Laser Beam Characterization And Fluid Flow Diagnostics</i>	<i>88</i>
<i>Trace Organic Chemical Detection Using an Ultraviolet Excitation Molecular Beam Fluorometer</i>	<i>90</i>
<i>We have Advanced Optical Parametric Oscillator Development</i>	<i>92</i>
Diagnostics and Characterization	94
Synthesis and Processing.....	95
Theory and Simulation	96
Recent Awards and Prizes.....	97

*Recent Measurements Define the Dispersion of
Shock-Waves in Highly Porous Solids*

by M. U. Anderson, R. A. Graham and G. T. Holman

Motivation -- Quantitative description of the deformation behavior of highly porous solids under shock compression is essential for a better understanding and utilization of shock-induced solid state chemical processes. Further, evaluation of wave dispersion in porous solids is crucial for evaluating the safety of nuclear weapons in an accident scenario in which the weapon has experienced sufficient damage to fracture the high explosive, directly affecting the sensitivity of the high explosives to subsequent thermal initiation. A detailed evaluation of wave dispersion in porous solids is now possible using the diagnostic capabilities of the piezoelectric polymer stress-rate PVDF to observe the risetime of the propagated waves.

Accomplishment -- Observations of shock wave dispersion in a number of selected, highly porous (60% dense) solids have been made in experiments utilizing the piezoelectric polymer PVDF. The materials studied include the ceramic, single component material rutile (TiO_2);

two component materials $2\text{Al} + \text{Fe}_2\text{O}_3$, $5\text{Ti} + 3\text{Si}$, and $3\text{Ni} + \text{Al}$, and the high explosive material HMX.

Significance -- The materials response data of the present report represents the most comprehensive study of wave dispersion effects in highly porous solids ever accomplished. The materials behaviors show that the deformation processes are far more complex than previously recognized. Such behavior is not presently incorporated in models of porous materials behaviors. Advancement of the predictive capabilities for ballotechnic energetic materials, materials processing and synthesis, and porous high explosives requires a recognition of the basic complexity of the processes and the development of improved materials models. The strongly material-dependent risetime characteristics appear to be both morphologically and starting density dependent for a given material.

Keywords: Porous solids, advanced energetic materials, PVDF, nuclear weapon safety.

Contact: Mark U. Anderson, Advanced Materials Physics & Device Research Department 1153
Phone: (505) 844-5726
Fax: (505) 844-5459
E-mail: maander@sandia.gov

***Roughening Instability and Surface Evolution During Ion Sputtering of Ge(001)
Have Been Measured and Explained by a New Model***

by E. Chason, T. M. Mayer and A. J. Howard

Motivation -- Controlling surface roughness on the nanometer scale is becoming increasingly important as device dimensions continue to decrease. Progress has been limited in part by a lack of probes that can measure roughness in this regime (0.1 - 10 nm), particularly probes that can be used to study the kinetics of roughness evolution. We have developed in situ X-ray reflectivity to allow us to measure the real-time evolution of roughness during sputter processing. Although sputtering is a commonly used processing tool, there is not a detailed understanding of the link between the development of surface morphology and the sputtering process. The observation of surface features such as sputter ripples indicate that the process is more than a simple stochastic removal of material. Quantitative studies of the roughening kinetics will allow us to critically evaluate models which relate the development of roughness to fundamental surface processes.

Accomplishment -- We have measured the kinetics of roughness evolution during sputtering of Ge (001) surfaces, thus extending our work from amorphous SiO₂ to a crystalline system. The temperature dependence of the roughening process is demonstrated in the accompanying figure. The observed kinetics are explained by a model which balances roughening by atom removal with smoothing by surface transport. At

the highest temperature shown, the surface roughens slowly due to smoothing by surface diffusion. At lower temperature, the surface roughness grows exponentially due to an instability related to the curvature dependence of the sputter yield. This instability leads to the development of a ripple topography on the surface which we have observed with atomic force microscopy (AFM). At the lowest temperature shown, the surface roughness reaches a steady state. In this instance, the sputtering process amorphizes the surface, enabling smoothing by a viscous flow mechanism. The kinetics obtained from this model are shown as solid lines in the figure. Similar behavior has been observed for Si surfaces.

Significance -- We have shown that the evolution of surface roughness can be understood quantitatively with a model combining sputter roughening with surface transport. This model explains the magnitude of the roughening as well as the development of surface ripples. Also, our results provide the first quantitative test of the kinetics predicted by the Bradley-Harper instability mechanism. Our approach provides the basis for developing predictive models of surface roughness during sputter removal which account for the complex interplay of ion beam and materials parameters.

Keywords: sputtering, surface roughness, X-ray reflectivity

Contact: Eric Chason, Semiconductor Physics Department 1112
Phone: (505) 844-8951
Fax: (505) 844-9185
E-mail: ehchaso@sandia.gov

Surface roughening kinetics at various temperatures (theory, solid line; experiment, circles).

A New Single Event Upset (SEU) Mechanism has been Discovered by Combining SEU-Imaging with Ion Beam Induced Charge Collection (IBICC) Microscopy of ICs

by B. L. Doyle, S. R. Lee, H. Schone, K. M. Horn, F. W. Sexton - Sandia and J. S. Laird, M. Cholewa, A. Saint, G. J. F. Legge - Univ. of Melbourne, Australia

Motivation -- The deposition of charge resulting from the passage of ions through integrated circuits (ICs) can cause a memory bit to change state, i.e. from a 1-0 or 0-1. These malfunctions are called Single Event Upsets (SEUs), and such upsets, caused by solar flare and cosmic ray particles, routinely plague advanced ICs in satellites and spacecraft. For example Voyager, Magellan, INSAT, and GOES/TRDS series satellites have all suffered such problems. While space and nuclear weapon applications currently require the most radiation resistant ICs, with the continued shrinkage of both feature size and stored charge of microelectronic devices, even terrestrial applications of ICs are now starting to be affected by SEUs. We have developed two techniques to study SEU microscopically: Single Event Upset (SEU) imaging and Ion Beam Induced Charge Collection (IBICC) microscopy. Both techniques utilize scanned nuclear microprobes at Sandia and the University of Melbourne.

Accomplishment -- SEU imaging has been shown to provide detailed images of regions on ICs susceptible to ion-induced malfunctions. IBICC microscopy provides direct images of charge generation and collection efficiency in ICs and thereby examines microscopically the underlying physical processes which lead to SEU failures. An IBICC image is shown in the figure for a Sandia TA670 radiation hardened SRAM. Light (dark) regions show high (low) charge measurement regions. By combining SEU images with the IBICC micrograph shown in the

figure, we have discovered that 1) the highest IBICC signals result from center strikes to n-on FET sources and drains which are located in a p-well, and 2) that the amount of charge generated for such strikes can only be explained by invoking either a shunting or bipolar charge amplification mechanism, and 3) that such strikes probably result in SEU failures of the TA670. Spatially corresponding SEU and IBICC measurements have also recently been completed on a 1Mb commercial Paradygm SRAM. Recent improvements in beam spot resolution (down to 0.5 micron) and a new microprobe system which will have 0.1 micron resolution will make measurements of even higher density, state-of-the-art ICs possible.

Significance -- The combination of SEU-Imaging and IBICC Microscopy has proven to be a powerful combination making possible, for the first time, the microscopic examination and explanation of the SEU process. It was previously thought that the most charge was generated and collected when ions struck the perimeter of FET sources and drains, but our results clearly show that ions which strike the center of these components result in the most collected charge. Previous explanations of the source of upsets in the TA670 involved charge collection associated with ions striking reverse-biased n-off and p-off drains, but our results now indicate that the n-on drains are the most SEU-sensitive regions on this particular IC due to current shunting and parasitic npn transistor action.

Keywords: nuclear, microprobe, single event upset, integrated circuits, SRAM

Contact: Barney L. Doyle, Ion Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-7568
Fax: (505) 844-7775
E-mail: bldoyle@sandia.gov

Ion Beam Induced Radiation can be used for Medical Applications

by K. M. Horn, B. L. Doyle and D. S. Walsh

Motivation -- Radiation therapy is a commonly used tool in the clinical treatment of malignant cancer tumors. However, established techniques and equipment utilizing radioactive sources (brachithery), cyclotron-produced, high energy proton beams (proton radiotherapy and radiosurgery), and laser treatments are often not applicable in certain situations. Medical clinicians claim that the development of a radiation source that could be handled like a radiation "air-brush" to deliver relatively large doses of radiation to specific areas with hand-held control would provide an ease of use and flexibility that currently does not exist in traditional radiation therapies.

Accomplishment -- The micro-radiosurgery technique is based upon the concept that low energy ion-induced nuclear reactions can be used to produce high energy protons directly at a tumor site. During the past year, specially designed "proton tubes" have been fabricated and tested at Sandia which demonstrate that using the $D(^3\text{He},p)^4\text{He}$ nuclear reaction, 17.5 MeV protons can readily be produced at the tip of a small needle using only an 800 keV ^3He ion beam. When coupled with a small RFQ accelerator, a small, inexpensive proton radiotherapy system could be realized. Computer calculations and experimental measurements performed using the proton tubes demonstrate that lethal radiation doses can be delivered to a sphere of tissue 6.2 mm diameter in only 100 seconds using an 800 keV, 1 microampere, ^3He ion beam. Discussions with medical researchers at University of New Mexico and University of Texas Southwestern

Medical Center have suggested several applications for the new device. A patent application for the micro-radiosurgery device is currently being submitted by Sandia.

Significance -- Since first disclosure of this technique in November 1992, medical clinicians have suggested that this controlled, switchable source of radiation could be used for skin cancers, tumors on delicate structures that preclude operative solutions (such as vocal chord tumors), and other surgically inaccessible tumor sites. One of the most unexpected applications suggested involves a technique called inter-operative radiotherapy (IORT). IORT is normally conducted after the surgical removal of a large tumor from within the body; radiation exposures are performed, in vivo, in order to kill any isolated cancer cells left behind in the healthy tissue. Performing this radiation exposure normally requires that the patient be temporarily sutured and then transported to the local radiation facility - invariably in the basement of the hospital due to shielding requirements. Owing to the compact nature of the micro-radiosurgery radiation source, it is envisioned that IORT could alternatively be performed by wheeling a sterilized system into the operating theater so that radiative treatment of the tumor area could be performed in a much more controlled environment with far less risk to the patient. Such a compact, portable system could also be used for dermatological applications in a doctor's office setting to treat skin lesions with fractionated radiation treatments that would minimize or eliminate scarring.

Keywords: radiation therapy, cancer, ^3He , protons

Contact: Kevin M. Horn, Radiation Effects Experimentation Department 9351
Phone: (505)845-7944
Fax: (505)845-3471
E-mail: kmhorn@sandia.gov

The micro-radiosurgery technique can be used for the topical radiation treatment of tumors using proton transmission through air gaps. This radiation pattern is calculated for a 1 sec exposure of a 1milliamp, 800 keV ^3He ion beam in the micro-radiosurgery proton-tube.

Heavy Ion Backscattering Spectrometry is Setting Record Sensitivities because of a New Time-of-Flight Detector

by J. A. Knapp and J. C. Banks

Motivation -- With new generations of electronic devices reaching ever smaller dimensions, substantially decreased contamination levels are required in both materials and processes. Reliably quantifying the required cleanliness is straining the capabilities of available diagnostics. Heavy Ion Backscattering Spectrometry (HIBS), invented and patented at Sandia, is an analysis tool for measuring surface contamination which has already demonstrated sensitivity better than Total-reflection X-Ray Fluorescence (TXRF) for most elements. Furthermore, HIBS is standardless and has no matrix effects, measuring all elements above Ar with sensitivity increasing with atomic number. HIBS uses relatively low-energy, heavy ions for backscattering analysis, taking advantage of the increased yield which can be obtained by using high Z ion beams at lower energy. Background due to increased yield from the substrate is eliminated by a thin carbon foil in front of the detector, with a thickness chosen to range out ions scattered from the substrate and allow only ions scattered from impurities heavier than the substrate to reach the detector.

Accomplishment -- The time-of-flight detector for HIBS which has been developed gives substantially better mass resolution and sensitivity than our original HIBS detector, which used a Si surface barrier detector for measuring the backscattered particle energy. The new detector is optimized for large solid angle, unlike all previous time-of-flight detectors used in ion

beam analysis. Two versions were constructed this year, with the first fitting into our existing HIBS analysis chamber, while the second version was installed in a larger chamber specifically built to accommodate it. The second version uses 50 ohm collection fixtures, which take up considerably more room in the vacuum chamber. The second version has much better resistance to noise and eliminates spectral artifacts due to electronic ringing. With other improvements in electronics and shielding of stray ions scattered around the chamber, the new detector has allowed us to achieve sensitivities of $\sim 5 \times 10^8$ atoms/cm² for Au on Si and $\sim 5 \times 10^{10}$ for Fe. The mass resolution at low Z is now sufficient to separate Fe and Cu, which the solid-state-based detector was not able to do.

Significance -- The new time-of-flight detector is used in our research HIBS system, and the design is the basis for the detectors in a prototype stand-alone HIBS system which we are building under a CRADA agreement with SEMATECH. This latter system, with three parallel detectors, is expected to achieve detection limits of $\sim 5 \times 10^9$ atoms/cm² for Fe and $\sim 1 \times 10^8$ atoms/cm² for Au on Si. This sensitivity, especially for higher Z, is better than any tool now available to the microelectronics industry. The system will demonstrate the feasibility of using HIBS in a microelectronics fabrication environment, and serve as a user facility for SEMATECH member company researchers, both for contamination studies and as a calibration for other tools.

Keywords: ion beam analysis, microelectronics, contamination

Contact: James A. Knapp, Ion Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-2305
Fax: (505) 844-7775

HIBS spectra obtained from Si contaminated with three levels of Ni. Br and Sb contaminants were missed by TXRF.

Ion Irradiation Strongly Enhances the Vortex Pinning Potential of High-Temperature Superconducting YBa₂Cu₃O₇- Thin Films

by E. L. Venturini and M. P. Siegal

Motivation -- Several promising applications of high-temperature superconducting thin films require large current densities in high magnetic fields at liquid nitrogen temperatures. However, under these operating conditions, i.e., a strong Lorentz force (current density $\times$ magnetic field) plus significant thermal energy, there is substantial energy dissipation due to the rapid motion of magnetic vortices (giant flux creep). The solution to this problem is to understand and exploit those physical mechanisms which produce strong vortex pinning to suppress the motion. We are exploring the effects of high-energy ion irradiation on pinning energies in single crystal-like YBa₂Cu₃O₇ (YBCO) epitaxial thin films utilizing a combination of magnetic hysteresis loops and magnetization relaxation in the superconducting state.

Accomplishment -- Thin (100 nm) YBCO films grown on (100) LaAlO₃ substrates using the *ex situ* BaF₂ process exhibit exceptional crystallinity as determined by ion channeling and superconducting properties. In particular, the dependence of critical current density J_c on temperature and magnetic field is comparable to that in YBCO single crystals. Hence, these films are ideal materials to establish the potential enhancement of J_c and vortex pinning energies due to defects introduced by high-energy ion irradiation.

The figure shows the dramatic increase in the effective pinning potential in a 1 tesla magnetic field as a function of the superconducting current

density following ion irradiation by 2 MeV Xe⁺ ions to a total fluence of 1×10^{12} per cm². TRIM calculations indicate that this irradiation introduces both clusters and point defects at a concentration of 2.5×10^{20} defects/cm³. In contrast, irradiation with 2 MeV H⁺ to a fluence of 1×10^{16} per cm² generates only point defects and leads to a much smaller enhancement in the pinning potential.

Significance -- Understanding and controlling vortex pinning is one of the major challenges in several applications of high-temperature superconductors. The energy dissipation at a given current density and temperature varies exponentially with the ratio of the effective pinning potential to the thermal energy. Using data in the figure, for a practical current density of 1×10^6 A/cm² and a magnetic field of 1 tesla, Xe⁺ irradiation has increased the pinning potential from 400 to 700 K. Hence, the dissipation at 77 K is reduced by a factor of 50, while that at 40 K is reduced by nearly 2000. Further, comparison of changes in the pinning potential following H⁺ and Xe⁺ irradiations suggests that damage clusters are preferable to point defects. We will continue to explore this issue by examining the effects that artificially engineered, nanometer-sized "holes" have on vortex pinning in superconducting thin films. Our goal is to identify a practical process for enhanced pinning.

This work involved a collaboration with S. Y. Hou, Julia M. Phillips and A. E. White at AT&T Bell Labs.

Keywords: high-temperature superconductivity, vortex pinning, critical current density, ion irradiation.

Contact: Eugene L. Venturini, Advanced Materials Physics & Device Research Dept. 1153
Phone: (505) 844-7055
Fax: (505) 844-5459
E-mail: elventu@somnet.sandia.gov

Xe⁺ irradiation enhances the vortex pinning potential.

Ion Beam Analysis has found many important uses in Magnetic Fusion Energy Technology

by D. S. Walsh, B. L. Doyle and W. R. Wampler

Motivation -- Ion beam analytical (IBA) techniques can be important tools for the assessment of magnetic fusion energy technology. Various problems ranging from basic material properties to the manufacturing and performance of components for fusion devices continue to be addressed by the wide variety of IBA techniques available at Sandia.

Accomplishment -- IBA has been applied to several magnetic fusion energy problems in the past year. Analysis of erosion experiments on the DIII-D DIMES probe and the detection of high Z metal contaminants and tritium in DIII-D, measurements of deuterium retention in several components from the TEXTOR and DIII-D tokamaks - including the first Mo limiter used in a major fusion device, and the examination of a CREARE manufactured microchannel He flow cooling fixture following its failure during a high heat flux test here at Sandia are several program highlights.

Significance -- The tritium measurements of the DIII-D DIMES probe are the first on any DIII-D components. We now have measurements of tritium retention in tokamak first walls of the JET, TFTR and DIII-D tokamaks. Since the closure of the Tritium Research Lab (TRL) at Sandia our measurements are providing the only data for tritium retention in the fusion community.

In addition to the main goal of measuring erosion, IBA of the DIMES probe also detected the presence of Nb as a contaminant in DIII-D. This had been suspected by researchers at DIII-D but never before confirmed.

Ex-vacuo IBA (X-IBA) of the TEXTOR Mo limiter head showed that very little deuterium was retained in the limiter despite expectations that the siliconization of TEXTOR might increase deuterium retention. Further examinations of Mo and C limiters from the tokamak are planned to more closely study the effect of siliconization on the first wall.

CREARE designed and manufacturing an actively cooled first wall component which uses He flow through multiple Cu microchannels to cool a plasma exposed surface. The initial unit performed poorly during Sandia's high heat flux tests. X-IBA of the CREARE unit showed melted regions near the edges of the cooling fixture where subsurface metals had exuded through ruptured brazes to the surface. The information will be used to improve future active cooling designs using He as the primary coolant - a program which is currently considered very important to future of magnetic fusion energy.

Keywords: ion beam analysis, magnetic fusion energy, deuterium, tritium, metals, DIII-D, TEXTOR, CREARE

Contact: David S. Walsh, Idaho State University Contract Scientist, Ion Solids Interactions & Defect Physics Department 1111
Phone: (505)844-9590
Fax: (505)844-7775

The external-beam apparatus for in-air ion beam analysis of fusion reactor components. The system can currently be configured for either NRA, RBS or PIXE analyses and includes automated 3-dimensional mechanical scanning of the target

Hydrogen Retention at Radiation Damage in Graphite Depends on Both Composition and Microstructure

by W. R. Wampler and B. L. Doyle (Sandia National Laboratories) and
V. N. Chernikov, A. E. Gorodetsky, S. L. Kanashenko and A. P. Zakharov
(Russian Academy of Sciences, Moscow)

Motivation -- Graphite is the most widely used material for plasma contacting components in magnetic confinement fusion plasma experiments. The next generation of fusion reactors, now being designed, requires new materials, in part because of effects of irradiation by fusion neutrons. Retention of hydrogen isotopes in plasma facing components is a critical issue because it influences plasma fueling and tritium inventory in the first wall. Our previous work has shown that lattice damage in graphite greatly increases retention of hydrogen. Two new graphites, made in Russia, have improved properties for fusion applications. USB, containing boron, has low hydrogen retention, and RGT containing titanium, has high thermal conductivity. In recent experiments, conducted jointly with the Russian Academy of Sciences in Moscow, we have examined the influence of radiation damage on hydrogen retention in several graphites including USB and RGT. Comparison between the D retention in the various types of graphite with their differing compositions and crystalline microstructures indicates D is retained at strong traps associated with lattice damage, and that transport of D to the traps may be restricted by the microstructure in some graphites.

Accomplishment -- Samples of several types of graphite were irradiated with carbon ions to simulate lattice damage by fusion neutrons. The samples were exposed to D₂ gas at 1200°C to simulate exposure to a fusion plasma. The

concentration of D retained in the graphite was then measured using D(³He,p)α nuclear reaction analysis. The figure shows the concentration of retained D versus C⁺ ion dose (bottom scale) and the corresponding damage in displacements per atom (top scale). D retention increased with damage at low doses, but saturated at damage levels above ~ 1 dpa. D retention was much lower in USB, which contains 15 wt.% B, than in graphites containing no boron (solid symbols). Also, RGT with 0.5 wt.% B retained less D than RGT without B. These results show that the presence of boron reduces retention of D at radiation induced defects in graphite. Transmission electron microscopy shows that microstructure is also an important factor for D retention. In some graphites, such as USB and highly oriented pyrolytic graphite, D must diffuse normal to the graphite basal planes to reach some of the traps. Since diffusion of hydrogen in this direction is difficult in graphite, transport of D to the traps may be restricted by the microstructure in such materials.

Significance -- These results provide information needed to assess effects of hydrogen retention in first wall materials in a fusion reactor, and suggest ways to further improve materials. Addition of boron to RGT, or to carbon fiber composites, may alleviate hydrogen retention problems while maintaining favorable high strength and thermal conductivity. Another approach would be to use multilayered materials which could combine the best properties of USB and RGT.

Keywords: fusion energy, advanced materials, graphite, radiation damage, tritium

Contact: William R. Wampler, Ion-Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-4114
Fax: (505) 844-7775
E-mail: bldoyle@sandia.gov

High-Temperature Phase Equilibria Established for Tl-Ca-Ba-Cu-O Superconductors

by T. L. Aselage and E. L. Venturini

Motivation -- The chemistry of the Tl family of cuprate superconductors, in which at least eight different superconducting phases are found, is quite complex. The high-temperature synthesis of a particular phase and the properties of the superconductors are sensitively related to the ambient partial pressures of both thallous oxide and oxygen, $P(\text{Tl}_2\text{O})$ and $P(\text{O}_2)$, and to the cation stoichiometry and temperature of the samples. We have designed and implemented a two-zone furnace system, in which independent control of each of these variables is achieved. In particular, an independently regulated thallium oxide source allows us to accurately control $P(\text{Tl}_2\text{O})$.

Accomplishment -- We have identified stable ranges of thallium oxide source temperatures and $P(\text{O}_2)$ for the synthesis of the important superconductors. Our calculation of the vapor pressure of Tl_2O over the source as a function of temperature and $P(\text{O}_2)$ has allowed us to construct phase diagrams such as that shown in the accompanying figure. This figure, appropriate for a batch composition of Ca:Ba:Cu of 1:2:2, illustrates the critical nature of $P(\text{Tl}_2\text{O})$ control during synthesis. Based on similar diagrams for other batch compositions, we

predicted and experimentally verified the stability of the 2223 phase in 1 atm. of O_2 . This result established that low $P(\text{O}_2)$ was not crucial to prepare 2223, in contrast to the existing literature. The decreasing stability of the 1122 phase with decreasing $P(\text{O}_2)$ evident in Figure 1 appears to be a general feature of all phases with single Tl-O rocksalt layers. We have developed a qualitative understanding of the sensitivity to $P(\text{Tl}_2\text{O})$ and $P(\text{O}_2)$ based on the relative thallium content and formal oxidation state of the cations within the crystal. The superconducting transition temperatures of our equilibrated samples are reproducible to within about ± 1 K.

Significance -- High superconducting transition temperatures, low surface resistances in thin films, and good flux pinning properties are observed in some Tl superconductors. These properties are responsible for increasing interest in potential electronic device and bulk conductor applications. Reproducible processing of these materials remains a difficult hurdle, however. Our results should enable those engaged in the synthesis of bulk materials and thin films to reproducibly synthesize the technologically important superconductors.

Keywords: thallium superconductors, cuprates, phase diagrams

Contact: Terry Aselage, Advanced Materials Physics and Device Research Department 1153
Phone: (505) 845-8027
Fax: (505) 844-5459
E-mail: tlasela@somnet.sandia.gov

Equilibrium $P(\text{Tl}_2\text{O})$ - $P(\text{O}_2)$ diagram, $\text{Ca:Ba:Cu} = 1:2:2$

Improved Single Crystal Growth of Tl-containing Superconductors has been Achieved

by B. Morosin and E. L. Venturini

Motivation -- The intrinsic properties and anisotropy of superconductors can only be evaluated using single crystals, preferably of high perfection. In the case of the Tl-containing materials, different phases exist which depend on the ratio of both Tl-O and $\text{Cu}_n\text{Ca}_{n-1}\text{O}_{2n-1}$ layers in their stacking sequence. Crystal growth is achieved via a pseudo-flux technique for which parameters are currently not well established. Further, electrical transport and magnetization studies of superconducting and normal-state properties require large, high-quality plates.

Accomplishment -- Initial growth studies employed mixtures of the oxides (Tl_2O_3 , BaO, CaO & CuO) in various stoichiometries to form the different structural phases. Reproducibility was very poor even when growth parameters were idealized. More recently precursor powders without the Tl_2O_3 have been prepared and these are then reacted with the appropriate amount of Tl_2O_3 in a modified pseudo flux method. Although yield is still not very high, crystals grown to date show transition temperatures which

are much sharper (see figure) than our old growth procedure and which agree more closely with those obtained with our bulk ceramic studies. Such Meissner signatures suggest the present crystals are of much better quality. Several growth parameters still require refinement for the Tl-Ba-Ca-Cu system before those substituting some Sr for Ba and some Pb for Tl are examined. The latter systems may have better superconducting properties because of the reduction of the separation distance between the superconducting planes. This reduction increases the coupling along the crystallographic c-axis, leading to less anisotropy in the superconducting properties.

Significance -- The present modified growth technique appears to provide better quality single crystals to establish the intrinsic properties of various phases of the Tl-containing superconductors. These properties will serve as the bench mark goals for our film growth program, yielding parameters which govern various device applications.

Keywords: superconductors, crystal growth, intrinsic properties, anisotropy.

Contact: Bruno Morosin, Advanced Materials Physics & Device Research Department 1153
Phone: (505) 844-8169
Fax: (505) 844-5459
E-mail: bmorosi@sandia.gov

Our improved, modified psuedo flux growth technique has yielded crystals with a “sharp” Meissner signature as shown for a Tl-2212 single crystal.

Pressure Tuning Determines the Orientational Order and Phase Transitions in Solid C₆₀ and C₇₀

by G. A. Samara, B. Morosin and J. E. Schirber

Motivation -- The identification of the molecular structures of C₆₀ and C₇₀ and their subsequent synthesis and separation have generated tremendous interest in these exciting forms of carbon. Currently broad research efforts are being aimed at determining and understanding the properties of these van der Waals solids and at identifying potential applications. Detailed knowledge of the orientational and rotational properties of the molecules in the solids and of the orientational ordering transitions in both crystalline C₆₀ and C₇₀ are necessary. We have recently shown that high pressure allows the delicate and continuous tuning of the strength of the intermolecular potentials and rotational barriers which control the motions of the molecules. Thus, pressure results can provide new insights into the ordering process as well as vital data for testing proposed intermolecular potentials and models for the transitions.

Accomplishment -- We have studied the pressure dependence of the ordering transitions of C₆₀ and C₇₀ using several pressure-transmitting media including He and N₂. In C₆₀ the transition (T_c≈250K) is from the orientationally disordered fcc phase to a simple cubic phase where the soccerball-shaped C₆₀ molecules are orientationally ordered. The behavior of C₇₀ which consists of elliptical rugby ball-shaped molecules is more complex. In this case we observe two transitions. At the first (T_{c1}≈360K), the free random rotations of the molecules are reduced to free rotations around their long axes, and at the second transition (T_{c2}≈280K) these

latter rotations freeze out resulting in an orientationally ordered phase. Highlights of the work include: (1) Lattice compression hinders the librational motion of the C₆₀ and C₇₀ molecules in the low-temperature phases thereby increasing T_cs and stabilizing the ordered phases; the effects are larger for C₇₀ as expected (figure). (2) The T_cs and their pressure dependences are influenced by the presence of ambient species in the interstitial lattice sites. He diffuses readily into the two lattices whereas N₂ (and O₂) do not on the time scale of the experiment accounting for the large difference in slopes between He and N₂ (figure). (3) A two-peak structure in differential thermal analysis spectra was observed at each transition and is believed to be due to the partial occupancy of the interstitial sites by species such as N₂ and O₂. This occupation hinders molecular rotations and results in nearly degenerate orientational configurations in both solids.

Significance -- The temperature-pressure phase diagrams of solid C₆₀ and C₇₀ have been determined and compared. A significant finding is the large influence of interstitial species and of the pressure transmitting medium on the orientational ordering processes. The pressure results reveal different, nearly degenerate configurations in both solids, which are believed to be due to hindered molecular rotations by interstitial species, and possibly different stacking modes in C₇₀. These results are already being used by theorists to test models, and they have also shed considerable light on the potential use of these solids as gas storage and separation media.

Keywords: fullerenes, orientational order, phase transitions, high pressure

Contact: George A. Samara, Advanced Materials Physics & Device Research Department 1153
Phone: (505) 844-6653
Fax: (505) 844-4045
E-mail gasamar@somnet.sandia.gov

Gas Separation is Possible with C₆₀ "Lattice Sieves"

by J. E. Schirber, R. A. Assink, B. Morosin and D. Loy

Motivation -- Gas separation is an important technology. A recent DOE study of membrane separation systems cites potential savings of up to 1 quad/year with improved techniques and results in \$4.5M/year in DOE research in this area. Of particular interest is the separation of O₂ from N₂, and H₂ and He from other gases. Most filters involve polymers which by their nature have a spectrum of pore sizes. Fullerenes crystallize into relatively simple lattices which because of the large 10Å diameter of the molecules, have high, but precisely defined vias. These "lattice sieves" show potential for separation of technologically important gases.

Accomplishment -- We have studied the interaction of various gases with C₆₀ and discovered substantial differences in the diffusion and permeation in C₆₀ of these gases at room temperature. For example, using ¹³C magic angle spinning NMR techniques we have shown that O₂ easily penetrates the C₆₀ lattice and resides in the octahedral interstices leaving the tetrahedral sites vacant. Using high pressure gas techniques uniquely available in our laboratories, we have loaded large amounts of various gases such as H₂, N₂, CH₄ and O₂ into C₆₀ materials of various grain sizes and measured the subsequent emission of these gases upon release of the pressure. In addition to the NMR techniques mentioned above which are appropriate for studies of H₂ and O₂, weight loss measurements as a function of time have been used to measure diffusion and

permeation from which separation factors between various gases can be estimated. Our preliminary results indicated a separation factor of about a factor of 3 between O₂ and N₂. However, these results are complicated by problems of reactivity of O₂ with C₆₀, particularly in the presence of ultraviolet radiation. Very large separations of H₂ and He from N₂, O₂ or air appear to be quite feasible. We also have observed some intriguing "negative pressure" effects, particularly with O₂ in which the ordering temperature between the fcc and primitive cubic structures is substantially depressed. This is of considerable fundamental interest and may have practical implications with respect to the temperature at which an actual separation system might be utilized.

Significance -- Our preliminary results indicate great promise for C₆₀ and higher order fullerenes (which will allow tailoring of pore sizes) as lattice sieves for practical gas separation. This could have a large impact on energy conservation because of the large amounts of energy expended in gas separation. For example, separation of O₂ from N₂ while straightforward by cryogenic techniques expends 0.25 quad a year. It has been demonstrated by AT&T that free standing films of C₆₀, fractions of a square cm in area and only 2000 Å thick, can be fabricated. Our requirement of films of such thickness on porous substrates would seem to be relatively modest.

Keywords: gas separation, fullerenes

Contact: J. E. Schirber, Research Scientist for Solid State Science Department 1002
Phone: (505) 844-8134
Fax: (505) 844-4045
E-mail: jeschir@sandia.gov

Cut away of face centered cubic array of spheres. The cube face or 100 plane exposes the octahedral sites while the 111 plane exposes the tetrahedral sites. The octahedral sites are of the order of $4\text{\AA}$ in diameter and the tetrahedral, $2\text{\AA}$ so various gases can easily permeate this lattice.

*Phonon-Mediated Attraction Between Large Bipolarons Can Lead to
Formation of Charged Bose Liquid*

by D. Emin

Motivation -- Evidence that the charge carriers in superconducting oxides are mobile polarons or bipolarons that condense into a liquid grows. These observations prompt one to ask how the attraction required for liquid formation can arise between quasiparticles of like sign.

Accomplishment -- Through their polarizabilities, I find that large bipolarons reduce the atomic vibrational frequencies. This effect lowers the zero-point energy of the solid. The lowering of the zero-point energy of a given mode increases as the separation between bipolarons is decreased relative to the phonon wavelength. This effect constitutes a phonon-mediated attraction between bipolarons. The net

interaction energy between bipolarons has been calculated. The phase diagram for large bipolaron's condensation into a liquid is then obtained. Since the low-energy excitations of a charged liquid satisfy the Landau criterion for resistanceless flow in the groundstate, superconductivity occurs with the Bose condensation of the liquid into its ground state.

Significance -- A mechanism through which large bipolarons can condense into a liquid has been identified and developed. Since evidence of large bipolarons and liquid formation has been found in the oxide superconductors, this work may describe the mechanism for their superconductivity.

Keywords: bipolarons, superconductivity

Contact: David Emin, Advanced Materials Physics and Device Research Department 1153
Phone: (505) 844-3431
Fax: (505) 844-5459
E-mail: demin@sandia.gov

Left Figure: The interaction between bipolarons of radius R separated by the distance s , $V(s/R)$, is found to be the sum of a short-range repulsion and a phonon-mediated attraction.

Right Figure: Large bipolarons of volume V form a liquid at sufficiently low temperatures within a range of their concentrations.

Photoluminescence from Porous Silicon has been Related to Particle Size Measured in K-Map X-Ray Diffraction

by J. C. Barbour, S. R. Lee, J. S. Custer and J. W. Medernach

Motivation -- Visible light photoluminescence (PL) from electrochemically prepared porous silicon (PS) has excited technical interest because of its potential use in optical displays requiring light from blue to red (400 to 800 nm). Scientifically, interest in PS stems from the desire to understand the luminescence mechanism and its possible relationship to sample microstructure (which is also not well understood). One of the leading mechanisms proposed for luminescence assumes the PS contains a microstructure of small Si columns or possibly particles which act as quantum wells causing carrier confinement. The modification of band structure from quantum size effects is thought to produce an optical bandgap (~2-eV) suitable for visible light emission.

Accomplishment -- This work examined several categories of PS and related the PL signal to distributions of particle sizes measured by K-map x-ray diffraction. Three characteristic types of reciprocal space maps (K-maps shown at right) were observed for each of 13 samples. Analysis of the upper figure indicates that this PS is composed of highly oriented columnar structures which are 30-60 nm wide and 200 nm long. This size structure is inconsistent with quantum confinement and accordingly no PL was found.

The samples corresponding to the center figure exhibited weak but broad PL signal (peak position = 700 nm) suggesting a wide diversity in particle sizes. In comparison, this K-map shows more diffuse rings than the rod shape in the top figure; and the outermost ring indicates the sample is dominated by particle sizes of 10-50 nm. This size is too large for quantum confinement, but the low PL intensity suggests that the signal may only originate from a minor component of the film. The strongest PL signal (320 times larger signal, also peaked at 700 nm) originated from samples with the most diffuse rings (bottom K-map) which extend farther in reciprocal space (smaller particle sizes). Analysis suggests that the particle sizes vary from 2-4 nm which in accordance with quantum confinement produces PL emission from 620-820 nm, as observed.

Significance -- This K-map work is a significant step toward the development of a technique to understand the mechanism and the regions of a film which give rise to PL. Further, this technique will enable the optimization of processing parameters to obtain the most efficiently luminescent porous silicon.

Keywords: advanced materials and technology, porous silicon, photoluminescence, x-ray diffraction

Contact: J. Charles Barbour or Steve R. Lee, Ion Solid Interactions & Defect Physics
Department 1111
Phone: (505) 844-5517 or (505) 844-7307
Fax: (505) 844-7775

Strong Quantum-Size Effects Observed in a Layered Semiconductor: MoS₂ Nanoclusters

by J. P. Wilcoxon and G. A. Samara

Motivation -- Clusters are an exciting class of materials intermediate between atoms and molecules on the one hand and bulk materials on the other. They exhibit size-dependent physical and chemical properties a consequence of the confinement of their electrons and their unusual surface morphology. Recent research is aimed at understanding the evolution of cluster properties with cluster size. Especially interesting are the manifestations of electron and hole confinement in semiconductor clusters as the cluster size decreases below the excitonic Bohr radius, and the electronic band structure gives way to discrete molecule-like electronic states. In the present work we have studied these effects in semiconducting MoS₂. Our choice of MoS₂ was motivated by both scientific and applied interest. On the scientific side, bulk MoS₂ crystallizes in a layered structure composed of S-Mo-S sandwiches held together by weak van der Waals forces. A number of questions were of interest: Will nano-meter size clusters of MoS₂ form? Can cluster size be controlled? Will such clusters exhibit strong electron confinement effects? We are interested in the potential of MoS₂ as a hydrogenation catalyst and as an electrode material for photoelectrochemical solar cells. In both applications, clusters have significant advantages over bulk material.

Accomplishment -- Using our patented synthesis technique in which clusters are grown inside inverse micellar cages, we have successfully grown size-selected MoS₂ clusters varying in size from 2 to 15 nm in diameter and studied their optical properties. The figure shows

the optical absorption spectra of 4.5 and 2.5 nm clusters. The spectrum of the 4.5 nm clusters is remarkable in the richness of its spectral features which have a one-to-one correspondence to excitonic features in the spectrum of bulk MoS₂ except that the cluster features are blue shifted by 0.78 eV due to size confinement. This result is consistent with the fact that these clusters are somewhat larger than the size of the exciton (2 nm radius) in the bulk. The spectrum of 2.5 nm clusters is qualitatively different from that of the 4.5 nm clusters and of the bulk crystal. For the 2.5 nm clusters, the excitonic features in the spectrum give way to a ladder of three well-defined peaks. This is the expected behavior in crossing over from the weak (excitonic) confinement regime to the strong (free-carrier) confinement regime where the cluster size (in this case $R = 1.25$ nm) is considerably smaller than the excitonic radius. For these very small clusters there simply is not sufficient density of states in the conduction and valence bands to observe excitonic features, and the allowed energy levels change from essentially continuous bands to a ladder of discrete levels as in molecular systems.

Significance -- We have demonstrated for the first time large blue shifts in the optical absorption (and emission) with decreasing cluster size for the layered semiconductor MoS₂ thereby affording great tailorability of the band gap and the ability to optimally match the solar spectrum. In a separate study these MoS₂ clusters have resulted in significantly enhanced catalytic activity in coal hydrogenation.

Keywords: nanoclusters, optical absorption, quantum confinement

Contact: Jess P. Wilcoxon, Advanced Materials Physics & Device Research Department 1153
Phone: (505) 844-3939
Fax: (505) 844-5459
E-mail: jpwilcox@sandia.gov

***Midwave (4 μm) Infrared Emitters have been Demonstrated with
Biaxially Compressed InAsSb Active Regions***

by R. M. Biefeld, S. R. Kurtz and K. C. Baucom

Motivation -- Strained InAsSb heterostructures offer the promise of new III-V based, infrared detectors and emitters. As-rich InAsSb heterostructures may display unique electronic properties that are beneficial to infrared emitter performance. The heavy-hole ground state ($|3/2, \pm 3/2\rangle$) in a biaxially compressed InAsSb layer can increase the in-plane, electron-hole effective mass ratio to $m^*_e/m^*_h = 0.5-0.4$. This effective mass ratio should increase the threshold energy of the dominant Auger process. With this improvement, the wavelength of diode lasers operating at room temperature may be extended from recently demonstrated 2.1-2.3 μm devices in unstrained InGaAsSb to the 3-5 μm range where devices are presently limited by Auger processes.

Accomplishment -- We have prepared the first prototype emitters, an optically pumped laser stripe and a light -emitting diode (LED), constructed from InGaAs/InAsSb strained heterostructures. This chemical system was chosen because of its high photoluminescence (PL) efficiency. The emitters were grown using metal-organic chemical vapor deposition

(MOCVD). Composition control necessary for lattice matching to InAs was achieved through use of a thermodynamic model. Growth conditions were optimized using an iterative procedure to maximize the PL. An SLS light-emitting diode was constructed which emitted at 3.6 μm with 0.06% efficiency at 77 K. An optically pumped, single heterostructure SLS / InPSb laser emitted at 3.9 μm with a maximum operating temperature of approximately 100 K. The performance of our first SLS midwave laser compares favorably with other prototype lasers constructed in these material systems.

Significance -- We have demonstrated the first midwave emitters that utilize biaxially compressed InAsSb. These devices should enable us to construct electrically injected lasers. We anticipate that with improvements in material quality through further MOCVD process optimization, we may soon realize a reduction of Auger rates and higher temperature operation of midwave emitters with biaxially compressed InAsSb.

Keywords: infrared laser, photonics, advanced materials, strained-layer superlattices

Contact: Robert M. Biefeld, Chemical Processing Sciences Department 1126
Phone: (505) 844-1556
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

PL and lasing spectra for an SLS / InPSb "single heterostructure" up to 100 K. The 95 K and 75 K lasing spectra were obtained at lower spectral resolution than the 14 K lasing spectrum. Laser emission occurred at approximately 320 meV (3.9 μm). Emission occurred at higher energy than PL.

*A New Capability for MBE Growth has been Applied to
Bandgap-Engineered Group IV SiGeC Alloys*

by J. A. Floro, E. H. Chason, S. T. Picraux, K. J. Penn, J. W. Strane and H. J. Stein

Motivation -- The ability to mix and match the III-V semiconductor compounds in many clever permutations allows for the development of novel high performance devices through the custom tailoring of optical and electronic properties. Not only are a wide range of optoelectronic properties firmly within the designer's grasp, but the strain is also independently controllable. The versatility of such a bandgap engineering approach in the III-V's is currently unmatched by Si. Attempts to extend these concepts to Si by alloying with Ge have proven fruitful, but are inherently limited by the inability to independently control strain, and because the bandgap can only be narrowed. True Si-based bandgap engineering requires another ingredient in the Group IV mix - carbon (see accompanying figure). SiGeC ternary alloys should allow independent control of strain while tailoring the bandwidth wider or narrower than that of Si. Since the solubility of carbon in Si is only 10^{-3} atomic percent, the real challenge is in the synthesis of this material

Accomplishment -- A Molecular Beam Epitaxy (MBE) system has been brought on line to study the growth of technologically relevant Group IV alloys. MBE offers the ability to precisely monitor and manipulate alloy growth. SiGeC alloy growth will be the first application of the system, which is capable of simultaneous evaporation of up to six materials. Carbon may

alternatively be delivered to the growing film from a microwave plasma source, with athermal kinetic energy which provides further control over metastable growth. *In situ* diagnostics include Reflection High Energy Electron Diffraction (RHEED) for real time surface structure/morphology measurement, and Auger Electron Spectroscopy (AES) to monitor chemical composition of the growing films. The system will handle 2 inch wafers, allowing for subsequent patterning and device processing of the films. Concurrent with system construction, we have performed x-ray, infrared absorption, and TEM studies of alloys grown by ion implantation and solid phase epitaxial regrowth. Single crystal regrowth of SiGeC alloys is obtained for C concentrations up to 1.5%. IR absorption shows the C is substitutional and x-ray shows the strain follows Vegard's law. The alloys are stable to temperatures $> 850^{\circ}\text{C}$.

Significance -- 1) Solid phase regrowth demonstrates the feasibility of C incorporation into Si. 2) *In situ* growth science studies of Group IV alloys can be performed in the new MBE system. 3) Addition of a microwave plasma source provides a novel capability for extending the range of metastable C introduction. 4) Layered film structures with sharp interfaces and controlled compositional grading are possible with this new capability.

Keywords: microelectronics, growth science, silicon bandgap engineering, molecular beam epitaxy

Contact: Jerrold A. Floro, Semiconductor Physics Department 1112
Phone: (505) 844-4708
Fax: (505) 844-9185

Bandgap vs. lattice parameter for the Group IV elements, compared with several of the III-V compounds. The solid line is a guide to the eye.

Pulsed-Laser Deposition has been used to Deposit Diamond-Like Carbon Thin Films

by T. A. Friedmann, M. P. Siegal, D. R. Tallant and F. Dominguez

Motivation -- A major impediment for the use of diamond films in semiconductor device applications has been the lack of a process for the growth of smooth diamond films without the need to polish a substrate surface with diamond grit for the creation of nucleation sites. The nucleation of diamond grains on a given substrate surface is generally the rate-limiting step for growth as well as the advent for rough morphologies (10-15 μm) and poor surface coverage for films < 10-20 μm thick. In addition, diamond films are generally grown at high temperatures (900 $^{\circ}\text{C}$) that are incompatible with most device processing technologies. Diamond-like carbon (DLC), on the other hand, can grow on most surfaces at room temperature without any substrate pretreatment. DLC can be thought of as an amorphous mixture of sp^2 - and sp^3 -bonded carbon atoms with physical and electronic properties intermediate between diamond and graphite.

Accomplishment -- A new pulsed-laser deposition (PLD) system has been assembled for the growth of DLC thin films. An excimer laser ($\lambda = 248 \text{ nm}$) is used to ablate a pyrolytic graphite target under high-vacuum. The energetic carbon

species (12 - 50 eV) generated in the PLD process condense on the cold substrate with a high fraction of sp^3 -bonded carbon atoms. DLC films have been grown on both silicon and sapphire substrates which are maintained at ambient temperatures (< 50 $^{\circ}\text{C}$) during deposition. The resulting films have mirror-like surfaces and are highly-resistive. These films are both relatively hydrogen-free and highly-strained. This strain can be relieved by the use of $\sim 100 \text{ mTorr H}_2$ during film deposition, enabling the growth of much thicker films. However, the C species in the ablated plume are cooled by collisions with the hydrogen gas. Thus, as the gas pressure is increased, the sp^3 fraction in the deposited film decreases, ultimately leading to the deposition of sp^2 -bonded glassy carbon (See Figure).

Significance -- Electronic and optic properties approaching those of diamond in a film material that is both optically smooth and can be grown at room-temperature (therefore, on nearly any substrate material) is expected to impact a wide variety of device programs. This new film deposition capability provides the ability to deposit high quality DLC films and control their structural and electronic properties.

Keywords: advanced materials, microelectronics, photonics, diamond-like carbon

Contact: Thomas A. Friedmann, Advanced Materials Physics & Device Research
Department 1153
Phone: (505) 844-6684
Fax: (505) 844-5459
E-mail: tafried@sandia.gov

KMAP Reciprocal Space Analysis has been Used to Nondestructively Observe the Ordering of III-V Compound Semiconductors

by S. R. Lee, D. M. Follstaedt and R. P. Schneider

Motivation -- Ordered III-V alloys are expected to have unique properties relative to their disordered counterparts. These properties can include substantial reductions of the bandgap and increases in electron mobility. Since ordering may modify the electrical and optical properties of compound semiconductor materials, it is important to be able to characterize both the degree of ordering and the microstructure of ordered materials. TEM is presently the most widely used technique for characterizing ordered compound semiconductors. TEM reliably indicates the presence of ordering, and it can directly image the ordered domains. However, TEM is destructive, labor intensive and does not fully quantify the degree of ordering. We have therefore evaluated KMAP x-ray diffraction analysis as a complementary alternative approach for detecting and characterizing order in III-V alloys.

Accomplishment -- In doing so, we have made the first (to our knowledge) quantitative reciprocal space map of an ordered III-V compound semiconductor. The material analyzed is epitaxial $\text{In}_{0.48}\text{Ga}_{0.52}\text{P}$ grown by MOCVD on GaAs. The upper right adjacent figure shows a TEM diffraction pattern verifying ordering in $\text{In}_{0.48}\text{Ga}_{0.52}\text{P}$. The oblong superstructure spots (circled at $(1/2, 1/2, -1/2)$, for example) are due to

CuPt-type ordering of Group III atoms along $\{111\}$ planes. We performed KMAP reciprocal space scans about the $(1/2, 1/2, -5/2)$ position in order to determine if the KMAP technique is sensitive enough for the investigation of ordered materials. The result is the reciprocal space map of the $(1/2, 1/2, -5/2)$ superstructure spot of ordered $\text{In}_{0.48}\text{Ga}_{0.52}\text{P}$ shown in the lower right figure. Both KMAP and TEM show an unusual "twist" of the elongated reflection to $\sim 8^\circ$ from the $\langle 100 \rangle$ growth direction.

Significance -- Since KMAP produces fully quantitative intensity maps of localized regions of reciprocal space, it may provide an accurate measure the order parameter (i.e., the *degree* of ordering). This parameter has not yet been determined for any of the ordered III-V compound semiconductors. The size and shape of the KMAP intensity distribution also provides quantitative information about the real-space microstructure of the ordered domains. We are presently analyzing and extending the initial measurements reported above in order to obtain a first measurement of the order parameter of $\text{In}_x\text{Ga}_{1-x}\text{P}$. These results will be used to further our understanding of the relationship between materials processing and the resulting band-gap and ordered structure of epitaxial $\text{In}_x\text{Ga}_{1-x}\text{P}$.

Keywords: ordering, microstructure, compound semiconductors, x-ray diffraction, reciprocal space

Contact: Stephen R. Lee, Ion-Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-7307
Fax: (505) 844-7775

The Strength of the Ge-H Surface Bond on Germanium was Determined Through Studies of Internal Microvoids

by S. M. Myers, H. J. Stein and D. M. Follstaedt

Motivation -- The formation of Si-H and Ge-H on the surfaces of Si and Ge and their alloys is important in the growth and passivation of these materials for devices. Although the surface states of the H have been extensively investigated, the strengths of the S-H and Ge-H surface bonds were not previously determined. This situation resulted from two difficulties with external semiconductor surfaces: 1) the complexity of thermal desorption prevents the bond dissociation energy from being deduced from the measured desorption activation energy, and 2) a large activation barrier for dissociative H₂ adsorption prevents observation of equilibrium between the surface and molecular gas under ultrahigh-vacuum conditions.

Accomplishment -- We used internal microvoid surfaces to determine the dissociation energy of the Ge-H monohydride bond on the Ge surface, giving 1.8 ± 0.2 eV. This follows our similar evaluation (with W. R. Wampler) of the Si-H bond energy on the Si surface, giving 2.6 ± 0.1 eV. These determinations were possible because the use of internal surfaces circumvented both of the difficulties with external surfaces discussed above. In particular, 1) thermal release from internal surfaces is controlled by the simply interpretable promotion of H atoms from chemisorption to solution, and 2) diffusion-mediated thermodynamic equilibrium between the internal surfaces and external H₂ gas can be achieved using elevated gas pressures. The

cavities were formed by He ion implantation and annealing and observed by transmission electron microscopy (see figure). The bonding of the H on the internal surfaces was characterized by infrared spectroscopy, and thermal release of the H during heating was observed by nuclear-reaction analysis.

Significance -- 1) Since the binding energy per atom of H in the H₂ molecule is 2.26 eV, our results indicate that the chemisorbed state of H on the Si surface is energetically stable with respect to H₂ gas while the chemisorbed state on Ge is not. 2) The composition of Si-Ge alloys grown from hydrogenated reactants is strongly influenced by the relative difficulties of detaching H atoms from Si and Ge surface atoms, so that knowledge of the Si-H and Ge-H bond strengths should facilitate a more predictive understanding of such growth. 3) The activation barrier for dissociative adsorption of H₂ on Si and Ge was previously not known. It can be shown, however, that the magnitude of this barrier is $E_D - 2E_B + E_R$ where E_D is the previously measured activation energy for recombinative desorption of H₂, E_B is the Si-H or Ge-H bond-dissociation energy measured in this work, and E_R is the dissociation energy of the H₂ molecule. By using the above expression we find that the adsorption activation barrier is about 2.0 eV for Si and 2.4 eV for Ge. These large barriers account for the difficulty of dissociatively adsorbing H₂ on Si and Ge.

Keywords: germanium, silicon, surface, hydrogen

Contact: Sam M. Myers, Semiconductor Physics Department 1112
Phone: (505) 844-6076
Fax: (505) 844-7775
E-mail: smmyers@somnet.sandia.gov

Cross-section TEM of cavities in Ge formed by implanting 1×10^{17} He/cm² and then annealing for 30 min at 973 K.

Theoretical Calculation of the Direct to Indirect Transition in InAlGaP

by J. S. Nelson

Motivation -- The InAlGaP alloy system is one of the most promising materials for visible light emission from red to yellow-green. As the emission wavelength is shortened further into the green by increasing the Al concentration, the material suffers a drastic decrease in emission intensity; at high Al concentrations InAlGaP becomes an indirect gap semiconductor. An accurate estimate of the direct - indirect (Γ -X) crossing with increasing Al concentration is needed to place an upper bound on short wavelength characteristics on the InAlGaP alloy, as well as provide physical insight into alternate band gap engineering schemes to achieve strong green light emission.

Accomplishment -- We have used first principles self-consistent pseudopotential band structure techniques, based on the local density approximation (LDA), to predict the Al concentration dependence of the Γ -X crossing in $\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{P}$. A model of the quarternary alloy based on special-quasi-random structures (SQS's) is utilized to treat the ternary end points,

InGaP and InAlP. The SQS provides a realistic model of the local disordered found in alloy systems, without the need to treat extremely large unit cell representations. Based on a SQS-4 representation of the ternary alloys, the calculations predict a Γ -X crossing at an Al concentration of $x=57\%\pm 5\%$. The dispersion of the X band is found to be much smaller than the Γ band due to its predominant P s-state character; the larger dispersion of the Γ band is a result of its cation (Al, Ga, and In) s-state character.

Significance -- This study has provided a more complete atomic level understanding of the direct - indirect transition in InAlGaP. Work is currently under way to apply this knowledge to optimize the short wavelength properties of InAlGaP, in hopes of increasing the intensity of light emission in the green portion of the visible spectrum. Such advances would have significant impact through new light emitters diode as compact and highly efficient light sources for display and related applications.

Keywords: microelectronics, photonics, computational material science

Contact: J. S. Nelson, Semiconductor Physics Department 1112
Phone: (505) 844-4395
Fax: (505) 844-1197
E-mail: jsnelso@cs.sandia.gov

Calculated band gap of $\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_y\text{P}$ versus Al concentration x . The upper set of curves is the corrected local density approximation (LDA) results. The direct to indirect transition occurs at an concentration of 57%.

SiGeC Alloys Stability Shown to be Sufficient for Device Processing

by J. W. Strane, H. J. Stein, S. R. Lee and S. T. Picraux

Motivation -- Si-based technology continues to dominate the semiconductor industry due to its inherent processing advantages and maturity. Silicon's prominent role could be greatly extended if the success in building bandgap engineered heterostructure devices using the III-V compounds could be transferred to the Group IV's. True Si-based bandgap engineering is possible if SiGeC ternary alloys can be successfully grown and incorporated into devices. SiGeC alloys offer independent control of lattice parameter and bandgap (not possible using SiGe binary alloys). Since the solubility of carbon in Si is only 10^{-3} atomic percent, the alloys of interest with of order 1%C must be sufficiently stable to not precipitate out the C during processing.

Accomplishment -- $\text{Si}_{1-y}\text{C}_y/\text{Si}$ and $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ heterostructures with C contents over three orders of magnitude higher than equilibrium values have been formed using ion implantation followed by solid phase epitaxial regrowth. The stability of these heterostructures to thermal treatment was studied to determine process limitations in device fabrication. During 30 min. anneals to temperatures below 800°C, the heterostructures do not exhibit any loss in stability. During high temperature anneals the

alloy layers or $\text{Si}_{1-y}\text{C}_y$ and $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ equilibrate by precipitation of SiC. The aligned but incoherent interfaces between the diamond host lattice and the carbide precipitates allow the strain due to the C in the alloy to relax. The thermal activation energy of the precipitation process was determined using a time to 50% loss in substitution C measured by absorption measurements on the localized vibrational mode of C in Si (figure 1). The activation energy of 3.3±0.5 eV corresponds closely to the diffusion of C in Si (3.1 eV). Rapid thermal annealing was used to investigate the stability at higher temperatures. At 1000°C, the heterostructures behaved as expected from the lower temperature furnace anneals (figure 1). At still higher temperatures (1075°C and above), there was no residual C after anneals as short as 30 seconds.

Significance -- These results provide the necessary information to predict the loss of stability for SiGeC alloys as a function of time and temperature for both furnace and rapid thermal annealing (RTA) treatments. They indicate that sufficient stability exists to meet the processing requirements of such current high performance Si devices and heterostructures bipolar transistors. These materials thus look promising for continued development.

Keywords: silicon, semiconductor materials, bandgap engineering

Contact: H. J. Stein, Ion Solid Interactions and Defect Physics Department 1111
Phone: (505) 844-6279
Fax: (505) 844-9185

One Nonlinear Electrical Phenomenon in RF-Excited Plasmas has been Explained and Controlled

by P. A. Miller, L. R. Romero and P. D. Pochan

Motivation --Electrically excited plasmas are widely used in the manufacture of microelectronic circuits. Previous workers have largely ignored the electrical nonlinearity of the voltage-vs.-current characteristics of plasmas. Recent industrial results have demonstrated the importance of nonlinear interactions between the plasmas and their rf power supplies. However, little is presently understood in detail of the use, control, or mitigation of most such phenomena.

Accomplishment -- One important nonlinear phenomenon is "period doubling" and the accompanying generation of subharmonics of the excitation frequency. This consists of an alternation between two states of the plasma on successive cycles of the excitation waveform. This behavior is a fundamental mathematical property of essentially all dynamical systems with two or more degrees of freedom, and it is generally a precursor to chaos. Period doubling (PD) has occurred in plasma etching reactors in industry and in Sandia's Microelectronics Development Laboratory (MDL), but we were the first to appreciate the source and nature of the phenomenon. In a typical reactor excited at 13.56 MHz, PD occurs above some threshold power level. Thus, PD is most often encountered as engineers attempt to increase reactor throughput by raising reactor power. PD is associated with signal generation at 6.78 MHz and integral multiples thereof. Problems arise because, at the onset of PD, many unexpected changes occur in the process, such as changes in dc bias, etch rate,

and optical emission (used for endpoint detection in etching). We first diagnosed the occurrence of PD in an industrial reactor in the MDL. We then developed an analytical model of the key aspects of plasma behavior that cause PD. Based on model predictions, we modified a laboratory research reactor to lower the threshold power for PD so that we could study period doubling in detail in our research laboratory. Using the modified laboratory reactor, we demonstrated that our model was essentially correct and that we could understand and control period doubling. Control is achieved by modifying the frequency-dependent resistive and reactive components of the impedance of the rf circuitry that couples power to the plasma (i.e. "tuning" the circuitry). PD has the lowest threshold if the circuit is resonant at the subharmonic frequency and has low losses.

Significance -- We now are in a position to exploit in two different ways the understanding gained from the model and the laboratory experiments. First, we know how to suppress PD in systems in which its presence is undesirable. Second, we can induce PD (and also higher levels of period multiplication) to achieve different processing conditions that may yield superior process performance. This second approach is equivalent to expanding the dimensionality of control space and, thus, provides an important opportunity for taking advantage of electrical nonlinearity.

Keywords: period-doubling, subharmonics, plasma, etching, nonlinearity, control

Contact: Paul A. Miller: Laser, Optics and Remote Sensing Department 1128
Phone: (505) 844-8879
Fax: (505) 844-3211
E-mail: pamiller@somnet.sandia.gov

Threshold of PD for different gases and pressures when rf circuits were tuned to induce PD. Although we understand the tuning techniques and behavior, we do not understand in detail the pressure dependence or the species dependence of the PD phenomenon which are shown in this figure.

Diamond CVD Growth Models have been Developed

by M. E. Coltrin

Motivation -- Low-pressure and low-temperature growth of diamond films *via* chemical vapor deposition opens up many potential markets. Diamond's unique properties include high thermal conductivity for thermal management applications, extreme hardness and low friction for protective coating applications. CVD diamond is usually grown from hydrocarbon sources like methane. However, halogenated sources offer the possibility of reduced growth temperatures, thereby increasing the range of material types that can be coated. We are developing quantitative computer models of diamond CVD to aid in process optimization. These complex models require as input information about the fundamental mechanisms of diamond growth. We have obtained the Molecular Mechanics program MM3 and are using it to calculate thermochemical properties of diamond surface structures.

Accomplishment -- We have proposed a surface reaction mechanism for diamond growth on the (100) (2x1):H surface which combines previously proposed mechanisms by Brenner and Garrison and by Harris and Goodwin. By examining the

growth at a step site we have obtained a mechanism that reproduces itself after one "cycle" of deposition. This property is required for the mechanism to be valid at steady state, and was not accomplished in the previous work. The theoretical technique of Molecular Mechanics (and a program called MM3) is being used to calculate energetics of bond breaking and formation during the elementary steps of this mechanism. With MM3 we have calculated the temperature dependent entropies and enthalpies of the 40 different surface structures appearing as intermediate configurations in the mechanism.

Significance -- Temperature dependent thermochemistry of the surface species are needed to calculate reaction energetics and reverse reaction rate constants (through the equilibrium constant) in a CVD kinetic mechanism. The MM3 calculations provide a reliable and systematic method for calculating this information. Having developed this methodology initially for systems containing only C and H atoms, we can extend it to fluorinated diamond surfaces.

Keywords: advanced materials, microelectronics, chemical vapor deposition, modeling

Contact: M. E. Coltrin, Chemical Processing Sciences Department 1126
Phone: (505) 844-7843
Fax: (505) 844-3211
E-mail: mecoltr@sandia.gov

Infrared Spectroscopy of Adsorbates on GaAs Surfaces has been Developed

by J. R. Creighton

Motivation -- Organometallic and hydride compounds are widely used as precursors for epitaxial growth of GaAs and other compound semiconductors. We are investigating the surface chemical and physical properties of these precursors on compound semiconductors in order to develop a fundamental understanding of the epitaxial deposition processes (e.g. MOCVD).

Accomplishment -- We have added a new experimental tool that significantly improves our ability to identify and characterize adsorbates. By interfacing an FTIR to our UHV system, we can now perform surface infrared spectroscopy (SIRS) on GaAs in a multiple internal reflection geometry. In addition to chemical species identification, by varying the polarization of the radiation this technique can be used to probe the adsorbate bonding geometry with respect to the surface. We examined the vibrational and structural properties of methyl (CH_3) and methylene (CH_2) adsorbates on GaAs(100). Reaction of trimethylgallium (TMGa) with the GaAs(100) surface at 300-400°C creates an ordered CH_3 adlayer that exhibits a (1 X 2) LEED pattern. The CH_3 adsorbate exhibits relatively sharp ($\text{FWHM} < 10 \text{ cm}^{-1}$) vibrational modes at 1192 and 2889 cm^{-1} , corresponding to the symmetric C-H bending and stretching modes, respectively. The polarization dependence of the symmetric modes gave the bond orientation of the CH_3 adsorbate with respect to the surface. The carbon-surface bond lies exclusively in the [-1,1,0] plane, which is parallel to the surface Ga-Ga dimer bond direction. This demonstrates that the CH_3

adsorbate is bonded to surface gallium (rather than arsenic) atoms. The Ga- CH_3 bond is tilted away from the surface normal by $50 \pm 10^\circ$, in good agreement with a tetrahedral bond angle. Using these results we have proposed a structure of the CH_3 -covered surface that consists of 1/2 monolayer of methyl groups bonded to a complete monolayer of dimerized Ga atoms. The proposed structure is consistent with the CH_3 orientation obtained by SIRS, the observed LEED pattern, the electron counting scheme for compound semiconductors, and ALE results. Extended reaction of TMGa with the GaAs(100) surface at 400-500°C produces an ordered CH_2 adlayer exhibiting a (1 X 4) LEED pattern. The CH_2 adsorbate is an important intermediate in the carbon incorporation mechanism. This adsorbate is characterized by a C-H bending mode at 1328 cm^{-1} and a symmetric and asymmetric C-H stretching mode at 2882 and 2943 cm^{-1} . Preliminary experiments indicate that this adsorbate is an unusual orientation tilted away from the surface normal and also out of the [-1,1,0] plane.

Significance -- In addition to our previous investigations of compound semiconductor surface chemistry using techniques (e.g. TPD) which detect desorbing products or scattered reactants, we now have a powerful tool (surface infrared spectroscopy) that directly probes the chemical and structural nature of adsorbates. This technique greatly enhances our ability to reveal the fundamental chemical and physical principles governing compound semiconductor epitaxy.

Keywords: surface chemistry, infrared spectroscopy, compound semiconductors, trimethylgallium, gallium arsenide, MOCVD

Contact: J. Randy Creighton, Chemical Processing Sciences Department 1126
Phone: (505) 844-3955
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

SIRS of monomethylgallium state on GaAs(100) recorded at 120K using unpolarized light.

Laser Measurements of Si Atoms Lead to an Improved Reaction Mechanism for Silane CVD

by P. Ho, W. G. Breiland and M. E. Coltrin

Motivation -- Chemical Vapor Deposition (CVD) is a widely used technology for the production of microelectronic devices, solar cells, protective coatings, and advanced materials. The chemistry of most CVD processes is poorly understood - successful processes have generally been developed through cut-and-try empirical methods. In recent years, however, researchers have begun using numerical models based on the science underlying CVD to improve the design of commercial processes and equipment. These models require an understanding of the chemistry occurring during a CVD process.

Accomplishment -- Extensive laser-induced fluorescence measurements of Si atoms were taken in our rotating-disk research CVD reactor and compared with predictions of our previously-developed numerical model for silane and disilane CVD. Significant disagreements were observed that could not be resolved by altering rate constants in the model, indicating that the reaction mechanism needed to be changed. For example, the model predicted that the shape of the Si atom profile (as a function of height

above the heated susceptor) should change dramatically as hydrogen was added to the gas mixture, but this was not observed experimentally. As long as $\text{SiH}_2 \leftrightarrow \text{Si} + \text{H}_2$ was the primary reaction affecting the Si atom concentration in the model, this disagreement persisted. When the $\text{H}_3\text{SiSiH} \leftrightarrow \text{Si} + \text{SiH}_4$ reaction was substituted, the proper trends were predicted for the Si atom profiles as a function of gas mixture, pressure, and temperature.

Significance -- This work provides a good demonstration of how detailed laser-based measurements can be used to test kinetic mechanisms for CVD. In this case, the experimental data showed that a straightforward reaction leading to Si atoms could not be important, and that less-obvious paths needed to be considered. This alteration in mechanism will be fed directly into models currently used for equipment design in SEMATECH programs. Our reaction mechanism for silane decomposition is also being used by a number of research groups in the US and in Japan who may be affected by this change.

Keywords: chemical vapor deposition, laser-induced fluorescence, silicon atoms, silane, disilane, reaction mechanism

Contact: Pauline Ho, Chemical Processing Sciences Department 1126
Phone: (505) 844-3759
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

Model predictions of Si atom profile shapes as a function of added hydrogen using the original silane reaction mechanism.

Experimental measurements of Si atom profile shapes as a function of added hydrogen agree well with predictions using the revised reaction mechanism.

Stimulated Chemistry of Ammonia (NH₃) on Surfaces

by A. R. Burns, D. R. Jennison and E. B. Stechel

Motivation -- Nitridation of substrate surfaces (e.g. GaN) is critical in the development of barriers in electronic and optoelectric devices. Since a chemically reactive form of nitrogen must be generated for nitridation, current technologies depend on plasma excitation of gas-phase NH₃ or thermal decomposition of adsorbed NH₃. Device performance can be limited by the quality of the nitride layers. Nitride layers have been less than ideal, either because of high substrate temperatures during thermal decomposition or the introduction of impurities generated in a plasma. Both problems may be eliminated by the use of stimulated (non-thermal) activation of adsorbed NH₃ by electrons or energetic photons; an added benefit would be direct nitride writing with submicron spatial selectivity. Thus we are motivated to study the fundamental processes, dissociation and desorption, which occur as a result of electronic excitation of adsorbed NH₃.

Accomplishment -- We have succeeded in characterizing in detail the electronically-excited processes which give rise to both dissociation and desorption of adsorbed NH₃ on Pt(111). We were able to unambiguously show that desorption and dissociation arise from two distinct excited states: (1) Desorption occurs via ~6 eV excitation of the lone-pair electrons at the N atom. (2) Dissociation occurs via the ~12-15 eV excitation of the N-H bonding electrons. Both excited states are molecular in origin and thus should be relevant to other surfaces such as GaAs, although the yields

are expected to increase on GaAs due longer excitation lifetimes. Dissociation is discussed in a separate report on the detection of neutral H. Desorption, meanwhile, is an "unwanted" reaction that lowers the nitridation efficiency. With quantum-resolved laser detection of desorbed NH₃ and ND₃, we were able to use internal and translational energies, and changes in yield due to isotopic substitution, to show that *desorption is a direct result of a change in molecular geometry in the excited state*. As shown in the figure, NH₃ goes from a pyramid to a plane or, possibly, to an inverted pyramid. This can be seen in part by the significant excitation of the "umbrella" vibrational mode. The change in molecular geometry with respect to the surface reduces the binding energy and causes desorption. Our results indicate that the molecule experiences a "hard wall" repulsion due to the hydrogen motion towards the surface. This motion is much slower for D atoms; thus the desorption yield is lower for ND₃.

Significance -- Our results directly impact the understanding of how the many degrees of freedom of a polyatomic molecule can determine the fate of electron- or photon-driven surface processes. These experimental results guide our theoretical efforts to model both the ground and excited-state potential energy surfaces. A separate report addresses our efforts to model the potential energy surfaces for this molecular adsorbate system.

Keywords: nitridation, film growth, non-thermal chemistry, reactive precursors

Contact: Alan R. Burns, Surface and Interface Sciences Department 1114
Phone: (505)844-9642
Fax: (505)844-5470

desorption

planar excited state

adsorbed pyramid

Desorption of NH_3 induced by excited-state changes in the molecule/surface geometry.

Direct Observation of Substitutional-Atom Trapping on a Metal Surface

by G. L. Kellogg

Motivation -- The ability to achieve atomically smooth surfaces during crystal and epitaxial growth processes is becoming increasingly more important as scientists and engineers attempt to create new materials by controlling crystal growth at the atomic level. Although it is often assumed that layer-by-layer growth occurs when the rate of diffusion across single crystal terraces exceeds the rate of nucleation events, there is indirect evidence from macroscopic growth studies that isolated surface defects can serve as nucleation sites and inhibit uniform growth. To probe this effect more directly, we have carried out an atomic-level investigation of how one such defect, a substitutional impurity atom, influences migration on an otherwise perfect single-crystal terrace.

Accomplishment -- Investigations with the field ion microscope show conclusively that Rh adatoms on a Rh(100) surface are trapped in the four lattice sites adjacent to an Ir substitutional atom. The trap site is created by intentionally substituting an Ir atom on the surface for a Rh atom within the top layer of Rh atoms. In the temperature range from 250-320 K, a Rh adatom migrates freely around the four sites neighboring the substitutional Ir atom, but does not move away. The energetics associated with the trap

site, determined from detailed investigations of the hopping rates to locations around and away from the impurity atom, are shown in the accompanying figure. A simple pairwise bond model with a stronger Ir-Rh bond compared to Rh-Rh explains the observed trapping as well as differences in the desorption fields for Rh and Ir atoms. A second Rh adatom added to the trap site forms a stable dimer with the first and becomes even more strongly attached to the Ir impurity atom. This suggests that the Ir substitutional atom indeed serves as a nucleation site for further growth on the terrace.

Significance -- A comprehensive, atomic-level understanding of crystal growth processes is one of the primary goals in our Basic Energy Sciences program on Tailored Surfaces and Interfaces for Materials Applications. Impurity atom trapping is undoubtedly an important element in the growth of crystalline solids and epitaxial overlayers. The quantitative energy barriers derived from this study will provide valuable input into more realistic growth-simulation models. Moreover, the direct observation of impurity atom trapping will serve to stimulate advanced theoretical modeling of adatom-impurity atom interactions, some of which has already begun.

Keywords: advanced materials, artificially structured materials, crystal growth, thin film growth, surface diffusion, surface alloying, atomic exchange, impurity atom trapping, field ion microscopy

Contact: G. L. Kellogg, Surface and Interface Science Department 1114
Phone: (505)844-2079
Fax: (505)844-5470
E-mail: glkello@sandia.gov

The energetics involved in self-diffusion on Rh(100) near an Ir impurity atom. The lower graph shows the binding energy of a Rh atom along line AB of the schematic. The lightly shaded circles represent top-layer Rh atoms, the darkly shaded circle is the Ir impurity, and the striped circle is the diffusing Rh adatom.

Direct Patterned Deposition of Adherent Copper on Teflon

by R. R. Rye, A. J. Ricco, A. J. Howard and D. J. Rieger

Motivation -- Because of its low dielectric constant and low power loss, Teflon is an ideal substrate for electronic applications, especially for very high frequency applications where capacitive coupling becomes a major problem. The major barrier to Cu on Teflon applications, however, is the well-known chemical inertness of Teflon; current state-of-the-art high frequency Radar technology depends on Cu clad Teflon produced by hot-pressing etched Cu foil and Teflon. We have developed a family of three-step processes for direct patterned deposition of adherent Cu onto Teflon with resolution, to date, of 20 μm , and with adhesion sufficiently strong that failure is near-cohesive in the Teflon and not adhesive.

Accomplishment -- Our previous methods have depended on Cu deposition (Cu CVD or electroless Cu deposition) onto surfaces pattern etched with sodium naphthalenide by either pre-irradiation or post laser ablation. The potential limitation of these approaches is that the isotropic nature of Cu deposition, while specific to the patterned etched layers, can be expected to introduce problems with control of resolution and side wall definition. In anticipation of these problems we have developed a new approach which combines chemical etching with standard photoresist technology. Chemical etching determines copper adhesion while standard

photoresist technology is used to define the electronic features. The chemical etching step produces a highly porous surface that allows deep penetration of copper for the mechanical interlocking which is the main factor in supporting strong adhesion. We have shown that failure in this case is near-cohesive in the Teflon and not adhesive failure. The limiting factor in feature resolution and definition is the photolithographic processing which is capable of sub micron resolution in contrast to the current industry standard for Cu on Teflon of 75 μm . We have shown that both electroless metal deposition and electroplating is selective to the active surface and not to the photoresist, a result which allows generalization of this approach to any metal which can be deposited by either electroplating or electroless metallization.

Significance -- This photoresist approach allows electronic circuits to be produced on Teflon using only techniques currently available in the electronics industry. As a test of this, we have produced a Lang divider circuit (designed by the SARs Radar Group at Sandia) in the CSRL. In our first attempt, we produced this circuit with 17 μm resolution (industry capabilities are 75 to 125 μm) between gold conductors with excellent side wall definition and adhesion. This circuit is currently being electronically tested.

Keywords: teflon, Cu, printed wiring boards

Contact: Robert R. Rye, Surface & Interface Sciences Department 1114
Phone: (505)844-9194
Fax: (505)844-5470

Optical micrographs at several different magnifications of a Lange coupler which was fabricated using Process III. Note the uniform fine metal edge definition along the 17 μm space that exists between the adjacent 200 μm -wide microstrip lines.

Interfacial-Force Microscopy Probes The Mechanical Properties Of Single, Nanometer-Size Grains On Various Substrates

by P. Tangyunyong, R. C. Thomas, J. E. Houston and T. A. Michalske

Motivation -- Considerable excitement has recently been generated in the potential for creating unique materials that are constructed from nanometersize building blocks--the so-called "nanophase materials." Such materials show promise of being stronger, lighter, more resistant to hostile environments and easier to form into complex shapes. The newly developed interfacial force microscope (IFM) is ideally suited for studying these unique materials. This technique is capable of measuring the force to break a single bond in a molecule and can determine position to less than an atomic diameter. These capabilities permit the determination of the mechanical properties (for example, elastic modulus, inter-granular motion, threshold for plasticity and the defect mode of plastic deformation) of a single, nanoscale grain in these materials.

Accomplishment -- We have applied the IFM to the first study of the mechanical behavior of individual grains in polycrystalline Au films deposited on various substrates. The tungsten probe has a nanometer scale tip and can be rastered across the surface to produce repulsive force images. In addition, the probe can be ramped into surface contact to measure the interfacial force necessary to produce local deformation (loading curves). An illustration of this type of measurement is given in the figure where repulsive-force images show a protruding grain (a). When loaded at its center, this grain produces the force-displacement behavior shown in (d) which is a fingerprint of grain-boundary

sliding, as can be seen in (b). Higher loading (e) dents the grain as illustrated in (c). By a detailed analysis of scanning-force images and loading curves, we can obtain quantitative values for the modulus of elasticity and maximum shear-stress at the threshold for plastic deformation of individual grains. These measurements are made possible by the unique capabilities of the self-balancing force sensor used in the IFM. No present scanning force microscopy or conventional nanoindentation instrument employs this unique sensor design. We have compared the values obtained from measurements of these parameters from a survey of single-crystal Au(111) and thin films of Au grown on glass, mica and Si(001) covered by adhesion layers of Ti and Cr. Although the measured modulus values vary from 36 to 110 GPa for Au/Mica and Au/Cr/Si(001), respectively (the value of 70 GPa for Au(111) is very near the "text-book" value), the results for the maximum shear-stress at the plastic threshold turned out to be near 4% of the modulus for all samples. These various values were correlated with parameters such as the grain size, mean surface roughness and qualitative measures of the film adhesion.

Significance -- Measurements such as these will permit an accurate evaluation of the mechanical properties for nanophase materials as a function of the details of the fabrication processing. This, along with modeling, will permit fabrication to be finely tuned to tailor materials for specific applications.

Keywords: nanophase materials, scanning probe microscopies, force sensors

Contact: J. E. Houston, Surface and Interface Science Department 1114
Phone: (505)844-8939
Fax: (505)844-5470
E-mail: jehoust@somnet.sandia.gov

400 x 400 nm IFM repulsive-force images of a typical protruding grain in thin Au films on glass substrates (a) before loading, (b) after a loading cycle to a peak load of $\sim 35 \mu\text{N}$ and (c) after a second loading cycle to a peak load of $\sim 75 \mu\text{N}$; Load-cycle data taken (d) in the center of the protruding grain shown in (1) to a peak load of $\sim 35 \mu\text{N}$ and (e) in the center of the grain shown in (b) to a peak load of $\sim 75 \mu\text{N}$. There are five distinct regions with different deformation behavior for the load-cycle curves shown in (d) and (e).

The First Direct Observation of Boron-Hydroxyls Enhancing TEOS Chemisorption in Boron-Doped SiO₂ CVD has been Made

by M. E. Bartram and H. K. Moffat

Motivation -- The addition of dopants for the modification of materials properties is often accompanied by changes in the deposition kinetics. This altered chemistry suggests that the dopant precursors increase the complexity of the CVD process. For example, the addition of trimethyl borate (TMB) to a thermal tetraethyl orthosilicate (TEOS) CVD process produces boron-doped SiO₂ with a lower reflow temperature for surface planarization in VLSI devices but also increases the overall deposition rate of SiO₂. As such, the study of this system is a unique opportunity to advance the important technology of boron-doped SiO₂ CVD as well as expand the rich science behind the effect of dopants on growth.

Accomplishment -- New information about the reaction synergy in doped CVD processes has been obtained by using FTIR to make the first direct observation that boranols increase the rate of TEOS chemisorption over a wide range of temperatures. At 300K, silanols (SiOH) and boranols (BOH) coadsorbed on SiO₂ were reacted with TEOS in the mtorr pressure regime to show that BOH has a rate constant infinitely greater than SiOH. At 1000K, coadsorbed deuterated silanols (SiOD) and boranols (BOD) were reacted with TEOS to circumvent limitations imposed by the concurrent hydroxyl

consumption and reformation which accompany TEOS reactions at this temperature. As shown in the figure, the reaction with TEOS at 1000K diminishes the concentrations of both SiOD and BOD. However, changes in the normalized areas of the vibrational peaks indicate that the reaction rate constant for boranols is better than twice that of silanols.

Significance -- These surface specific studies have demonstrated for the first time that the relative rate constants for boranols and silanols reacting with TEOS are dramatically different at 300K (BOH/SiOH $\approx \infty$) and 1000K (BOD/SiOD = 2). This suggests that $E_{a\text{TEOS+boranol}} < E_{a\text{TEOS+silanol}}$. This is valuable information for microelectronics fabrication since the deposition rates for the growth of boron-doped SiO₂ from TMB and TEOS have been shown here to be sensitive to the temperature as well as the relative concentrations of boranols and silanols. Consideration of this is important to achieve process reliability. For example, this suggests that non-uniform boranol concentrations on the deposition surface, that can arise from effects such as gas-phase depletion, may be a major cause of non-uniform growth. In addition, these studies provide one of the first examples of the specific manner in which dopants can effect deposition kinetics.

Keywords: CVD, tetraethyl orthosilicate, trimethyl borate, boron-doped, SiO₂, microelectronics

Contact: Michael E. Bartram, Chemical Processing Sciences Department 1126
Phone: (505) 844-1619
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

Rapid Methods for Calculating Reflectance Spectra of Growing Semiconductor Films are Being Developed for Applications in Process Control

by W. G. Breiland

Motivation -- Much of semiconductor processing involves the deposition of thin films for device applications. Existing deposition equipment typically uses a "recipe" approach to thin-film manufacturing: Set the process parameters to empirically determined values and run the process for an empirically determined amount of time. If the deposition apparatus runs the same as it did during the calibration runs, a successful thin film will result. A superior approach would be to actively control the thin film properties such as thickness and composition during deposition using *in situ* sensors. We are currently exploring the use of normal-incidence reflectance to serve as such a probe. To be successful as an active control, however, a model-based control strategy must be able to rapidly compute the reflectance spectra expected for a given semiconductor multi-layer film under processing conditions such as elevated temperature. Advances in sensor technology place heavy demands on such computations. It is now possible to collect a 2048-point reflectance spectrum every quarter-second during a growth run. This data must be analyzed and materials-properties extracted in real time in order to provide a basis for control.

Accomplishment -- An efficient method for calculating the reflectance (or ellipsometry) spectrum of an arbitrarily complex multi-film structure for any incidence angle and polarization has been devised, with particular emphasis on calculating the spectral reflectance of a growing film. Advantage is taken of the fact that

spectra are required at evenly-spaced thickness intervals within each layer. Under these conditions, a recursion relation may be used for the layer matrix used to describe propagation of light through the film, significantly reducing the number of complex-number transcendental computations required to calculate the spectrum of the growing film.

Another aspect of spectral reflectance calculations is being addressed by developing simple semi-empirical models for the dielectric functions of semiconductors that allow one to rapidly compute the optical constants of a material for a specific temperature and composition. Preliminary success has been achieved with modifications of the standard multiple-harmonic-oscillator model to provide n and k above the bandgap, as well as n below the bandgap.

Significance -- Modern semiconductor electronic and optoelectronic devices require very stringent control over a wide variety of materials properties such as thickness, composition, strain, doping level, and interface abruptness. These controls place severe demands on existing film deposition equipment, resulting in low product yields and tedious calibration runs. Successful implementation of active control of these properties through the use of *in situ* sensors and model-based control will have a dramatic impact on device manufacturing yield and will provide increased capability for the fabrication of novel complex film structures.

Keywords: microelectronics, optoelectronics, CVD, MOCVD, MBE, *in situ* monitors

Contact: William G. Breiland, Chemical Processing Sciences Department 1126
Phone: (505) 844-7029
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

Calculated reflectance vs film thickness curves at two (out of 1024) wavelengths during the growth of three quantum wells (10, 5, and 1 nm) at 650C.

Determination of the Direct to Indirect Band-to-Band Transitions in $\text{In}_x(\text{Al}_y\text{Ga}_{1-y})_{1-x}\text{P}$ Alloys by Pressure Dependent Photoluminescence Measurements

by E. D. Jones, S. M. Myers, J. S. Nelson, J. E. Schirber and R. P. Schneider, Jr.

Motivation -- Light emitting diodes (LED) made from $\text{In}_x(\text{Al}_y\text{Ga}_{1-y})_{1-x}\text{P}$ alloys lattice matched to GaAs, represent an important class of semiconductor devices for industrial applications and consumer products. Currently, the usable wavelength of this alloy system ranges from red (650 nm) to yellow-green (530 nm). A determination of the physical mechanisms which limit the attainment of shorter wavelengths would have a major impact upon the commercial market. The major limiting mechanism has been identified to crossing of the direct and indirect energy bands in these alloy systems. Indirect transitions are weak, and hence, represent the major limiting factor towards the attainment of shorter wavelengths.

Accomplishment -- In order to distinguish indirect from direct transitions, pressure dependent photoluminescence measurements were made in a series of $\text{In}_x(\text{Al}_y\text{Ga}_{1-y})_{1-x}\text{P}$

alloys with varying aluminum concentrations. Direct transitions have positive pressure coefficients of about 9 meV/kbar while indirect transitions have negative pressure coefficients of about -2 meV/kbar. Thus the sign of the pressure dependence of the photoluminescence energy quickly identifies the nature of the observed optical transition. Figure 1 shows the result of these measurements at 76 K and it is to be noted that for those samples with the largest bandgap energy, the photoluminescence signals rapidly disappear with applied pressure. This phenomena then is used to pinpoint the energy that the direct and indirect transitions are equal.

Significance -- The pressure dependent photoluminescence data show that the shortest attainable wavelength is about 550 nm, e.g., yellow-green. Further investigation in parameter space, i.e., designing non-lattice matched LED's may prove to be helpful.

Keywords: microelectronics, photonics, advanced materials

Contact: Eric D. Jones, Semiconductor Physics Department 1112
Phone: (505) 844-8752,
Fax: (505) 844-8985
E-mail: edjones @sandia.gov

PRESSURE DEPENDENCE OF BANDGAP ENERGIES:
 $\text{In}_x(\text{Al}_y\text{Ga}_{1-y})_{1-x}\text{P}$ ALLOYS

Figure 1. Pressure dependence of the photoluminescence determined bandgap energies for several $\text{In}_{0.48}(\text{Al}_y\text{Ga}_{1-y})_{0.52}\text{P}$ alloys lattice matched to GaAs. The from top to bottom, the Al/Ga ratio varies from 0.5 to 0.0.

Real Time Control of MBE by Optical-based Flux Monitoring (OFM)

by K. P. Killeen and S. A. Chalmers

Motivation -- Deposition of compound semiconductor materials for fabrication of optoelectronic devices by molecular beam epitaxy (MBE) is an imprecise art. Numerous test and calibration runs are required to develop acceptable growth recipes for each target device structure.. Subsequent depositions are subject to drift in the process causing reproducibility errors. This reality indicates the need for development of new *in situ* monitors for epitaxy that are correlated to the important parameters of film thickness and composition. These sensors can then be used as real time input to allow closed loop control of the deposition system. Such sensors and process control methods are becoming essential due to increasing device performance demands from both commercial and weapons component customers.

Accomplishment -- We have developed and demonstrated a new method for controlling molecular beam epitaxy (MBE) of compound semiconductors based on the vapor-phase optical absorption of group III elemental sources (i.e., Al, Ga and In). Angle resolved, high resolution laser excitation and absorption experiments were conducted on Ga and Al to measure the spectral overlap between the Doppler shifted beam absorbance and hollow cathode lamp emissions of these elements. A monitor was then designed and implemented on the CSRL's Riber 32P MBE system with the lamp probe light passing parallel and adjacent to the GaAs substrate. The absorbance

signal was scaled by a beam velocity correction factor to yield an instantaneous reading proportional to the beam flux. Since the sticking coefficients for the group III sources are essentially unity, this relative flux signal can be used to directly determine growth rates and group III lattice composition once calibrations to material properties are established.

To demonstrate controlled growth with the system, 12 period distributed Bragg reflectors (DBRs) of AlAs/GaAs were grown with target center wavelength of 980 nm. Our *in vacuo* spectral reflectance diagnostic was used to calibrate the OFM to material growth rates and determine the DBR characteristics. The optical monitor, interfaced to a PC based control system, was used to automatically activate the Al and Ga source shutters thereby compensating for the different AlAs and GaAs deposition rates with varying deposition times. The DBRs grown over several days with purposely different Al and Ga effusion cell temperatures exhibited wavelength deviations of less than 0.5% of the target 980 nm..

Significance -- This technique promises to supersede the traditional indirect methodology of MBE control (extrapolation of pre-growth calibrations), by providing a new procedure for the deposition of III-V epitaxial structures with unprecedented precision and efficiency.

Keywords: MBE, OFM, flux monitor, in situ, diagnostics, real-time control

Contact: Kevin P. Killeen, Chemical Processing Sciences Department 1126
Phone: (505) 844-5164
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

OFM Controlled Growth of AlAs/GaAs 980 nm DBRs

Inter-Quantum-Well Tunneling in a Double-Well Structure with In-Plane Magnetic Fields

by S. K. Lyo and J. A. Simmons

Motivation -- Nanoelectronic structures based on two-dimensional (2D) tunneling offer the possibility of new device concepts. In a double-quantum-well structure (DQWS), the current flows into one end of one QW and flows out of the other end of the other QW. We have demonstrated recently that tunneling current-paths and source-drain resistances can be locally controlled on a submicrometer scale using built-in gates. The basic new physics in a typical widely-separated DQWS is the concept of incoherent 2D-2D tunneling. Because there has been no microscopic theory which yields tunneling currents as a function of in-plane magnetic fields, it is necessary to develop a 2D-2D tunneling theory and compare with our data.

Accomplishment -- We have developed a microscopic theory of 2D-2D tunneling based on Kubo's linear response formalism. The tunneling conductance is found to show two sharp resonances as a function of the magnetic field for the QW's with unequal electron densities. The turn-on (turn-off) field where the first (second) peak appears is proportional to the square-root of the difference (sum) of the densities. The

densities in the QW's can therefore be obtained from the turn-on and turn-off fields. The widths and heights of the resonance peaks depend sensitively on the intra-well scattering times and the temperature (see the figures). Tunneling occurs not only through the ground sublevels but also through the higher sublevels at high temperatures. Analytic relationship between the source-drain conductance and the tunneling conductance are derived, using a differential transmission-line model. The theoretical results yield good agreement with the tunneling conductance data obtained from this relationship.

Significance -- Microscopic processes responsible for 2D-2D resonant tunneling are satisfactorily understood through reasonable agreement between the data and the theory. Since the width of the tunneling current as a function of the magnetic field is very sensitive to the lifetime of the electrons at the Fermi level, the lifetime can be deduced from the tunneling-current data. Macroscopic source-drain transport including tunneling is well explained within the frame of a differential transmission-line model.

Keywords: two-dimensions, tunneling, magnetic field, scattering lifetime, temperature

Contact: S. Ken Lyo, Semiconductor Physics Department 1112
Phone: (505) 844-3718
Fax: (505) 844-1197
E-mail: sklyo@sandia.gov

The tunneling conductance data (a) from GaAs/Al_{0.3}Ga_{0.7}As DQWS with 150Å-wide QW's separated by a 150Å-wide barrier are compared with the theoretical results for several damping parameters (i.e. inverse scattering lifetime) at 0 °K (b) and also at several temperatures for zero damping (c). The densities of the QW's are 0.953 and 1.74310¹¹ cm⁻².

Thermal Stability Studies Demonstrate Usefulness of Diamond-like Carbon as a Coating Material up to 250° C

by J. E. Parmeter, D. R. Tallant and M. P. Siegal

Motivation -- There is currently much interest in amorphous carbon/hydrogen films grown from plasma CVD of hydrocarbons, the films being alternatively referred to as diamond-like carbon (DLC) or a-C:H. The DLC films are potentially a useful coating material that can serve as an economical replacement for diamond films in a number of applications, since the DLC films can be grown at much higher rates and with hardness or optical band gap values that are quite close to those of diamond. However, the suitability of DLC for a specific application will depend to a large degree on the thermal stability of this material, an issue which has not previously been investigated thoroughly. In order to gauge the temperature regime in which DLC will serve as a useful coating material, we have performed a multi-technique experimental investigation of the thermal stability of these films.

Accomplishment -- The thermal stability of DLC films deposited onto tungsten and aluminum substrates was investigated in a variety of environments using Raman spectroscopy, Auger spectroscopy, and thermal desorption measurements. The net result of these studies is that DLC films can be expected to be stable up to at least 250° C, even in rather extreme conditions.

Raman spectra of films annealed in air show negligible changes up to 300° C, with conversion to micro crystalline graphite (glassy carbon) occurring between 300° and 450° C. Auger spectra of unannealed DLC films suggest an sp^3/sp^2 carbon ratio in the films of 60:40. Auger measurements also confirm that a structural transition occurs near 400° C, with the carbon peak fine structure indicating a conversion of the bulk of the sp^3 carbon to sp^2 between 300° and 500° C. Thermal desorption studies indicate that hydrogen evolution from the films commences near 260° C. Additional Raman studies show that DLC is stable for several days in boiling (95 C) water, and for hours at 200° C in a high humidity environment.

Significance -- Our results show that DLC should be a usable, economical substitute coating material to replace diamond coatings in a variety of applications where substrate temperatures in excess of 250° C are not required. Film degradation due to atmospheric water, a concern raised in some previous studies, appears to be negligible under these conditions. In the case of applications where temperatures over 250° C will be encountered, alternative coating materials will need to be developed.

Keywords: Advanced materials, chemical vapor deposition, surface chemistry

Contact: John E. Parmeter, Chemical Processing Sciences Department 1126
Phone: (505) 844-8594
Fax: (505) 844-3211
E-mail: c/o esheric@sandia.gov

Auger (top) and Raman (bottom) spectra illustrating changes in DLC films as the result of annealing.

New Technique Developed for High-Accuracy Measurement of Two-Dimensional Electron Density in Pseudomorphic HEMT Structures With Highly Doped Contact Layers

by **J. A. Simmons and M. L. Lovejoy**

Motivation -- The two dimensional electron density n in the strained quantum well of pseudomorphic high electron mobility transistors (HEMTs) is an important parameter for device performance. Essential figures of merit such as the source-drain current and transconductance are for the most part proportional to n . Accurate measurements of n are thus needed for reliable device modeling and for the development of materials growth strategies. The measurement of n in these structures is complicated by two characteristics. First, high-performance PHEMT structures require a heavily doped cap layer for the fabrication of low resistance ohmic contacts. This layer presents a conduction path parallel to that of the quantum well, severely distorting its classical Hall response. Etch-removal of the layer introduces additional bandbending, changing the original n . Second, PHEMT structures also require for high performance a value of n large enough that several subbands are typically occupied. While Shubnikov-de Haas (SdH) oscillations from the first subband are readily observed, those from higher subbands are much more difficult to routinely detect, requiring magnetic fields up to 20 Tesla.

Accomplishment -- We have developed a new technique for the measurement of 2D electron density in PHEMT structures with multiple occupied subbands. The technique utilizes a hybrid of SdH and photoluminescence (PL) measurements to provide an accurate value for n , even in the presence of severe parallel conduction. SdH measurements provide a value for the Fermi energy relative to the first subband, while PL measurements give the subband energy spacings. Combining these values allows determination of n to within $\sim 2\%$, without etching the cap layer.

Significance -- This hybrid analysis technique will prove valuable in the design, modeling, and epitaxial growth of PHEMTs and other quantum well device structures such as laser diodes, which must incorporate a heavily doped bulk layer for low resistance contacts. The technique allows one to accurately ascertain the electron density prior to device fabrication. Because Hall effect and PL measurements are routinely used to characterize device material, no additional device processing is required, and since only the lowest subband is measured with SdH, magnetic fields of only a few Tesla are sufficient.

Keywords: microelectronics, strained quantum wells, materials characterization

Contact: Jerry A. Simmons, Semiconductor Physics Department 1112
Phone: (505) 844-8402
Fax: (505) 844-1197
E-mail: jsimmon@sandia.gov

Hall and longitudinal resistances for PHEMT structures with and without heavily doped cap layers. The sample with an undoped cap layer exhibits SdH oscillations of two periods, allowing determination of the electron densities of both occupied subbands. Independently, the densities can be obtained by values of the quantized Hall plateaus, and by the slope of the classical Hall resistance at low magnetic fields. For the sample with a doped cap layer, however, only the SdH oscillation due to the first subband is visible, and the classical Hall resistance is highly non-linear due to parallel conduction. By combining this data with PL data the total quantum well electron density from both subbands is readily obtained, even in the presence of severe parallel conduction.

Gate-Controllable "Artificial Impurity" Fabricated By Use of a Nanostructure Air--Bridge Technique

by J. A. Simmons, M. E. Sherwin and J. F. Klem

Motivation -- As present day electronic devices are scaled down to increasingly smaller sizes, understanding of the quantum effects which dominate in the small limit is becoming increasingly crucial. In the small-size limit the electron wavefunction remains coherent across the entire device, and the presence of a single impurity can determine the device's behavior. Detailed knowledge of quantum transport phenomena, can improve the design of conventional electronic devices, and will also provide the operating principles for the devices of the future.

Accomplishment -- We have developed a new electron-beam lithographic technique, and used it to fabricate single "artificial impurities" with diameters down to 100 nm. The artificial impurities are defined by dropping a post from a metallic airbridge suspended over the device's active region. The impurity potential is thus controllable through the application of a gate bias. We have fabricated impurities in the center of narrow gate-defined constrictions on GaAs heterojunctions with mobilities on the order of 2×10^6 cm²/Vs, so that the electron mean free path is larger than the constriction width and length. The resulting "island-in-the-strait" device

exhibits a conductance quantized in units of $(n_1 + n_2) 2e^2/h$, where n_1 is the number of occupied subbands on one side of the impurity, and n_2 is the number of occupied subbands on the other side. We control n_1 and n_2 by biasing the three different gates and depleting the 2D electrons laterally. At high magnetic fields B , transport through the device is dominated by edge state phenomena, and tunneling across the device occurs resonantly through the "impurity" energy levels. At high B these levels are determined by self-interference of electrons encircling the impurity. We are presently extending the study to lower electron density devices, which are expected to shed light on the nature of the quasiparticle states in the fractional quantum Hall effect.

Significance -- The ability to fabricate gate-controllable regions of submicron diameter will greatly increase the range of experiments possible in quantum transport. In particular, these structures will allow the study of resonant magneto-tunneling through 0-dimensional "quantum dot" and "quantum anti-dot" potentials, and should provide fundamental information on electron-electron interactions in systems containing only a few electrons.

Keywords: nanostructures, quantum interference, magnetotransport, quantum dot

Contact: Jerry A. Simmons, Semiconductor Physics Department 1112
Phone: (505) 844-8402
Fax: (505) 844-1197
E-mail: jsimmon@sandia.gov

$\times 20,000$ $1\ \mu\text{m}$

Top: Electron micrograph of the artificial impurity, defined by an airbridge with a descending post of 200 nm diameter. The impurity resides in the middle of a narrow constriction defined by two additional gates. **Bottom:** Device resistance as a function of the voltage on all three gates together. Converted to conductance, quantized steps occur at low bias in units of $4e^2/h$, with each quantum channel on either side of the impurity contributing $2e^2/h$ per occupied subband. At high bias, one channel pinches off before the other, and the step size switches to $2e^2/h$.

A Localized Vibrational Mode for Nitrogen has been identified in ZnSe using Ion Implantation and Infrared Absorption

by H. J. Stein

Motivation -- Nitrogen doping to obtain p-type activity has made ZnSe a strong candidate for development of blue-light-emitting devices. The development is currently limited, however, by insufficient activation of N at high concentrations. Little is known about the site location for the N in ZnSe, or about N-N and N-impurity interactions. A low mass atom such as N bonded into the ZnSe lattice can give rise to a localized vibrational mode (LVM) detectable by infrared absorption. Thus, an infrared absorption study of N-ion-implanted ZnSe was initiated.

Accomplishment -- The first observation of a LVM for N in ZnSe has been made. Assignment of absorption to a N mode was verified by isotopic substitution. The vibrational frequency for the N mode is similar to those for substitutional N in Ge, Si and GaP, and is,

therefore, consistent with N on Se sites. Coimplantation with deuterium reduced the intensity for the LVM of N and introduced a LVM for Zn-D. The Zn-D absorption intensity increased while the N absorption decreased markedly upon annealing between 200 and 300°C in the coimplanted sample. It is suggested that deuterium breaks Zn-N bonds and bonds to Zn, while N relaxes toward threefold coordination with the remaining Zn atoms as sketched in the accompanying figure.

Significance -- The results of this study with controlled introduction of deuterium and N isotopes by ion implantation has provided information on N and N-deuterium(hydrogen) interactions which may help understand limitations on activation of N acceptors in MBE and MOCVD ZnSe.

Keywords: Vibrational mode for N in ZnSe, bonding site for N in ZnSe, Zn-H complex in N-doped ZnSe. Schematic illustrations of substitutional N in ZnSe, and of Zn-H complex in N-doped ZnSe.

Contact: Herman J. Stein, Ion Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-6279
Fax: (505) 844-9185

SUBSTITUTIONAL N
IN ZnSe

Zn-H COMPLEX
IN N-DOPED ZnSe

Measurements have been Made of the Electrical Properties of Implantation-Induced Nanocavities in Silicon

by C. H. Seager, S. M. Myers, R. A. Anderson, W. A. Warren and D. M. Follstaedt

Motivation -- Silicon implanted with high energy He ions develops nanometer-scale cavities when annealed at high enough temperatures to drive out the helium (seen in the figure). Previous work has shown that the internal surfaces of these nanocavities possess a high density of silicon dangling bonds. These dangling orbitals are extremely chemically reactive and can serve as gettering sites for impurities in the silicon host lattice, which suggests the possibility of using nanocavities to getter undesirable transition metal ions in silicon IC wafer processing. The energy levels of the Si dangling orbitals and the details of how they become charged are expected to affect the band structure in the vicinity of these cavities; this, in turn, could affect the aggregation and binding of impurity atoms at the cavity surfaces. In addition, precise determination of Si dangling orbital properties at free, external silicon surfaces has been hampered by the limited electrical measurements that can be made at free surfaces; when these dangling orbitals are located on internal surfaces, a whole variety of bulk semiconductor characterization methods like DLTS can be employed to characterize their properties.

Accomplishment -- We have prepared He implanted and annealed Si samples with ohmic and Schottky electrical contacts to characterize the transport of charge across regions containing a high density of these nanocavities. Both p- and n-type samples have been utilized to study the trapping of electrons and holes at the internal

cavity surfaces. Measurements of the impedance offered by cavity layers demonstrates that they trap majority carrier charge in both types of silicon. Capacitance techniques were used to probe the resulting depletion layer widths due to the trapping of holes or electrons. Our data shows that these depletion layers are ~ 1 -2 m wide; this width increases as the layers are biased due to injection of more majority carrier charge into the cavity traps. In conjunction with these measurements we have applied a simple theoretical model to the cavity charging problem to predict the equilibrium and biased band structure in the vicinity of the cavity layers. This model gives a semi-quantitative fit to our measured conductance and capacitance data. Capacitance-based studies of hole and electron emission from cavity states were also used to provide estimates of acceptor and donor transitions of the Si dangling orbitals. These measurements indicate that the lower state is 0.17 eV above the valence band maximum while the upper level is 0.38 eV below the conduction band minimum. Finally, electron spin resonance data verified the Si dangling orbital character of the cavity traps.

Significance -- These studies represent the first comprehensive account of Si dangling orbital properties on clean internal surfaces. They have verified the ambipolar nature of the Si dangling bond states and have located their energy positions with a precision unavailable from studies of external surfaces.

Keywords: implantation, gettering, microelectronics

Contact: Carleton H. Seager, Ion Solid Interactions & Defect Physics Department 1111
Phone: (505) 844-9168
Fax: (505) 844-4045

Development of a Massively Parallel Unstructured Finite Element Reacting Flow Code for Multiple Instruction Multiple Data Computers

by H. K. Moffat, J. S. Shadid and S. A. Hutchinson

Motivation -- Solving reacting flow problems in multiple dimensions is a very large computational problem that demands the most powerful computers. In fact, there are many complex reacting flow problems in chemical vapor deposition involving 2D and 3D complex geometries that are beyond the capabilities of current serial codes. The solution of these problems will require massively parallel computers and codes specifically tailored to run on them. In the past few years, Sandia has invested heavily in Multiple Instruction Multiple Data (MIMD) massively parallel computers. We are currently developing a complete new suite of codes, based on an unstructured finite element code that solves the compressible reacting flow equations, plus associated utilities for handling massively parallel data structures. The first target application for the code, called SALSA, will be to model complex 2D and 3D CVD processes.

Accomplishment -- Using SALSA as a test bed, we have implemented robust load-balanced algorithms for breaking up the mesh data on MIMD computers and have tested them on a wide range of problems. Metrics used to optimize the partitioning have been proven to be correct for many classes of problems, though incorrect for certain special classes. Additional kernel programs for getting mesh and solution data on and off of MIMD computers efficiently have been constructed and implemented. An example of a challenge in the latter problem is how to broadcast 64 megabytes of data to 1024

processors through a serial front end while minimizing the time each processor must wait for its requisite data.

In computational problems like these, the matrix-vector multiply used in the Krylov solvers, i.e. iterative solvers like conjugate gradient method, are the most time and communications intensive part of the calculations. We have shown that our Krylov solvers achieve up to 96% efficiencies (defined as the amount of time doing calculations versus communications) for large problems. SALSA can now solve the time dependent heat transfer equation with multiple material types and as many as 1 million grid points. Hooks and solution strategies have been implemented for the full set of reacting flow equations.

Significance -- A working tool for solving CVD problems in 2D and 3D complex geometries has been made. In the past, the complexity of implementing unstructured finite element problems on MIMD computers has hampered the migration of these problems to MIMD computers. The kernel algorithms provided by SALSA for handling unstructured finite elements on MIMD computers and for solving the resulting linear algebra problems with iterative methods are providing a catalyst for migrating additional Sandia codes (e.g. the heat transfer program, COYOTE, and the incompressible flow solver, NACHOS) to MIMD computers. Additionally, we have demonstrated superior scaled parallel performance on this problem class.

Keywords: chemical vapor deposition, numerical modeling, parallel processing computers

Contact: Harry K. Moffat, Chemical Processing Sciences Department 1126
Phone: (505) 844-6912
Fax: (505) 844-3211
E-mail: hkmoffa@cs.sandia.gov

Figure 1: Load balance of vertical CVD reactor for 28 processors constructed with Chaco using spectral quadrisection and KL refinement.

Figure 2: View of streamlines showing detrimental recirculation and a temperature profile in a vertical CVD reactor.

2-Dimensional Photonic Lattices Demonstrate Lateral Control of Photon Propagation

by P. L. Gourley, J. R. Wendt, G. A. Vawter, T. M. Brennan and B. E. Hammons

Motivation -- A thresholdless semiconductor laser produces a lasing photon with the first injected electron-hole pair. Such a laser would operate at ultralow current levels, millions of times lower than operating currents in existing semiconductor lasers. These low power lasers could compete with low power silicon devices used in computer technology and have the advantage of chip-to-chip communication. To realize such an advance, laser cavities with ultrahigh confinement must be developed. We propose to develop 2-dimensional photonic lattices to confine light in the wafer plane.

Accomplishment -- We have designed, fabricated, and experimentally studied the first honeycomb 2-dimensional photonic lattice for controlling the propagation of light. The honeycomb was patterned onto a wafer comprising (Al,Ga)As quantum wells on a AlAs/AlGaAs mirror grown by molecular beam epitaxy. The pattern was created by direct write electron beam lithography. The honeycomb was formed by etching holes with a reactive chlorine ion beam. The etch depth was about 1 micrometer. After fabrication surface normal

optical properties, including reflectance, continuous and time-resolved luminescence spectroscopy, and wavelength dependent light scattering, were investigated. The latter measurements show that light is resonantly scattering by the 2-dimensional lattice at selected wavelengths satisfying a Bragg condition. This scattering effectively controls the propagation of light through the lattice.

Significance -- Future generations of ultra-low threshold laser diodes require materials which eliminate all channels of energy loss, including spontaneous emission losses. To this end, we have used recent advances in electron beam lithography and reactive ion etching to synthesize new photonic lattice structures. Photonic lattices provide control over spontaneous losses and have potential to impact laser diode technology. Through the design, synthesis, and experimental study of these new nano/micro-engineered semiconductor structures, we endeavor to develop the science of photonic nanostructures that will enable a new generation low threshold, high efficiency and high brightness lasers.

Keywords: semiconductor laser, photonic lattice, nanostructures

Contact: Paul L. Gourley, Semiconductor Physics Department 1112
Phone: (505) 844-5806
Fax: (505) 844-1197

Upper figure - Scanning electron micrograph of a 2-dimension honeycomb structure. Lower figure - light scattering at 850 nm from honeycomb.

Binary Optics Have Been Used To Make Optical Phase Sensors With Extremely Large Dynamic Range, High Bandwidth And Sensitivity For Laser Beam Characterization And Fluid Flow Diagnostics

by D. R. Neal and M. E. Warren

Motivation -- Optical technology has long been limited to those optics that could be fabricated using some variation of grinding and polishing. This generally limited the optics that could be fabricated to a narrow group of conic sections. While this technology is very mature, it could not be used to fabricate arrays of optics, or arbitrary surfaces without going to extreme lengths. Using photolithographic techniques adapted from the semiconductor industry it is possible to make much more general optics. The optics are limited only by the size and depth of surface profile that is achievable with modern etching and processing machines---a few microns over a 6--9 inch diameter. Since these optics are fabricated from a number of discrete mask and etch steps with heights differing by factors of two, they are often called *binary optics*. It is not difficult to etch features that are smaller than 1 mm, which allows both diffractive and refractive optics to be built. The CSRL (1300) has complete facilities for fabricating advanced semiconductor devices up to a few inches in diameter. These includes mask aligners, Reactive Ion Etch (RIE) machines and wet etch equipment. In 1128, a number of optical design techniques have been developed over several years. We have combined these two areas of expertise to design and construct several binary optics applications.

Accomplishment -- Phase measurement is a problem that lends itself well to binary optics applications. We have invented several different types of phase measuring systems, including a static phase shift interferometer, a one-

dimensional wavefront sensor, and a multi-tiered wavefront sensor. Binary optics is well suited to making the arrays of optics that these devices require.

We have designed and fabricated a 40 element cylindrical lenslet array for use in a one-dimensional wavefront sensor. A surface profile of a few of the lens elements are depicted in Figure 1. The fabricated array has less than 1/20 wave of residual surface error for the 16 level surface. Two different arrays were fabricated with different etch profiles to test different design techniques.

Significance -- Binary optics fabrication techniques allow the production of various optics to be limited by the imagination of the designer rather than the fabrication technology. The applications that we have already developed are beginning to have impact in other Sandia and outside programs. For example, the one-dimensional sensor has been demonstrate to be capable of making extremely large dynamic range phase measurements at high bandwidth. We have demonstrated the sensor by measuring gasdynamic turbulence and droplet evaporation clouds directly. Phillips laboratory has initiated a WFO contract to purchase several of these wavefront sensors, and WYKO Corp. has begun discussions on tech transfer and a possible CRADA. We expect to continue to develop new optical devices for phase measurement and other applications.

Keywords: binary optics, diffractive optics, micro-optics, wavefront sensor, phase measurement, phase sensor

Contact: Daniel R. Neal, Lasers, Optics and Remote Sensing Department 1128
Phone: (505) 845-0854
Fax: (505)844-8985
E-mail: drneal@somnet.sandia.gov

Surface profile of cylindrical lenslet array fabricated using binary optics techniques.

Trace Organic Chemical Detection Using an Ultraviolet Excitation Molecular Beam Fluorometer

by B. L. Preppernau and P. J. Hargis

Motivation -- Detection of air-borne organic compounds requires sensitive unambiguous identification. Such compounds typically have electronic transitions in the ultraviolet with near-featureless broad spectra when recorded at atmospheric conditions. Expanding atmospheric samples in a supersonic molecular beam acts to cool the gas to within a few degrees of absolute zero which lessens the spectral density in a fluorescence or photoionization spectrum by reducing the effective rotational and translational temperatures of the molecules. This provides a sharply defined spectra which can be used to unambiguously identify specific molecules.

Accomplishment -- We have constructed a pulsed supersonic molecular beam apparatus which can be synchronously probed with a pulsed ultraviolet (UV) high resolution dye laser tunable from 210-400 nanometers. A mixing manifold on the atmospheric pressure inlet to the system is used for partial pressure mixing of organic compounds vapors and allows for manufacture of mixture ratios down to ten parts-per-billion (ppb) in air. Three techniques can be used to record spectra; laser-induced fluorescence (LIF) is

detected using a photomultiplier tube, a DC biased plate and charge sensitive amplifier collects photoionization (PI) signals, and light collected by an optical fiber is coupled to a spectrometer equipped with an intensified CCD camera for dispersed wavelength fluorescence measurements. Figure 1 shows the effect of supersonic expansion cooling on the LIF spectrum of acetone. The upper trace shows data obtained at atmospheric conditions. As the vacuum base pressure drops, broad spectra narrow due to cooling. The lower traces were acquired at 2×10^{-3} and 6×10^{-6} Torr respectively. The signal to noise ratio has improved by nearly two orders of magnitude since the laser probe energy is distributed among fewer rovibrational transitions. Figure 2 shows LIF and PI spectra for toluene recorded at a concentration of 10 ppm demonstrating the complementary value of recording simultaneous spectral signatures by different methods.

Significance -- This system gives uniquely sensitive surveys of UV spectra for organic compounds; for enhanced detection of environmental contaminants.

Keywords: chemical detection, molecular beams, laser-induced fluorescence

Contact: Bryan Preppernau, Laser, Optics, and Remote Sensing Department 1128
Phone: (505) 844-9425

Figure 1. Supersonic Expansion Acetone LIF Spectra.

Figure 2. LIF and Photoionization Spectra of Toluene.

We have Advanced Optical Parametric Oscillator Development

by A. V. Smith, W. J. Alford and T. D. Raymond

Motivation -- Optical parametric oscillators (OPO's) provide a means of generating widely tunable coherent light from pump laser light with high efficiency. This technology has the promise of compact, rugged and broadly-tunable sources of coherent light. OPO's were first demonstrated over 25 years ago but were not widely used due to technical difficulties. Recent developments in pump laser technology and nonlinear crystal growth have renewed the promise of OPO's. Despite their long history and potential wide applicability, they have not been carefully modeled nor fully characterized in the laboratory. In particular, the issues of beam quality and spectral linewidths and shifts are crucial for many remote sensing applications. They are the subject of our thorough studies via computer modeling and laboratory measurement.

Accomplishment -- We have developed a computer model for nanosecond duration pulsed OPO operation and have built a laboratory capability for thorough characterization of OPO's. The model includes the effects of light diffraction of the three interacting waves in an OPO cavity, the effects of beam walkoff due to the birefringence of the nonlinear mixing crystal, and strong exchange of energy among the three waves. This is the first time that all three of these important effects have been incorporated in a single model. In the laboratory we have built a ring-cavity KTP crystal OPO and surrounded it

with the many diagnostic probes necessary for thorough characterization of its performance. Although the modeling and laboratory measurements are just reaching the level of refinement necessary for pioneering work, we have already demonstrated gratifying agreement between calculation and measurement. Our results indicate that the OPO's built according to the usual methods can be seriously flawed for many applications. In particular, we find significant degradation of beam quality and spectral purity if the device is pumped hard to obtain high efficiency. In addition, slight misalignment of the nonlinear crystal can lead to frequency shifts.

Significance -- In addition to providing insight into the operation of current OPO designs, our model should make possible the design of a new generation of OPO's that overcomes some of the current limitations. We hope to be able to generate tunable output more efficiently while maintaining good beam quality and spectral purity. In addition, our models can be applied to other nonlinear frequency conversion processes such as sum and difference frequency mixing. This allows us to optimize the design of coherent sources for LIDAR applications and for chemical identification and measurement applications. The latter should prove useful in developing diagnostics for monitoring semiconductor growth processes.

Keywords: optical parametric oscillator, tunable solid-state laser, LIDAR, remote sensing, nonlinear optics, chemical sensing.

Contact: A. V. Smith, Laser, Optics, & Remote Sensing Department 1128
Phone: (505) 844-5810
Fax: (505) 844-3211

Second harmonic generation is a parametric process that can be studied with OPO code. This figure shows the fluence profiles for (a) an input fundamental beam and (b) the second harmonic beam generated in a nonlinear crystal as calculated with the code. The elongation in the second harmonic profile is caused by walk off in this critically phase matched process. The high intensity portion of the second harmonic beam appears on the side towards walk off and is generated near the entrance face of the crystal before the fundamental beam is significantly depleted.

— Diagnostics and Characterization —

Materials Characterization

Our capabilities in this area include optical microscopy, scanning, electron microscopy, analytical transmission electron microscopy, double crystal x-ray diffraction, ion beam analysis of materials (RBS, channeling, ERD, PIXE, NRA), Hall measurements, photoluminescence, light scattering, electronic transport, deep level spectroscopy, magnetization, and dielectric and magnetic susceptibilities.

Chemical Vapor Deposition (CVD)

We have a wide range of experimental tools for investigating CVD which include optical probes for gas-phase and surface processes, a range of surface analytic techniques, molecular beam methods for gas/surface kinetics, and flow visualization techniques. Carefully chosen experiments provide the critical information on chemical species, gas temperatures, and flows necessary for model development and validation.

Surface and Interface Spectroscopies

We maintain strong capabilities in auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), thermal desorption spectroscopy (TDS), infrared reflectance-absorbance spectroscopy (IRAS), and quantum state resolved laser surface probes.

Sandia Nuclear Microprobe

The Sandia Nuclear Microprobe is used to study and evaluate the radiation hardness of microelectronic devices using two new advanced diagnostic techniques invented at Sandia: Single-Event-Upset Imaging and Ion-Beam-Induced-Charge-Collection Imaging.

Vision Science Laboratory

We have developed a vision science laboratory with state-of-the-art hardware and software capabilities for carrying out video inspection, multi-spectral image analysis, and sensor-based pattern recognition. These capabilities can be applied to applications ranging from microsensor-based chemical detection and recognition to automated video/SEM inspection of semiconductor materials and circuits.

Xternal Micro Ion Beam Analysis (X-MIBA)

This unique facility is designed for the multi-elemental analysis and ion irradiation of samples which are vacuum incompatible or extraordinarily large. Detection of elements ranging from all three isotopes of hydrogen to the transuranics is possible with sensitivities of 0.01 to 100 ppm.

Growth Science Laboratory

We have unique capabilities for in situ characterization of materials during molecular beam epitaxial growth, low energy ion bombardment on ion beam simulated growth using intensity profile sensitive reflection high energy electron diffraction (RHEED) for surface structure, energy dispersive x-ray reflectometry for in situ surface and interface structure, and Auger electron spectroscopy for surface composition.

KMAP X-Ray Diffractometer

KMAP X-Ray Diffraction Analysis is used to determine the lattice constant, strain relaxation, composition, layer orientation, and mosaic spread of a large variety of advanced epitaxial semiconductor materials.

Tandem Van de Graaff Ion Accelerator

This 6 MV EN accelerator provides ion species from hydrogen to bismuth for quantitative ion beam analysis of materials containing light elements (hydrogen to fluorine) using elastic recoil detection (ERD) and heavy elements using Rutherford backscattering spectrometry (RBS). This facility has also been used for high energy ion irradiation studies of high temperature superconductors.

Atomic-Level Imaging and Spectroscopy

We have developed unique capabilities in scanning tunneling microscopy (STM), field Ion microscopy (FIM), atom probe microscopy (APM), and interfacial force microscopy (IFM). Selected analysis is possible in both high temperature and ultra-high vacuum.

Nanoelectronics Laboratory

We have capabilities for characterizing nanoelectronic structures (also fabricated at

Sandia by e-beam lithography) through electrical transport measurements at low temperatures and high magnetic fields.

Lasers and Optics

We have extensive capabilities in characterizing and advancing the understanding in the area of solid-state lasers and non-linear optics, especially as coherent sources of broadly tunable light in rugged, compact geometries. We have established expertise in long-term and transient radiation effects characterization of optical materials.

Laser Spectroscopies

We have extensive capabilities for characterizing semiconductor materials by photoluminescence and magnetoluminescence down to low temperatures by optical laser imaging and laser microscopy, by laser excitation spectroscopy, and by time-resolved measurements of optical emission.

— Synthesis and Processing —

Nanocluster Laboratory

We have developed and patented a process based on the use of inverse micelles for the synthesis of large quantities of monodisperse clusters of metals, semiconductors, and oxides.

Electron Cyclotron Resonance (ECR)

This plasma facility has been built for studying fundamental processes governing the growth of oxide and nitride dielectric films used in optoelectronics and used as hard coatings.

400 kV Ion Planter

This system is equipped with a variety of sources (gas, sputter, and metal vapor). This facility provides ion species from hydrogen to bismuth which can be used for studying fundamental

irradiation mechanisms and selective chemical doping in semiconductors, ferroelectrics, and superconductors.

Molecular Beam Epitaxy

We have state-of-the-art commercial semiconductor growth laboratories for MBE growth of III-V and II-VI materials. In addition, we have research systems for Group IV semiconductor growth, including conventional and beam-enhanced epitaxial growth.

Metal-Organic Chemical Vapor Deposition (MOCVD)

We maintain state-of-the-art materials growth and characterization facilities with unique capabilities in MOCVD of compound semiconductor

materials. Our facilities include commercial production MOCVD reactors as well as research reactors designed specifically for studies of CVD chemistry and for the development of advanced in situ diagnostics.

High Pressure and Shock Wave Physics and Chemistry Laboratories

Our capabilities in this area include large volume static high pressure apparatus which can be operated at temperatures ranging from 2° to 700° K and in magnetic fields; gas gun and explosive loading facilities with state-of-the-art, time-resolved diagnostics.

Shock Wave Synthesis

Recovery fixtures have been developed for use with gas gun and explosive shock loading facilities which allow unique material synthesis

over broad ranges of shock pressures and temperatures.

Crystal and Thin Film Growth

Capabilities in this area include a pulsed laser deposition chamber, a thin film oxide deposition chamber, a diamond-like carbon deposition chamber, a hot filament chemical vapor deposition chamber, and various apparatus for single crystal growth.

Low-Temperature Plasma Analysis

We have state-of-the-art capabilities for the analysis of low-temperature plasmas as found in commercial processing reactors. These include emission spectroscopy, electrical characterization, laser and microwave-based measurements of species concentrations, electric field measurements (in situ), and others.

— Theory and Simulation —

CVD Reactions

We have extensive capabilities to model complex chemically reacting flows such as occur in chemical vapor deposition manufacturing processes. Our numerical simulations can include the coupled gas-phase and gas-surface chemistry, fluid dynamics, heat, and mass transfer to provide predictive models of a chemical process.

Low-Temperature Plasmas

We have extensive capabilities in simulating the time and space evolution of low-temperature plasmas, focusing on new theoretical techniques for achieving rapid convergence and on direct comparisons with experimental results.

Optical Design

We have capabilities in novel optical designs, including resonators for application-driven laser geometries and in the application of binary optics.

These capabilities are coupled to in-house micro-optics construction facilities and state-of-the-art optics testing.

Wave Propagation

We have developed advanced simulation codes for understanding wave propagation in optical parametric oscillators and amplifiers for the purpose of designing efficient, mission-oriented tunable laser sources.

Electronic Structure and Linear Scaling

Our capabilities in this area include First Principles Surface Impurity Code, a Pseudo-Potential Band Structure Code and the ability to perform total energy and full potential electronic structure calculations. We are also developing linear scaling algorithms to replace current algorithms which scale as the cube of the number of particles.

Semiconductor Calculations

Expertise in this area includes: Ab initio pseudopotential bandstructure, semi-conductor transport and photo-luminescence, Monte Carlo surface epitaxial growth and sputtering, and

binary collision TRIMRC code to simulate ion-solid interactions. Workstations, CRAY-YMP, and massively parallel computational facilities are used.

—Recent Awards and Prizes in the Physical and Chemical Sciences Center—

1994 — R&D 100 Award to J. E. Houston and T. A. Michalske for “*Interfacial Force Microscope.*”

1992 — Department of Energy Materials Science Award for Significant Implication in Metallurgy and Ceramics to J. E. Houston and T. A. Michalske for “*Interfacial Force Microscope.*”

1992 — Department of Energy Materials Science Award for Sustained Outstanding Research to P. L. Gourley, I. J. Fritz, E. D. Jones, S. K. Lyo, J. S. Nelson, R. P. Schneider, G. C. Osbourn, R. M. Biefeld and L. R. Dawson for “*Strained-Layer and Artificially Structured Materials.*”