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FWP Executive Summaries

Basic Energy Sciences

Materials Sciences Programs

G. A. Samara

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FWP EXECUTIVE SUMMARIES

BASIC ENERGY SCIENCES
MATERIALS SCIENCES PROGRAMS
(SNL/NM)

G. A. Samara
Program Manager

Sandia National Laboratories
Albuquerque, New Mexico

January 1995

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I. Budget

Basic Energy Sciences/Materials Sciences Funding for FY94-97 Sandia National Laboratories - Albuquerque, New Mexico

Active Programs	Title	AFP FY94 (\$K)	AFP FY95 (\$K)	Projected FY96 (\$K)	Projected FY97 (\$K)
KC020101	Physics & Chemistry of Ceramics	950	967	996	1,026
KC020101	Polymer Composites (Center)	-	88	91	94
KC020101	Materials Joining (Center)	-	30	31	32
KC020102	Science of Adhesion	479	481	495	510
KC020102	Wetting and Flow of Liquid Metals	-	96	99	102
KC020103	Energetic Particle Synthesis	810	775	798	822
KC020103	Surface Hardness (Center)	-	80	82	84
KC020103	Advanced Growth	357	340	350	361
KC020105	Artificially-Structured Semiconductors	644	370	381	392
KC020105	Ceramic Hi T Superconductors	68	96	99	102
KC020105	Materials Joining	17	-	-	-
KC020105	Surface Hardness	50	-	-	-
KC020105	S&P Center (Performance Meas.)	140	-	-	-
KC020202	Tailored Surfaces for Materials Application	581	562	579	596
KC020202	Physics & Chemistry of Novel Superconductors	328	539	555	572
KC020202	Nanoclusters (Center)	10	-	-	-
KC020205	Boron-Rich Solids	461	490	505	520
KC020205	High Temp. Superconductivity	231	145	149	153
KC020205	Synthesis & Processing Center	194			
KC020302	Polymer Composites (Center)	50	-	-	-
KC020303	CVD Sciences	679	651	671	691
KC020303	Nanoclusters	<u>242</u>	<u>232</u>	<u>239</u>	<u>246</u>
	TOTALS	6,291	5,942	6,120	6,303
Equipment	- Programmatic	504	1052	500	500
	- Awards	100	200		

New Initiative Proposal

Electrorheological Fluids500K*

*This activity proposed for FY97 start ups could start in FY96 if funds become available.

II. Capital Equipment Requests

Mid Year (FY95) Requests (In priority Order)

1. Elemental Analysis Instrument \$65K

New elemental analysis equipment is needed for our thin films program. An essential part of determining identity and purity of new compounds is elemental analysis. Currently the in-house facilities at Sandia can not handle air sensitive compounds at an acceptable level. In addition, in-lab analysis will speed up compound identification and progress of our program. Delay and costs with contracted analysis preclude use of external sources of analysis.

2. Dual Port Glove Box \$64K

A very large effort is currently underway to develop and characterize unique mixed ceramic compound systems so that the properties of the solutions and the thin films generated from them can be understood and ultimately controlled. The compounds supported by the BES Ceramics Program contribute to a wide number of other projects currently underway. At present we have one, single-man glove box to perform all of our air sensitive reactions (upgraded by alternative funds) and this fact represents a serious limitation. By addition of another glove box, we will be able to exceed our current level of productivity in a number of areas.

Major Equipment Needs for FY96 (In Priority Order)

1. Scanning Near-Field Optical Microscope \$250K

Justification - Optical probes have great versatility for characterizing a wide range of materials in conditions ranging from ultra high vacuum to liquid environments. The numerous contrast mechanisms that are unique to light (e.g., absorption, reflection, polarization, emission, non-linear effects, etc.) provide both phase and composition sensitivity. Both linear and non-linear optical techniques are established tools for studying thin film growth and recent developments in ultrafast lasers provide new approaches to examine surface kinetics such as diffusion, reactions, and desorption. Despite the great utility of optical probes, an inherent disadvantage with regard to surface and interface characterization has always been the limited lateral or spatial resolution determined by the diffraction limit (250 nm for visible light). Thus all conventional optical techniques are necessarily macroscopic or "averaged" over many surface features below this limit.

With precise lateral and vertical motion control in the sub-Å range, coupled with sophisticated digital image processing, scanning probe microscopies (i.e., STM and IFM) have revolutionized nm-scale imaging of surfaces. The same technology is now available for optical characterization using the scanning near-field optical microscopy (SNOM). Near-field optics is based on using an aperture for light that is significantly smaller than the wavelength. Typically, the probe is an optical fiber (or micropipette) that has been

drawn to an extremely fine point. By scanning the fiber tip over the surface within the near-field optical condition one can produce optical images with nanometer-scale resolution.

We will integrate the SNOM capability into several BES Materials Science programs at Sandia. Specifically, we will characterize the optical properties of nano-size clusters, perform in-situ characterization of chemical vapor deposition to provide unique dynamical information on thin film nucleation and growth, and by incorporating the SNOM probe with an Interfacial Force Microscope, we can obtain direct structural information for lubricant and adhesive layers exposed to contact loading. In general, we will take full advantage of optical spectroscopies in the nanometer realm to provide the information needed for predictive models of corrosion, propagation of defects, and stability of nanometer-scale structures.

If not purchased - Sandia's BES Materials Science program will not have the capability to apply our expertise in optical spectroscopies to examine materials and growth processes on the nanometer-scale. Since electron-based spectroscopies are limited in their range of operating environments, we will not be able to directly study and model nanometer-scale processes important to technologically important processes such as CVD, aqueous corrosion, and thin film lubrication.

III. General Programmatic Overview and Institutional Issues

The goals of the BES Materials Sciences Program at Sandia are:

- Perform basic, forefront interdisciplinary research that also demonstrates relevance of basic science to technology.
- Choose programs which support DOE interests and are complementary to Sandia's multiprogram laboratory mission.
- Perform research in a setting which enhances technological impact because of Sandia's spectrum of coordinated basic research, applied research and development engineering.
- Take advantage of a wide range of large, capital-intensive research facilities not usually found at universities.

Our BES Materials Sciences Program has the central theme of Scientifically Tailored Materials. The major objective of this program is to combine Sandia's expertise and capabilities in the areas of solid state sciences, advanced atomic-level diagnostics and materials synthesis and processing science to produce new classes of tailored materials for U.S. energy applications, for critical defense needs and for industrial applications.

Current research in this program at SNL/NM includes the physics and chemistry of ceramics synthesis and processing, the use of energetic particles for the synthesis and study of materials, high-temperature and organic superconductors, tailored surfaces and interfaces for materials applications, chemical vapor deposition sciences, artificially structured semiconductor materials science, advanced growth techniques for improved semiconductor structures, boron-rich solids, atomic level science of interfacial adhesion, and the synthesis and processing of nano-size clusters for energy applications. Considerable synergism exists among these program elements, and most of them share a number of common themes based on either the science or the use of common synthesis and processing approaches. These themes are: Synthesis and Processing, Epitaxial Growth, Surfaces and Interfaces, Energetic Beams and High Tc Superconductivity. Several of the technical activities of the program have been incorporated into the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials.

Two new activities were initiated in late FY 94 after DMS allocated some funding for each. The first is a collaboration with the National Renewable Energy Laboratory and is entitled **"Composition Modulated Semiconductor Structures for Photovoltaic and Optical Technologies."** DMS provided \$200K to initiate this activity and hire a post doc. The work deals with compositional structuring and alloy ordering in III-V semiconductors to enhance their performance for photovoltaic and other optical applications. Several visits between the involved staffs at the two laboratories have taken place to coordinate the planned work. Programmatically this activity is included as one of the tasks under our core program on Artificially Structured Semiconductor Materials Science.

The second new activity is entitled **"Wetting and Flow of Liquid Metals and Amorphous Ceramics at Solid Interfaces."** DMS provided \$100K and, by agreement with DMS, we redirected \$100K of FY 94 funding from the Tailored Surfaces and Interfaces Program to initiate this activity. The goal of this work is to perform experiments and model the atomic-scale processes that control fluid flow at solid interfaces and use these understandings to develop

predictive models for macroscopic wetting and flow behavior. Collaborators include Roland Cannon of LBL/U. C. Berkeley and Uzi Landman of Georgia Tech. The results of this work are expected to be relevant to the Materials Joining Project of the Synthesis and Processing Center, and interactions with the Project will be initiated.

Our interdisciplinary program utilizes a broad array of sophisticated, state-of-the-art experimental capabilities provided by other programs as well as this program. The major leveraged capabilities include several molecular beam epitaxy and chemical vapor deposition facilities, a broad range of materials synthesis and processing facilities, clean rooms, ion-beam accelerators, laser-based diagnostics, advanced optical and surface spectroscopies, unique combined high-pressure/low-temperature/high-magnetic-field facilities, and electron, scanning tunneling and atomic force microscopies.

A. The DOE Center of Excellence For The Synthesis and Processing of Advanced Materials. (S&P Center)

In addition to being involved in the technical program of the S&P Center, Sandia is responsible for the overall coordination of Center activities. Summaries of our coordination efforts and a description of the projects which constitute the technical focus of the Center are given in Sec. IV, p. 9.

B. Industrial Interactions/Technology Transfer

Our DMS-funded program has been responsible fully or in part for the generation of over 30 cooperative research and development agreements (CRADAs) with industrial partners. We also have several less formal collaborations. A summary is provided in Sec. V, p. 16.

C. New Initiative Proposal

This year we are submitting a new proposal entitled "Electrorheological Fluids." Materials synthesis and characterization will be combined with experimental measurements and analytic theory to guide the synthesis of new materials that have applications of interest to the DOE. Electrorheological fluids are particle suspensions that rapidly solidify when subjected to large electric fields. Solidification is due to the chaining of dispersed particles chain along the electric field lines. Because induced dipolar forces are involved, the strength of the solid increases as the square of the field. This fast, reversible liquid-solid transition has applications in clutches, continuously variable transmissions, active vibration damping materials, and valveless hydraulic systems. However, to be used for practical applications the available fluids must have a greater yield stress at a lower applied electric field. Current methods of preparing these materials are largely empirical since there is very little scientific understanding of the phenomena, but key findings in a Sandia LDRD have demonstrated that it is now possible to understand and control the properties of these materials. This proposal builds on these findings. A summary of the proposal is provided in Sec. VI. A. p. 22.

D. Technical Program Highlights

The technical accomplishments of the Program during the past year are summarized in Sec. VI.B. Highlights of the work include:

- Development of and implementation of two new optical monitors for thin film growth that can potentially revolutionize the process control of epitaxial thin film growth. These monitors provide the grower with the first in-situ measure of film thickness and composition. (pp. 25 and 57)
- Development of an ambient pressure process for producing thin film and bulk aerogels. This process may be the enabling technology that opens up new fields of cost-effective, ultralow dielectric constant dielectrics and superinsulants. (pp. 26 and 37)
- Discovery that microscopic cavities in silicon formed by helium ion implantation provide strong sinks for metal atoms (Fe, Co, Ni, Cu and Au) that, if allowed to remain mobile within the silicon lattice, would severely degrade electrical properties. Results have important implications for meeting the very low (1 in 10^{14}) future metal-impurity tolerances of advanced microelectronics. (pp. 27 and 44)
- Demonstration and explanation of the extraordinary radiation hardness of semiconducting icosahedral borides as contrasted with other boron-rich solids. This result is significant for the development of electronic devices that can operate in radiation environments that preclude use of conventional semiconductors. (pp. 28 and 55)
- Synthesis of superconducting Tl-Ba-Ca-Cu-O thin films with significantly enhanced properties using controlled, scalable, two-temperature-zone furnace processing. This represents a significant advance toward the manufacturing of these materials. (pp. 29 and 50)
- Development of a comprehensive understanding of the atomic mechanisms controlling ion-assisted thin film growth based on in-situ electron diffraction measurements in conjunction with computer simulations. Ion bombardment during growth helps control surface morphology, a key issue in the development of ultra-small structures. (pp. 30 and 46)
- Application of the interfacial force microscope to the first study of the adhesive bonding force as a function of separation between controlled surfaces of self-assembling monolayer films deposited on both substrate and probe surfaces. The quantitative understanding of chemical bonding so obtained represents a significant step towards the ability to design adhesives for specific applications. (pp. 31 and 40)
- New understanding of the semiconductor bandstructure alignments induced by ordering in InGaP_2 which is important for developing this material for high efficiency photovoltaic devices. (pp. 32 and 48)
- Demonstration of a universal scaling relation for the dynamic spreading of liquids of widely different chemical properties on solid surfaces. The results are important for joining technologies as well as for the synthesis and processing of advanced metal-ceramic composites. (pp. 33 and 42)
- New understanding of the complex surface chemistry in the metal-organic chemical vapor deposition of GaAs. (pp. 34 and 57)

E. Program Reviews

1. BESAC Review

The BESAC members met in Albuquerque on February 25-27, 1994. Our DMS program was one of the main agenda items. A broad review of the motivation, organization, management and technical highlights of the program was given. Very favorable comments were received, but we have not received the written report. Particularly noteworthy was the strong Committee support for the concept and objectives of the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials.

2. Expert Panel

Several elements of our DMS-funded program were reviewed on September 14-15, 1994 by an expert review panel organized by the management (W. T. Oosterhuis and J. J. Smith) of DMS.

The panel members were Prof. Ivan Schuler (UCSD), Prof. Douglas Finnemore (Ames/Iowa State University); Prof. Sam Liu (UCSD); and Prof. F. DiSalvo (Cornell)

W. T. Oosterhuis, J. J. Smith, H. L. Davis and D. Koelling from DMS participated in the review. Although we have not yet received the panel's written report, the verbal feedback we received from the DMS staff and panel members commented on the high quality, productivity and broad interactions of our program.

The program elements reviewed were

- CVD Sciences
- Physics and Chemistry of Novel Superconductors
- Tailored Surfaces for Materials Applications
- Boron-Rich Solids
- The Synthesis and Processing of Nanoclusters for Energy Applications

3. DMS Management On-Site Reviews

- On June 24, 1994 Dr. J. J. Smith of DMS visited and reviewed the above program elements.
- On June 15-16, 1994 Dr. A. L. Dragoo of DMS visited and performed his annual reviews of the following program elements
 - Physics and Chemistry of Ceramics
 - Atomic-Level Science of Adhesion
 - Energetic Particle Synthesis and Science of Materials
 - Advanced Growth Techniques and the Science of Epitaxy
 - Artificially-Structured Semiconductors

4. Germantown Management Review

The annual management review of our program was held in Germantown on March 8, 1994.

5. In-House Management Reviews

Each element of our program is evaluated on a continuing basis with respect to objectives and performance by the responsible line management. Each involved participant is evaluated on his/her contributions in a formal annual review process with feedback.

F. Program Changes

The Ceramics Program has changed significantly over the last year, while maintaining its central mission: to understand the chemical and physical processes that link precursors to the properties of ceramics and glasses. These changes were in program leadership and task focus. Alan Hurd took over the management of the program in May 1994 when Dale Schaefer accepted an assignment in Defense Programs in Washington. While Dale's leadership is missed, he continues to contribute technically to the program, especially in the area of glass dynamics. Hurd is a familiar participant, having been involved in the BES Ceramics program since its inception.

The technical focus of the program has been narrowed to three areas: Porous Materials, Complex Precursors, and Glass Dynamics. Each area has active theoretical input, although deeper interactions are sought.

G. Program Quality/Recognition

1994 was another excellent year in terms of the significant accomplishments and productivity of our DMS program (as detailed in Sections IV.B and V.B of this Executive Summaries booklet) and in terms of the professional recognition received by our staff, both of which reflect on the quality of our BES program.

We received four DMS awards as follows:

1. *Sustained Outstanding Research in Metallurgy and Ceramics*: "Science of Surface Processes in Beam-Enhanced Growth," E. Chason, J. Y. Tsao, J. A. Floro, K. M. Horn, T. M. Mayer, P. Bedrossian, D. K. Brice and S. T. Picraux.
2. *Significant Implication for Department of Energy Related Technologies in Metallurgy and Ceramics*: "Ambient Pressure Aerogels: Thin Film and Bulk," C. J. Brinker, S. S. Prakash (UNM), D. M. Smith (UNM), and R. Deshpande (Armstrong World Industries).
3. *Sustained Outstanding Research in Solid State Physics*: "Surface Atom Energetics," P. J. Feibelman.
4. *Significant Implication for Department of Energy Related Technologies in Materials Chemistry*: "Real Time *In Situ* Materials Growth Monitors Using Remote Optical Probes," K. P. Killeen, S. A. Chalmers, and W. G. Breiland.

We also organized symposia, chaired sessions, and presented numerous invited papers at national and international conferences (see individual program summaries for details).

IV. The DOE Center of Excellence For The Synthesis And Processing of Advanced Materials

The Center was established by the Division of Materials Sciences and the DOE Laboratories in recognition of the importance of materials synthesis and processing (S&P) to present and future technologies. It is a coordinated, cooperative venture among the following laboratories: Ames Laboratory (Ames), Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), Idaho National Engineering Laboratory (INEL), University of Illinois Seitz Materials Research Laboratory (UI/MRL), Lawrence Berkeley Laboratory (LBL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), Pacific Northwest Laboratory (PNL), and Sandia National Laboratories (SNL). The Center will also include appropriate university grant research.

Sandia is responsible for the overall coordination of Center activities.

The overall objective of the Center is,

"To enhance the science and engineering of materials synthesis and processing in order to meet the programmatic needs of the Department of Energy and to facilitate the technological exploitation of materials".

Synthesis and processing are those essential elements of materials science and engineering (MS&E) that deal with (1) the assembly of atoms or molecules to form materials, (2) the manipulation and control of the structure at all levels from the atomic to the macroscopic scale, and (3) the development of processes to produce materials for specific applications. Clearly, S&P represent a large area of MS&E that spans the range from fundamental research to technology. The goal of basic research in this area ranges from the creation of new materials and the improvement of the properties of known materials, to the understanding of such phenomena as diffusion, crystal growth, sintering, phase transitions, etc., in relation to S&P. On the applied side, the goal of S&P is to translate scientific results into useful materials by developing processes capable of producing high quality, low-cost products.

Sandia has incorporated appropriate research from its DMS-funded program into the Center. In addition we have responsibility for the overall coordination of Center programs and activities.

A. Center Workshops and Coordination Meetings

1. Workshops

Much effort involving all of the laboratories' Center coordinators and DMS staff was spent during the spring of 1994 on organizing and planning the seven Center projects which were identified in January 1994. This effort resulted in a workshop for each project (described below).

2. Germantown, May 24, 1994

The Center's Project coordinators met to review the results of the workshops and the restulging plans for hte Projects. A set of recommendations to DMS was agreed upon, and Iran Thomas and the DMS staff were briefed on the results.

3. Boston, November 29, 1994

A coordination meeting involving all the Laboratories' coordinators and many DMS staff was held in conjunction with the MRS meeting. Agenda items included a Center update, and initial discussions on Center Performance Measures and potential future Center projects in photovoltaics and amorphous metals.

4. Dallas, January 31, 1995

The Laboratories' coordinators, Dr. Robert Gottschall and Dr. Jerry Smith met in Dallas. Agenda items included the membership of and next meeting with the Center's Industrial Steering Group, review of the strawman on Center Performance measures, a format for reporting the Center's research highlights, and potential new Center project. Several decisions were reached and follow-on actions and responsibilities defined.

B. Materials and Processes Focus of the Center

The current emphasis of the Center is on seven focused multilaboratory Projects developed in FY 94 which draw on the complementary strengths of the member institutions in their ongoing research programs. These seven Projects were selected from among many potential choices within the DMS program on the basis of the following criteria:

- Scientific excellence
- Clear relationship to technology
- Involvement of several laboratories
- Strong existing or potential partnerships with DOE Technologies
- Strong existing or potential partnerships with industry.

Thus, the emphasis of the Projects is on technological relevance and the potential for making near term impact. Each Project held a workshop during the spring 1994 attended by principal investigators (PIs) from the laboratories and by representatives from DMS staff. The main purpose of these workshops was to bring together the PIs to define the objectives, scope and participants of each Project. Invitations to these workshops were extended to appropriate DOE Technologies Offices and industrial representatives. We had limited, but helpful participation by these groups. Each Projects is coordinated by an appropriate representative from one of the participating institutions. George A. Samara (SNL/NM) is the overall Center coordinator.

A brief description of each project follows:

1. Conventional and Superplastic Metal Forming

Participating Labs: Ames, LBL, LLNL, LANL, ORNL, PNL, SNL/CA

Coordinator: W. G. Wolfer (SNL/CA)

This project is motivated by the goal of improving fuel efficiency in transportation systems. Achieving this goal requires the use of light weight structural materials which in turn necessitates consideration of aluminum alloys. Unfortunately, compared to steels, Al alloys are more difficult to form and exhibit rougher surfaces after forming.

The major objective of the project is to concentrate on those aspects of deformation mechanisms which control formability in conventional metal forming and which contribute to superplasticity in fine-grained materials. Because of the desired impact of this research on automotive technology, the research will be carried out on alloys based on the Al-Mg and Al-Cu systems. The intent of the research is to advance the understanding of the compositional and microstructural aspects which improve formability for conventional forming on the one hand, and which lead to superplasticity on the other hand. The results of this research are expected to assist the materials industry in the development and improvement of aluminum alloys for high-rate forming applications, and to contribute to efforts in the automotive sector to overcome some of the present limitations encountered in the use and in forming of aluminum sheet metal for automotive components.

2. Materials Joining

Participating Labs: Ames, INEL, LBL, LLNL, ORNL, PNL, SNL/CA, SNL/NM

Coordinator: R. Bruce Thompson (Ames)

Materials joining is an enabling technology in virtually all industrial sectors, and often the reliability of joints is the factor that limits performance. Welding is an old technology, but weld failures are common and some technologically important materials such as aluminum alloys are difficult to weld. Advanced high temperature ceramics have tremendous potential in energy and related technologies, but there are no reliable methods of joining them. These realities provide the motivation for this project.

The project consists of two tasks. The first entitled "*The effects of Gradients on Weld Reliability and Performance*," will use advances in experimental, analytical and computational tools to develop an integrated and quantitative understanding of the origin and extent of gradients in composition, stress, microstructure and properties which occur during various welding processes. Strategies will also be developed to control these gradients which are often the cause of failure. Initial emphasis is on Al-Cu alloys and on Fe-Ni-Cr alloys.

The second task, "*Ceramics and Dissimilar Materials Joining*," focuses on critical issues in the non-welding joining area which include property mismatch between members to be joined; use temperature limitation; poor wetting, adhesion and/or chemical bonding; and manufacturing and/or joint reliability. Some of the initial emphasis is on silicon carbide joining, an area of strong interest to the Fossil Energy program. This part of the work will be done in collaboration with research sponsored by the Office of Advanced Research, Fossil Energy program.

3. Nanoscale Materials For Energy Applications

Participating Labs: ANL, LBL, LLNL, UI/MRL, NREL, ORNL, SNL/NM

Coordinators: D.S. Chemla/Mark Alper (LBL)

Nanosize materials offer exciting opportunities in many areas of technology. These materials have properties very different from those of the bulk and the surface, and are also unlike those of individual atoms or molecules. They are expected to have size-dependent electronic, optical, mechanical, surface (lubricative, adhesive, hardness), magnetic and energy storage and transfer characteristics. Some of these properties result from their enormous surface area-to-volume ratios. Additional properties result from quantum size effects which appear when the dimensions of a system become comparable with or smaller than the wavelength of the corresponding quantum excitations in the bulk. Other properties results from altered surface, magnetic, and storage characteristics. 3D networks of these materials, besides enhanced connectivity enabling integration of functions, can exhibit collective responses different from those of the constituents.

Consistent with what are believed to be the most pressing needs to advance and utilize this new area of materials science, the project consists of three closely related tasks:

- synthesis and processing for controlled size,
- surface passivation and interface properties, and
- interconnections and assemblies.

Metal, semiconductor and oxide clusters are of interest, and the synthesis routes being pursued include inverse micelles, arrested precipitation, ball milling, colloidal dispersions, ion implantation, gas condensation, sputtering and sol-gel methods. Initial targeted applications are catalysis, optoelectronics and soft magnets.

4. Tailored Microstructures in Hard Magnets

Participating Labs: Ames, ANL, BNL, INEL, LBL, LLNL, LANL, ORNL

Coordinator: Bob Dunlap (ANL)

Improvements in the properties of permanent (or hard) magnetic material can lead to lighter, more efficient and longer life motors for energy, transportation and many other industries. A figure of merit for permanent magnet materials is the maximum energy product, W . In some of the best current commercial materials W is $\leq 50\%$ of its theoretical value. The problem is generally attributed to a lack of understanding of the role of microstructure in determining magnetic properties. Other limitations of current commercial magnetic materials are relatively poor mechanical and corrosion-resistant properties. These properties are also determined largely by microstructure.

The overall objective of this project is to improve hard magnets by understanding, in terms of the microstructures achieved, the magnetic and mechanical properties of materials produced by a number of synthesis and processing (S&P) approaches.

Initial focus is on the technologically important material $\text{Nd}_2\text{Fe}_{14}\text{B}$ as a model system. Specifically, this material will be produced in single crystal, powder, bulk and thin film forms and characterized by state-of-the-art tools. The microstructures developed by the different S&P methods will be compared and modeled. The relationship between microstructure and domain wall pinning, magnetic properties and mechanical properties will be determined. The ultimate goal is to identify S&P approaches which optimize material properties for specific applications.

5. Microstructural Engineering with Polymers

Participating Labs: Ames, BNL, INEL, UI/MRL, LBL, LLNL, PNL, SNL/NM

Coordinator: Gregory J. Exarhos (PNL)

The manipulation of polymer chain structure underlies the current, "age of polymers." Although discoveries of new polymers continue, it is widely recognized that emerging technologies will use multiphase polymers, structurally designed to achieve properties inaccessible by simple, single-component materials. These materials will exploit phase separation phenomena, restricted to submicron scales by clever design of precursors and processing protocol. This project seeks to establish the scientific basis for tailoring such structurally engineered materials.

The goal of this project is to develop new multiphase materials that retain the processability of organic polymers but share the properties normally associated with inorganic materials. The project seeks a foundation for multiphase polymers similar to the knowledge base in small-molecule chemistry that underlies the current generation of commodity polymers. Initial emphasis will be on the development of advanced synthesis and processing approaches for mesostructured polymers, polymer blends and polymer ceramic/glass composites.

6. Processing for Surface Hardness

Participating Labs: LBL, LLNL, LANL, ORNL, SNL/CA, SNL/NM

Coordinator: James B. Roberto (ORNL)

There exists a broad range of applications for which the ability to produce an adherent, hard, thin, wear-resistant coating plays a vital role. These applications include engine and machine components, orthopedic devices, textile manufacturing components, hard disk media, micromachined sensors and actuators, optical coating, and cutting and machining tools (e.g., punches, taps, scoring dies, and extrusion dies). Emphasis is being placed on development and improvement of processes which are environmentally benign and which provide flexible control over the surface structure and chemistry.

Plasma-based processing is an important component of processes used for the applications listed above. The ability to provide flux, energy, and temporal control of a variety of ions, which is characteristic of plasma-based processing, provides the means to tailor surface structure and chemistry necessary to solve current and future problems that relate surface hardness and other tribological properties.

The goal of the project is to address critical issues which limit the use of plasma-based processing for surface hardness. Initial emphasis is on plasma ion immersion processing (PIIP), a relatively

inexpensive non-line-of-sight-implantation process capable of treating complex-shaped targets without complex fixturing, and on boron-based superhard coatings where the focus is on cubic boron nitride and boron suboxides.

7. Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance

Participating Labs: ANL, INEL, LBL, LLNL, ORNL

Coordinator: Linda L. Horton (ORNL)

Protection from corrosion and environmental effects arising from deleterious reactions with gases and condensed products is required to fully exploit the potential of advanced high-temperature materials designed to improve energy efficiency and minimize deleterious environmental impact. The resistance to such reactions is best afforded by the formation of stable surface oxides that are slow growing, sound, and adherent to the substrate and/or by the deposition of coatings that contain or develop oxides with similar characteristics. However, the ability of brittle ceramic films and coatings to protect the material on which they are formed or deposited has long been problematical, particularly for applications involving numerous or severe high temperature thermal cycles or very aggressive environments. This lack of mechanical reliability severely limits the performance or durability of alloys and ceramics in many high-temperature industrial applications and places severe restrictions on deployment of such materials. The beneficial effects of certain alloying additions on the growth and adherence of protective oxide scales on metallic substrates are well known, but satisfactory broad understandings of the mechanisms by which scale properties and coating integrity (that is, corrosion resistance) are improved by compositional, microstructural, and processing modifications are lacking.

The objective of this task is to systematically generate the knowledge required to establish a scientific basis for the design and synthesis of improved (slow growing, adherent, sound) protective oxide coatings and scales on high temperature materials without compromising the requisite bulk material properties. Specific objectives are to (1) systematically investigate the relationships among substrate composition and properties and scale/coating adherence, damage tolerance, and micromechanical properties, (2) use such information to predict scale/coating failure, and (3) identify conditions leading to more damage-tolerant coatings and scales that are amenable to legitimate synthesis routes. The initial emphasis is on alumina scales and coatings, and the work will be co-sponsored by the Office of Advanced Research, Fossil Energy Program. Some of the work in the project is also in collaboration with the Electric Power Research Institute (EPRI).

C. The Center's Industrial Steering Group

The Center has an industrial perspective provided by an Industrial Steering Group (ISG). The role of ISG is to become familiar with the Center's technical activities and comment on their value to industry, provide information from an industrial perspective, help identify technological barriers, influence the direction of the Center's programs, and help develop ideas which can make the Center more effective.

Current ISG membership is as follows:

<u>Member</u>	<u>Specialty</u>
Dr. Thomas R. Anthony (GE)	Emerging Materials and Processes
Dr. Uma Chowdhry (Dupont)	Ceramics
Dr. Thomas C. Clarke (IBM-Almaden)	Polymers, Electronic Materials
Dr. David W. Johnson, Jr. (AT&T Bell Labs)	Ceramics
Dr. Hylan B. Lyon, Jr. (Marlow Industries)	Emerging Materials and Processes
Dr. Neil E. Paton (Howmet)	Metals and Alloys

This membership was established before the formation of the above-discussed Center Projects. Appropriate additional members will be added in FY 95.

D. Center Performance Measures

A small project has been set up to develop performance measures for the Center. The project, under the direction of Dr. Gretchen Jordan of Sandia National Laboratories, will research methods for annual performance measurement that capture progress and socio-economic impacts in addition to measures of the quality of science. A model will be documented for possible transfer to other OBES activities.

V. Industrial Interactions and Technology Transfer

A. CRADAs and Contracts

The research results and capabilities of our DMS-sponsored program have been responsible fully or in part for the generation of over 30 cooperative research agreements or contracts with industrial partners. Details are given in the Table on the following pages.

While all projects in our Program are involved in industrial interactions and technology transfer, two projects, CVD Sciences and Physics and Chemistry of Ceramics, stand out in being involved in over half of the industrial agreements. Over the last three years our CVD Science BES/MS program has directly led to several significant DOE/DP Technology Transfer Initiative (TTI) programs which serve to leverage the funding provided by BES. Our first TTI program, with Texas Instruments, applied the IRIS techniques developed in this program to the measurement of critical kinetic rates in plasma processes. Two major CRADA programs currently underway seek to improve MOCVD equipment and develop safer process chemistries for the growth of compound semiconductor materials. The first of these CRADAs, with Motorola, focuses on advanced precursors that can replace arsine and phosphine for growth of III-V materials via MOCVD. Motorola clearly recognizes the benefits of having a detailed, fundamental knowledge of process chemistries, and so in addition to developing safer processes, they are also asking Sandia to provide them with kinetic models that they can use in numerical simulations of their MOCVD equipment. The second CRADA, with EMCORE, seeks to apply Sandia's expertise in rotating-disk reactor technology to improve EMCORE's commercial high-speed rotating disk MOCVD reactor. Additional DP/TTI programs that help leverage Sandia's programs in chemical vapor deposition research include programs on optoelectronic device manufacturing with Hewlett-Packard, on the manufacturing of thick diamond films for heat sinks with Norton Diamond Films and on the growth of antimonide materials for magnetic sensors with GM as part of the Clear Car Initiative.

In the Ceramics project our research on ferroelectric thin films has led to two CRADAs with Radiant Technologies on nonvolatile memories and to our involvement with the ARPA-sponsored NCAICM initiative, also on nonvolatile memories. Superconductor Components, Inc. has obtained a license to market high quality superconductor powders produced by our patented solution process, and we continue to consult with this company. Our sol-gel films research has led to our involvement in two CRADAs and two contracts. One of the contracts is with the Gas Research Institute to develop membranes for gas separation. The other is ARPA-funded with 3M on fiber reinforcement. The CRADAs are with a 7-member industrial consortium on non-lithographic processing and with AMOCO on the development of membranes for gaseous separations. Other spin-offs from the Ceramics project are listed in the Table.

All of the industrial connections summarized above and in the Table point clearly to the value and impact of our DMS-funded research. It is critical that we maintain the focus of this research on the development and enhancement of new research tools and capabilities, for it is these tools that are the foundation of the applied programs.

Company	Agreement	Project	DMS-Funded Progenitor(s)
Radiant Technologies	DP/TTI-CRADA	Nondestructive Readout Nonvolatile Memories: (Semiconductor/Ferroelectric)	Ferroelectric Ceramics
Radiant Technologies	DP/TTI-CRADA	Optical Read-Write Memory	Ferroelectric Ceramics
SEMATECH	DP/TTI-CRADA	Benchmarking Microelectronics and Manufacturing Equipment	CVD Sciences
SEMATECH	DP/TTI-CRADA	Microelectronics Manufacturing Technology-Semiconductor Equipment Reliability Modeling and Design.	CVD Sciences; Strained Layer Semiconductors
SEMATECH	DP/TTI-CRADA	Contamination-Free Semiconductor Manufacturing	Energetic Part. Synthesis
Hewlett Packard	DP/TTI-CRADA	Advanced Manufacturing Techniques for Optoelectronics	Strained-Layer Semiconductors; Ceramics
Hewlett Packard	DP/TTI-CRADA	Electronic, Optical and Thermodynamic Properties of Visible Light Emitting Diodes	Strained-Layer Semiconductors
Texas Instruments	DP/TTI-CRADA	Measurements of Kinetic Rates in Plasma Processing.	CVD Sciences
DuPont	DP/TTI-CRADA	Diamond Film Synthesis and Processing.	CVD Sciences
Digital Instruments, AT&T, Univ. of NM	DP/TTI-CRADA	Non-Contact Atomic Level Interface Force Microscope.	Interfacial Adhesion
Conductus, Inc.	DP/TTI-CRADA	Confocal Resonator Imaging System for Surface Analysis	Novel Superconductors
Cray Research	DP/TTI-CRADA	Massively Parallel Electronic Structure Methods for CRAY's MPP Supercomputer	Strained-Layer Semiconductors
Charles Evans & Assoc.	BES/MS-CRADA	New Light-Element Depth Profiling Technique	Energetic Part. Synthesis
Motorola	DP/TTI-CRADA	Advanced SiGeC Materials for High-Performance Digital Microelectronics	Adv. Growth
NCAICM	ARPA-CRADA	Manufacturing Technology for 1 Megabyte Ferroelectric Nonvolatile Memory	Ferroelectric Ceramics
3M	ARPA-Joint Project	Drying of Fibers - Fiber Reinforcement Project	Sol-Gel Films
Amoco	IWRP-CRADA	Membranes for Commercial Separations	Sol-Gel Films
7-Member Display Consortium	ARPA-CRADA	Non-Lithographic Processing	Sol-Gel Films

Company	Agreement	Project	DMS-Funded Progenitor(s)
Gas Research Inst.	Contract	Porous Materials for Methane Storage	Sol-Gel Films
Dow-Corning	DP/TTI-CRADA	Silicone Microcomposites	'91 S&P Center Project
Dow Chem.	DP/TTI-CRADA	Processing of Chlorinated Polyethylene	'91 S&P Center Project
BIOSYM Technologies	DP/TTI-CRADA	Computer Software for Modeling Polymer Blends	ORNL/SNL Blends Program
Goodyear	DP/TTI-CRADA	Materials for Tire Technology	ORNL/SNL Blends Program
SCT Technologies	License	Solution Processing of High-Temperature Superconductors	Cermic Hi Tc
EMCORE	DP/TTI-CRADA	Metal-Organic Vapor-Phase Epitaxy of Compound Semiconductor Devices	CVD Sciences
Motorola	DP/TTI-CRADA	Advanced Precursors and Chemistries for Metal-Organic Vapor Phase Epitaxy	CVD Sciences
Dupont	DP/TTI-CRADA	Improved TI-Based High Temperature Superconductivity Films	Novel Superconductors
United Technologies	ARPA Contract	Model for Silicon Nitride Deposition - Scaling Up Commercial Reactors	CVD Sciences
Norton	ARPA Contract	Thick Diamond Films for Heat Sinks	CVD Sciences
Norton	DP/TTI-CRADA	Halide and Oxygen Chemistries for Diamond Film Synthesis	CVD Sciences
Schumacher Inc.	DP/TTI-CRADA	Development of Copper CVD	CVD Sciences
General Motors	DP/TTI-CRADA	Growth of Antimonide III-V Semiconductors	CVD Sciences; Strained-Layer Semiconductors
SEMATECH	DP/TTI-CRADA	Development of High Temperature Electrostatic Chucks	Ceramics; Sol-Gel

B. Other Industrial Interactions

Our DMS-sponsored research has also been responsible for several other less formal, but significant, industrial interactions and/or technology transfer activities. These include the following:

1. Semiconductor Heterostructure Mirrors for Vertical Cavity Surface-Emitting Lasers - The study of semiconductor heterostructure mirrors, leading to high Q Fabry-Perot laser cavities now used by industry (Bandgap Technology, Photonics Research), was initiated in our program on strained-layer semiconductors. The synthesis of these structures and the study of their physical properties was funded largely by DMS. The technology was transferred last year to Bandgap Technology Corporation which markets 860 nm lasers for optical communications and imaging applications.
2. Gettering of Impurities - Within the Energetic-Particle Synthesis and Science of Materials project it was discovered that microscopic cavities within a silicon wafer trap (more effectively than with other means) metal impurities that would otherwise be highly detrimental to electronic devices on the wafer. These cavities can be formed by ion-implanting He and then heating the material to 700°C or above. After this discovery was released in 1993, expressions of interest and requests for additional information were received from SEMATECH and twelve semiconductor companies, one of whom has proposed to initiate a CRADA.
3. Surface Treatments - Within the Energetic Particle Synthesis and Science of Materials project it was discovered that ion implantation of oxygen into aluminum can produce an extremely high density of nanometer-size aluminum-oxide particles, and that the resulting alloy has high mechanical strength (in the gigapascal range typical of high-strength steels), and substantially reduced friction and wear during sliding contact. Release of this discovery in trade journals led to requests for information from 41 companies, and at least two of these are known to be exploring technological applications.

Previously (more than 5 years ago) we discovered that the implantation of titanium and oxygen into ferrous alloys creates an amorphous layer with greatly reduced friction ($\times 1/2$) and increased wear ($\times 10$) resistance. This surface treatment process was transferred to industry, and, for example, is still used by Spire Corporation for surface treatment of hard bearing steels to achieve improved tribological properties.
4. Dodson-Tsao Model of Strained-Layer Stability and Metastability - This work provided a unified approach to understanding the stability limits of strained layer films and the kinetics of strain relaxation. It was crucial in the quantitative understanding of strain relaxation and stability in semiconductor structures. These types of structures are now used commonly in the edge-emitting diode lasers found in CD-ROM players and ultrafast pseudomorphic HEMT devices used in microwave applications.
5. Stress Corrosion of Ceramics - Our earlier DMS-funded work in this area led to an AT&T-funded project to apply fundamental models for glass fracture and glass surface reactivity to develop optical fiber cables with improved reliability. This interaction has brought in over \$400 K in direct funding from AT&T and has resulted in two patents.

6. Consortium for Advanced Synthesis and Processing of Electronic Materials - A consortium of 5 companies and 4 universities, led by Texas Instruments and Hughes Aircraft and funded by ARPA, has been formed to study ways to advance the synthesis and processing of new electronic materials. The major goal of this project is to enhance molecular beam epitaxy (MBE) technology to improve U.S. competitiveness in semiconductor structures. Sandia has been chosen as an associate member of this team. Reflection mass spectrometry (REMS), developed under the DMS Advanced Growth project, has been targeted for development as an on-line diagnostic for monitoring of surface reactivity during III-V quantum well synthesis.
7. SEMATECH Task Force on Surface Microroughness - SEMATECH has recognized the importance of monitoring and control of nanoscale surface roughness during semiconductor wafer production for next generation electronic devices. A task force has been formed to close the technology gap in particle counting and microroughness determination. SEMATECH has enlisted our help as a designated resource on surface roughness to help in the development and calibration of various techniques for determining surface roughness. We have used the EDXRR (energy-dispersive X-ray reflectivity) technique developed in the DMS Advanced Growth project to measure the surface roughness of as-prepared wafers.
8. Boron-Rich Solids for Energy and Radiation Applications - We have consulted extensively with two companies who have expressed strong interest in our DMS-funded work on boron-rich solids. One of the companies, High Z, is interested in the thermoelectric properties of these materials and already markets a product, and the other, Science and Engineering Associates (SEA) is interested in energy conversion devices and in the extreme radiation tolerance of borides.
9. Surface Science Codes - Discussions have been initiated with Biosym Corp., to develop commercial software based on computational methods developed in our DMS-funded Tailored Surfaces project.

VI. Research Program Summaries

A. New Initiative Proposal

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New Initiative Proposal

Electrorheological Fluids

Principal Investigators and Collaborators

P.I.'s: SNL/NM J. E. Martin, D. Adolf, M. Anderson, R. Anderson
Collaborators: Exxon T. Halsey; LANL R. Hjelm; Ford J. Ginder

Motivation and Objectives

We propose a fundamental research program into electrorheological fluids, in which materials synthesis and characterization will be combined with experimental measurements and analytic theory, to guide the synthesis of new materials that have applications of interest to the DOE. Electrorheological fluids are particle suspensions that rapidly solidify when subjected to large electric fields. Solidification is due to the chaining of dispersed particles along the electric field lines. Because induced dipolar forces are involved, the strength of the solid increases as the square of the field. This fast, reversible liquid-solid transition has applications in clutches, continuously variable transmissions, active vibration damping materials, and valveless hydraulic systems. However, to be useful for practical applications the available fluids must have a greater yield stress at a lower applied electric field. Current methods of preparing these materials are largely empirical since there is very little scientific understanding of the phenomena, but key findings in an exploratory Sandia Laboratory-Directed R&D (LDRD) program has demonstrated that it is now possible to understand and control the properties of these materials.

Our proposed program has four principal thrusts: Mechanisms of Particle Polarization; Nonohmic Conduction and Dielectric Breakdown; Fluid Synthesis and Stabilization; and Structure and Rheology of Concentrated Suspensions. In each of these areas we will conduct experiments and develop theories that aid in the design and understanding of better fluids. We will be responsible for every aspect of the research, from fluid synthesis and characterization, to structural, dielectric, and rheological measurements. We feel that being in control of all aspects of the program will increase our effectiveness and will accelerate the development of high performance fluids.

In each of these areas we will conduct fundamental experimental and theoretical studies, the success of which will best be judged by our ability to synthesize useful ER fluids. After all, the potential technological impact is the driving force behind the program.

Program Highlights

Mechanisms of Particle Polarization: Particle interactions obviously depend on the dielectric constants and conductivities of the dispersed particles and liquid phase, and these are functions of field frequency. We will develop an apparatus and techniques for measuring dielectric properties, using field components at two different frequencies to create and to probe, respectively, the time resolved structural organization that accompanies electrorheological effects in high concentration fluids in flow.

Nonohmic Conduction and Dielectric Breakdown: A primary factor that limits fluid performance is the onset of nonohmic conduction that is a harbinger of dielectric breakdown. These effects limit the voltages that can be applied and thus limit the yield strength. We will reduce charge injection at the electrode surfaces by polishing the electrodes, and by coating with a thin dielectric film, perhaps a diamond-like coating. We will use ac permittivity measurements to detect the onset of breakdown or conduction phenomena within the regions of enhanced electric fields between particles. If high local fields produce electroluminescence we will explore this as a measure of the field distribution in rough and smooth particle suspensions.

Fluid Synthesis and Stabilization: We will synthesize from solution smooth incipient ferroelectric particles as an alternative to hydrothermal synthesis, which produces rough surfaces. We will form particles of mesoporous silica by templating around cationic trimethylammonium surfactants and functionalized via uncondensed silanol groups so as to block the open pores. We will coat glass microballoons with a high dielectric or conducting material, and synthesize dielectric-coated metal spheres and test for ER effect. We will test deformable microgel particles as a means to reduce peak fields. We will explore relaxor ferroelectric fluids.

Structure and Rheology of Concentrated Suspensions: The rheology of concentrated ER suspensions is not understood. We use electroheology and light scattering to probe the instantaneous nonlinear response of concentrated fluids and use these to develop new theoretical concepts. We will investigate the electrorheology of novel planar structures using biaxial ac fields.

Budget

We request \$500K per year for a minimum of three years to carry out the proposed research. Part of these funds will be allocated to LANL, depending on the direction and emphasis of the program. No funds will be provided to Exxon or the Ford Motor Company.

B. Significant Accomplishments

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**Development Of Two Optically-Based *In Situ* Monitors For Thin Film Growth Of Materials
Using MBE and CVD
KC 02 03 03**

Scientific Accomplishment

We have developed two new optical monitors for thin film growth that can potentially revolutionize the process control of epitaxial thin film growth. These optical diagnostics are a direct outgrowth of our development of research tools for understanding the fundamental mechanisms of CVD. Our first monitor directly measures the flux of atoms effusing from a source oven in a molecular beam epitaxy (MBE) growth chamber. Because the growth rate of the film is directly proportional to the flux, real time monitoring and control of the growth rate was made possible. With this monitor controlling the deposition process, we have demonstrated control of growth rates to 0.3% even in the presence of purposely introduced transients that would have caused 10 to 15% deviations without control. Our second monitor employs spectral reflectance to directly measure film growth and optical constants during either MBE or metal organic chemical vapor deposition (MOCVD) of compound semiconductors. This monitor provides the first real-time *in situ* device for measuring high temperature growth rates and optical dispersion of thin films inside CVD reactors. We have also developed a method to extract film properties from these measurements independent of the underlying structure below the top-most film. We have installed this reflectance probe on a commercial reactor and it has rapidly become an essential workhorse tool for pre-growth calibration and real-time materials growth monitor. This work received the 1994 annual Significant Implication for Department of Energy Related Technologies in Materials Chemistry award.

Significance

These two optical monitors provide thin film growers with the first direct measure of film growth and composition. The monitors provide instantaneous feedback on the status of a deposition run. This eliminates the need for a large number of calibration runs and sets the stage for direct control of film thickness rather than the "timed recipe" approach presently used for thin films materials growth. The commercialization of these monitors will produce highly efficient thin film materials growth equipment capable of depositing with high yield precise structures of unprecedented complexity.

Performers: Kevin P. Killeen, Scott A. Chalmers, and William G. Breiland, Sandia National Laboratories New Mexico.

Ambient Pressure Aerogel Films

KC O2 01 01

Technical Achievement

Thin film and bulk aerogels have been made by ambient pressure techniques, work that won the 1994 BES award for Significant Implications for DOE Related Technologies. Conventional supercritical processing of aerogels is energy intensive, dangerous, and not amenable to continuous forming operations such as coating. The ambient pressure process overcomes these problems and could revolutionize aerogel manufacturing; most significantly we can prepare thin films on large substrates, previously impossible to perform within the constraints of an autoclave.

In the new method capillary pressure is decreased and chemical crosslinking is controlled by chemical modification of the gel. Resulting films are typically hydrophobic, increasing their stability.

In a side development, the phenomenon of "springback" in these films was observed unambiguously by imaging ellipsometry and environmental scanning electron microscopy. Springback is a mechanical dilation of the drying network as pores become empty of liquid, thus releasing the capillary pressure.

Significance

Aerogel films have long been sought for architectural windows, in which an aerogel film, sandwiched between two panes and evacuated or backfilled, would provide a very effective transparent thermal insulator. Highly porous films are also attractive as catalytic substrates and certain sensor applications. Their use in optics, as continuously variable refractive index layers, has been exploited with conventional sol-gel film processing.

Energy cost for the manufacture of aerogel films by supercritical processing has prevented them from being taken seriously for microelectronics and displays. The ambient-pressure process may be the enabling technology that opens up new fields of cost effective, ultralow dielectrics and superinsulants.

Performers

C. J. Brinker and A. J. Hurd (Sandia National Laboratories, NM) and S. S. Prakash (UNM)

Metal Impurities in Silicon Strongly Trapped by Cavities

KC 02 01 03

Scientific Achievement

Microscopic cavities in silicon formed by helium ion implantation have been shown to provide strong sinks for metal atoms that, if allowed to remain mobile within the silicon lattice, would severely degrade electrical properties. This "gettering" of metal impurities has now been demonstrated to occur for iron, cobalt, nickel, copper, and gold, which are the species of greatest concern in semiconductor technology. The effect has been understood at a fundamental level in terms of the attachment of metal atoms to unsatisfied silicon chemical bonds present on the walls of the cavities. Distinguishing characteristics of impurity gettering by cavities include, first, the exceptional strength of the trapping reaction and, second, kinetic features that cause the trapping to persist even when the starting impurity concentration in the silicon is infinitesimally small. The effectiveness of this process is illustrated by the observation that conventional gettering through precipitation of the metal impurity as a silicide phase actually undergoes reversal in favor of cavity gettering when cavities are introduced.

Significance

The detrimental effects of metal impurities in silicon are of ever greater concern as the evolution of modern microelectronics makes devices increasingly sensitive to such perturbations. For example, SEMATECH has projected that future metal-impurity tolerances may decrease to one metal atom in 10^{14} silicon atoms for some applications. In order to satisfy such unprecedented requirements reliably, it is highly desirable to develop new, more effective gettering processes for use in conjunction with stringent clean-room procedures. Results of the present research indicate that the new concept of gettering by cavities is very promising for this purpose.

Performers

S. M. Myers and D. M. Follstaedt, Sandia National Laboratories, New Mexico

Self-Healing of Irradiated Boron-Rich Solids

KC 02 02 05

Technical Achievement

Transmission electron microscopy observations were used to evaluate damage produced by irradiating boron-rich metals, semimetals and semiconductors of three different structure types with high doses of energetic electrons. Remarkably, the defect clustering and amorphization seen in solids generally and even in other borides was never observed in semiconducting icosahedral borides. In accord with studies of other icosahedral borides, we conclude that radiation-induced boron vacancies and interstitials spontaneously recombine in icosahedral borides. We explain this spontaneous self-healing as having its origin in the unusual structural and electronic stability of fragments of boron-rich icosahedra.

Significance

The self-healing of radiation damage in icosahedral boride semiconductors and insulators offers the potential that these materials can be exposed to radiation without suffering the rapid degradation of electronic properties that result from the presence of high densities of radiation-induced traps and defects. Thus, it is possible that electronic devices based on icosahedral borides can operate in radiation environments that preclude use of conventional semiconductors.

(Performed by D. Emin, T. Aselage, Sandia National Laboratories, M. Carrard, L. Zuppiroli, Ecole Polytechnique Federale de Lausanne, Switzerland)

Superconducting Tl-Ba-Ca-Cu-O Thin Film Synthesis Using Two-Zone Processing

KC 02 02 02

Scientific Accomplishment:

Superconducting Tl-Ba-Ca-Cu-O thin films with significantly enhanced properties have been synthesized using controlled, scalable, two-temperature-zone furnace processing. The two-zone furnace approach is based on BES-funded research at Sandia in recent years which demonstrated that independent control of both the thallous oxide and oxygen partial pressures is necessary for equilibrium growth of the numerous structural phases in this complex system. This research has now been successfully extended to the reproducible production of thin films required for advanced physics studies and electronic applications.

The advance in thin-film processing and our extensive equilibrium phase diagram work for cuprate superconductors have resulted in a Technology Transfer Initiative Defense Programs Dual Use CRADA with DuPont de Nemours & Company for the development of a manufacturable process for superconducting Tl-Ba-Ca-Cu-O thin film synthesis. This program enables Sandia to scale its processing technology for routine use and makes Tl-Ba-Ca-Cu-O thin films available to the growing superconductivity marketplace for electronic applications.

Significance:

Development of two-zone furnace processing for Tl-Ba-Ca-Cu-O thin film superconductors enables the manufacture of these materials by directly solving the key issues of process reproducibility and scalability. These problems have been the biggest drawback to widespread use of Tl-based films by the superconductivity community. The Tl-Ba-Ca-Cu-O system contains phases with $T_c > 125$ K, high J_c at temperatures above 77 K, and the lowest-reported microwave surface resistance at temperatures up to 100 K. The exploitation of these materials for a wide-range of active and passive microwave device applications is expected.

In addition, two-zone furnace processing allows the controlled growth of Tl-Ba-Ca-Cu-O thin films of any structural phase with the optimization of either T_c , J_c , or microwave surface resistance. Such "tailored" properties permit the first detailed studies correlating thin film microstructure (in terms of epitaxy), morphology, and phase-purity with both intrinsic and extrinsic superconducting properties, thus extending previous work on single crystals.

(Research at Sandia National Laboratories performed by M. P. Siegal, E. L. Venturini, P. P. Newcomer and B. Morosin)

Mechanisms of Ion-Assisted Growth Processes

KC 02 01 03

Scientific Achievement

Kinetic Monte Carlo computer simulations in conjunction with electron diffraction measurements have been used to develop a comprehensive understanding of the atomic-scale mechanisms controlling ion-assisted growth. In this technique, beams of low energy particles are used to bombard the surface during deposition to modify the growth process. We find that at typical growth temperatures, relatively large numbers of ion-induced adatoms and vacancies transiently exist on the surface before recombining with each other or with islands and adatoms produced by the growth beam. This picture is in contrast with previous indications that most of the ion-induced defects recombine in the bulk and only small numbers of surface vacancies are created. This result was determined by measuring the surface defect yield at low temperature where the defects are immobile on the surface and cannot recombine. As the temperature is raised, the number of surface defects created per ion decreases. Computer simulations confirmed that the decrease in the apparent surface defect yield is caused by recombination of mobile defects on the surface. These measurements of the surface defect yield are being incorporated into our simulations of ion-assisted growth to understand how these defects can destabilize small clusters and lead to dynamic smoothing of the surface morphology.

Significance

As advanced thin film structures continue to decrease in size, control of surface morphology becomes increasingly important. Ion bombardment during growth provides an additional avenue for controlling the kinetic processes that determine surface morphology. Fundamental studies of defect production tied in with growth studies and modeling enable us to determine the mechanisms of ion-assisted growth and make it possible to optimize these processes. Future applications of this technique for fabricating ultra-small structures include enhancing the sharpness of the interfaces between dissimilar layers and decreasing the temperature for epitaxial growth.

Performers

B.K. Kellerman^{a,b}, J.A. Floro^a and E. Chason^a

^aSandia National Laboratories

^bUniversity of Texas, Austin

Interfacial-Force Microscopy Probes Adhesive Bonding at the Molecular Scale KC 02 01 02

Technical Achievement

We have applied the interfacial force microscope (IFM) to the first study of the adhesive bonding force as a function of separation between controlled surfaces of self-assembling monolayer films deposited on both Au substrates and Au-probe surfaces. The peak value of the adhesive force and established adhesion models were used to obtain quantitative values for the surface energy of the films or the bonding energy per molecule when specific chemical bonds occur between the molecular end groups. By using various combinations of end groups (i.e., by changing the chemical nature of the interfaces between films), we were able to contrast the bonding between van der Waals, hydrogen and acid/base interactions. With methyl ($-\text{CH}_3$) end groups on both probe and substrate films the interaction involves totally saturated hydrocarbons and our measured values for the surface energies closely agree with values obtained by other researchers using contact-angle measurements for liquids of similar hydrocarbons. Carboxyl ($-\text{COOH}$) and amine ($-\text{NH}_2$) end groups permit the investigation of hydrogen bonding (both $-\text{COOH}$ vs. $-\text{COOH}$ and $-\text{NH}_2$ vs. $-\text{NH}_2$) as well as acid/base ($-\text{COOH}$ vs. $-\text{NH}_2$) interactions. For these chemically-active end-group combinations, which interact because these groups can act both as acids and bases, we find that the bond energies per molecular end group quantitatively scale according to that expected on the basis of earlier measurements made for gas-phase dimer formation of similar end-group combinations in smaller molecules. They also scale according to the acid/base strengths of the particular end-group combination, i.e., the strongest bonds are formed between the strongest acids interacting with the strongest bases.

Significance

The detailed understanding of chemical bonding between molecular groups across an adhesive interface that is provided by our unique approach represents the first step toward establishing a firm foundation for the development of predictive models for the design of adhesives for specific applications. Recent adhesion models have attempted to characterize the bonding interaction in terms of the acid/base character of the chemically active groups residing on the interfaces. It is often found that these chemically active groups can act as either acids or bases and for this reason, characterizing the individual acidities and basicities has proved to be possible in only a limited number of special cases. Our recent results show the potential of carefully controlled adhesion measurements to characterize these separate acid/base strengths and thus, lead to a predictive capability for adhesive interactions between surfaces containing various chemically active groups. In other words, if a standard monopolar acid or base group (one with only acid or base character) are adsorbed on the probe surface, the bonding strength between this surface and one covered with an arbitrary system of chemically active groups can be used to find the individual acid and base strengths for the system.

(Research performed by J. E. Houston and T. A. Michalske at Sandia National Laboratories.)

Excitonic and Band-to-Band Behavior In Ordered InGaP₂ Alloys

KC 02 01 05

Technical Achievement

Low temperature photoluminescence (PL) studies of InGaP₂ with well behaved ordering properties have revealed new understanding of the semiconductor bandstructure alignments induced by ordering and are important for developing such materials for high efficiency solar cells. At nominal laser excitation power densities the magnetoluminescence spectra show the expected behavior for free excitons. However, for ultra-low excitation levels ($\sim 1 \mu\text{W}/\text{cm}^2$) a continuous distribution of energy levels are observed between the free exciton PL peak and the luminescence energy edge. Further, the magnetic field shifts of the low-energy edge of the PL spectrum are found to be linear, while at higher power densities, quadratic. We have explained this behavior as arising from a particular type of offset (type 2) for the valence bands between the various ordered domains. In contrast, the previously assumed type of offset does not allow an explanation of the observed laser power, magnetic field, and temperature dependencies of the PL spectrum. Furthermore, the linear field dependence of the PL energy allowed the first measurement of the valence band effective mass $m_v \sim 0.2$, in agreement with simple theoretical expectations.

Significance

The InGaP₂ system has been identified as an important photovoltaic material system. Understanding the origins of the PL spectra allows a unique verification of the theoretical band structures and material properties for these kinds of systems. The valence band offset determined by these observations was not predicted by theory and new interpretations are now underway. These results clear up several previous experimental ambiguities, including "moving or power dependent PL spectra," and "wavelength dependent recombination lifetimes." Such basic understanding of the fundamental material parameters and band structure issues is important to realizing high-efficiency solar cells. This work is part of a new SNL/NREL BES collaboration.

(Research performed jointly by E. D. Jones, D. M. Follstaedt, J. S. Nelson, and R. P. Schneider, Jr. at Sandia National Laboratories and A. Mascarenhas at NREL, Golden, CO)

Universal Scaling Behavior Revealed by Dynamic Spreading Experiments KC 02 01 02

Scientific Achievement

Real-time video imaging experiments have been used to demonstrate a universal scaling relation for liquids of widely different chemical properties flowing in well-defined surface grooves. The spreading kinetics are shown to depend only on surface tension, contact angle, viscosity, and groove geometry. Quantitative spreading data are obtained by digitizing the video images measured as liquid is allowed to spread from a droplet reservoir into a narrow, V-shaped surface groove ~100 μm wide machined in flat copper substrates. The groove angle has been systematically varied and the groove shape is verified by profilemetric methods. For liquids ranging from chemically inert organic alcohols to reactive high-temperature tin-lead solders, excellent agreement with experiment is found using a simple continuum model based upon the Navier Stokes equation, no-slip boundary conditions, and the ratio of surface tension to viscosity for each fluid. Although fluid flow in closed capillary tubes has been extensively studied and modeled, similarly detailed studies of flow in open channels had not been performed. The quality of our real-time kinetic data now enables us to experimentally test the competing predictions from contemporary theoretical models for fluid flow.

Significance

The synthesis of advanced metal/ceramic composite materials and joining technologies such as soldering, brazing, and welding are all critically dependent upon the ability of a liquid metal to completely wet the interface between two solids. Microstructural defects that result from incomplete wetting can seriously limit the performance of materials in critical components. Prior spreading studies of liquid metal droplets on flat substrates have shown that kinetic processes, such as intermetallic formation at the wetting front, can be rate-limiting. Consequently, the spreading rate can be several orders of magnitude slower than predicted by contemporary theory. The universal scaling relation developed from our new measurements demonstrates how morphological surface modification can be used to engineer surfaces for wetting enhancement, thereby overcoming these previous kinetic limitations. Furthermore, we have shown that wetting on rough surfaces and groove spreading are analogous and have the same kinetic form. The ability to use surface modification techniques coupled with an accurate kinetic model will lead to more reliable predictions of wetting in these important materials synthesis and joining technologies.

Performers

R. R. Rye and F. G. Yost (Sandia National Laboratories)
L. Romero and J. A. Mann, Jr. (Case Western Reserve University)

Surface Chemistry of Chemical Vapor Deposition of AlGaAs Alloys

KC 02 03 03

Scientific Accomplishment

Our investigations of the surface chemistry of GaAs metal-organic chemical vapor deposition (MOCVD) have dramatically improved our understanding of this complex growth process. We have now made a significant extension of our studies of the surface chemistry of MOCVD to include the aluminum precursor trimethylaluminum (TMAI) and the AlAs surface.

We have found (the somewhat surprising result) that chemisorption of TMAI on GaAs(100) results in methyl group transfer from the Al atoms to surface Ga atoms. Thereafter the chemistry is virtually identical to the trimethylgallium (TMGa) behavior, with methyl radical desorption occurring at $\sim 440^\circ\text{C}$ during temperature programmed desorption (TPD). For chemisorption of TMAI on AlAs, the stronger Al-C bond (compared to the Ga-C bond) manifests itself with a CH_3 desorption peak at 470° during TPD. This increase in desorption temperature corresponds to a 2 kcal/mole increase in the CH_3 desorption activation energy. TMAI adsorption on AlAs also produces significantly more CH_3 dehydrogenation (resulting in carbon doping). The branching ratio of CH_3 desorption to CH_3 decomposition on AlAs is close to unity, whereas on GaAs it is approximately 100:1. These measurements provide the first detailed understanding from a surface chemistry perspective of why there is a higher propensity for unintentional carbon doping in AlAs (as compared to GaAs) during MOCVD.

Significance

$\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys and superlattices have major applications for optoelectronics and high speed integrated circuits. MOCVD is the leading manufacturing process for III-V compound semiconductor materials and is the subject of several separate DP/TTI funded CRADA projects that we have with industry. Results of this investigation are being used to support our first III-V heteroepitaxy MOCVD modeling effort which includes specific deliverables to Motorola in one such CRADA.

PerformerS: Charles M. Truong, Derrell W. Sloan, and J. Randy Creighton, Sandia National Laboratories New Mexico.

Atomic-Scale Processes Observed in Nucleation by Chemical Vapor Deposition

KC 02 02 02

Scientific Accomplishment

We have observed the evolution of atomic-scale morphology during the initial stages of Fe deposition on Si(100) by chemical vapor deposition (CVD). Fe on Si(100) is an excellent model system for investigations of the atomistics of CVD processes because the decomposition of the precursor $\text{Fe}(\text{CO})_5$ takes place in a temperature range accessible to our atomic-level probes. From a technological standpoint, Fe on Si is important in that Fe silicides are being considered as candidate materials for direct-gap semiconductors. Scanning tunneling microscope analysis of cluster location, density, average size, and size distribution allows us to deduce the importance of atomic-scale kinetic events in the nucleation process. Clusters of Fe are found to nucleate on the flat terraces of Si(100) during pyrolysis of $\text{Fe}(\text{CO})_5$, showing no preference for precursor dissociation at step or defect sites. Compared to growth by thermal evaporation of Fe atoms, CVD growth exhibits significantly larger cluster size and lower cluster density at equivalent coverage. Kinetic Monte-Carlo simulations of the growth process confirm that this effect is due primarily to selective dissociation of the precursor at existing Fe islands - an "autocatalytic" effect. Adsorption and diffusion of the precursor prior to decomposition may also be important in evolution of island morphology.

Significance

An atomic-level understanding of metal deposition on semiconductor surfaces is becoming increasingly more important as feature sizes in microelectronic circuits begin to approach dimensions on the sub-micron or even nanometer scale. This study represents the first attempt to use variable-temperature, scanning-probe techniques to examine the atomic-scale events involved in nucleation processes during CVD growth. We have identified specific reaction sites of precursors and directly confirmed the importance of an autocatalytic effect in the nucleation and growth of metals on Si and other less reactive substrates. Detailed measurements of island density and size have provided data that are necessary for development of accurate models of film growth, which will be useful in predicting properties of new materials prepared by CVD techniques. Identification of specific reaction sites and rate-limiting processes suggests new means for the modification of nucleation process by chemical alteration of the surface. Passivation of reactive sites can retard nucleation, while site-specific activation can be achieved through chemical alteration. This opens up the possibility of fabricating atomic-scale structures based on selective surface chemistry and scanning probe techniques.

(Research performed by D. P. Adams, T. M. Mayer, B. S. Swartzentruber, and E. Chason, Sandia National Laboratories)

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Physics and Chemistry of Ceramics

KC 02 01 01

Principal Investigators: R. A. Assink, T. J. Boyle, C. J. Brinker, R. K. Brow, K. Chen, P. F. Green, A. J. Hurd, W. C. Moffatt, D. W. Schaefer, P. R. Schunk, R. W. Schwartz

Goals: To understand the chemical and physical processes that determine the structure and properties of ceramics and glasses and to form a fundamental technology base for DP applications.

Recent Highlights

- **Ambient pressure aerogel thin films:** Using *in situ* imaging ellipsometry and environmental SEM, established that porosity is created at the final stage of drying by dilation or "springback" of the gel network as much as 600%. Silated precursors prevent crosslinking as the network is compacted by capillary pressure, allowing reversible shrinkage and wide porosity variation.
- **Cross-Condensation Reaction Rates** The cross-condensation kinetics of methyl-, ethyl-, and phenyl-modified silicates were measured using ^{29}Si NMR. A numerical model was developed to describe the effect of the substituent on the hydrolysis and condensation steps of the reaction.
- **Anomalous Diffusion Model of Ionic Motion:** Developed a description of the dielectric behavior of glasses which views ionic motion as anomalous diffusion; describes the dispersion found in both the conductivity and permittivity in ion-containing glasses. Model provides insight into the short-range glass structure, bond length scales and vibrational modes.
- **Mechanical/Electrical Relaxations in Mixed Alkali Glasses:** Demonstrated that, in mixed alkali ion-containing glasses, mechanical and electrical relaxations do not mimic each other as they do in single alkali glasses, suggesting different mechanisms for the two properties. This result offers new insight into the nature of the mixed alkali effect in glasses.
- **Elastic Porosity** With LLNL, developed a new idea for the origin of porosity in aerogels based on competition between enthalpy and elasticity. SAXS showed that, because of crosslinking, macroscale phase separation favored by mixing entropy is restricted to nanometer pores. This "new" nanoporosity accounts for inconsistencies in gas absorption analysis.

Future Directions

- **Thin film patterning and hydrophobic dilation:** Thermally-induced changes in liquid-vapor surface tension and chemical condensation rates will be used to create patterns of high and low refractive index in a continuous coating operation, and aerogel films will be prepared from water-alcohol mixtures as a drying dilation strategy based on water becoming progressively prevalent during the drying process.
- **Kinetics of titanate sol-gels:** ^{17}O NMR of liquids will be used to investigate the kinetics of model titanate sol-gels while solid state NMR will be used to characterize the structure of products prepared from the enriched reactants. ^7Li NMR will be used to study the effects of LiOCHMe_2 and LiCl on $\text{M}(\text{OCHMe}_2)_4$ ($\text{M} = \text{Ti, Zr}$). Identification of such species is critical for catalysts.
- **Microscopic Understanding of Anomalous Diffusion in Glasses:** high frequency mechanical relaxation dynamics by Brillouin spectroscopy will be correlated with low frequency mechanical relaxations and compared with electrical response in the same frequency range.

Interactions with DOE Technologies

- METC-funded ceramic membranes for methane/carbon dioxide separation exhibited separation (developed on basis of results from the BES program) flux 100 times greater than known polymeric membranes but with comparable separation.
- Tech transfer programs continually draw from the BES tech base: membranes (AMOCO), ferroelectric thin-film devices (RADIANT) and electrostatic chucks (SEMATECH).
- DP programs drawing from BES tech base include collaborations with LLNL on microscopic porosity in aerogels; protected volume technology; powder compaction. DP provides complementary funding for applied efforts.

Program Quality

- **1994 DOE/BES Award:** Significant Implications for DOE-Related Technologies for discovery of an ambient pressure process to prepare bulk and film aerogels.
- 7 invited papers, 5 invited presentations, 1 patent disclosure, new CRADA (w/AMOCO), ?? total CRADAs.

Physics and Chemistry of Ceramics

KC 02 01 01

Publications

Work Performed Under Present BES Program

1. "Cross-Condensation Reactions in an Organically Modified Silica Gel," S. Prabakar, R. A. Assink, N. R. Raman, and C. J. Brinker, in Better Ceramics Through Chemistry VI, eds. T. Cheetam, C. J. Brinker, M. L. Mecartney, and C. Sanchez (MRS Symp. Series, Pittsburgh, PA, 1994), to be published.
2. "Sol-Gel-Derived Silica Films with Tailored Microstructures," M. N. Logan, C. J. Brinker, in Better Ceramics Through Chemistry VI, eds. T. Cheetam, C. J. Brinker, M. L. Mecartney, and C. Sanchez (MRS Symp. Series, Pittsburgh, PA, 1994), to be published.
3. "Fundamentals of sol-gel dipcoating," C. J. Brinker and A. J. Hurd, J. Phys. III France, 4, (1994), 1231-1242.
4. "Structure-Property Relationships in Sol-Gel-Derived Thin Films," C. J. Brinker, N. K. Raman, M. N. Logan, R. Sehgal, R. A. Assink, D-W. Hua, and T. L. Ward, in ACS Symp. Series on Inorganic and Organometallic Polymers, eds., P. W.-Neilson, A. Allcock, and K. Wynn (ACS, Washington, D.C.), in press.
5. "Comparison of Two Methods for Analysis of the Electrical Properties of an Ion Conducting Glass," D. L. Sidebottom, P. F. Green, and R. K. Brow, J. Non-Cryst. Solids, (in press).
6. "Anomalous Diffusion Model of Ionic Transport in Oxide Glasses," D. L. Sidebottom, P. F. Green, and R. K. Brow, Phys. Rev. B, (in press).
7. "Structure And Topology of Silica Aerogels During Densification", D. W. Schaefer, B. J. Olivier, And C. S. Ashley, G. Beaucage, D. Richter, B. Farago, B. Frick, And D. A. Fischer, Journal Of Noncrystalline Solids, 172-173 (1), 647-655, 1995.
8. "General Routes to Porous Metal Oxides Via Inorganic and Organic Templates", C. Roger, D. W. Schaefer, C. B. Beaucage, And M. J. Hampden-Smith, J. Of Sol-Gel Sci. & Tech., 1994.
9. "Characterization of Porosity in Ceramic Materials by Small-Angle Scattering: Vycor Glass And Silica Aerogel", D. W. Schaefer, R. K. Brow, B. J. Olivier, T. Rieker, G. Beaucage, L. Hrubesh, and J. S. Lin, in Modern Aspects Of Small-Angle Scattering, ed Harry Brumberger, (Kluwer Academic Publishers, Dordrecht, 1994).
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12. "Structure of Organic Aerogels, 1, Morphology and Scaling", D. W. Schaefer and R. Pekala, Macromolecules, 26, 5487-5493 (1993).
13. "An Investigation of Group (IV) Alkoxides as Property Controlling Reagents in the Synthesis of Ceramic Materials," T. J. Boyle and R. W. Schwartz, Comments Inorg. Chem., Vol. 16 (5), pp. 243 - 278 (1994). (invited)
14. "Spinnability of Silica Sols: The Role of Alkoxy Group Exchange," S. Prabakar, R. A. Assink and A. D. Irwin, in Better Ceramics Through Chemistry VI, Mat. Res. Soc. Symp. Proc., Vol. 346, pp. 433 - 437 (1994).
15. "Cross-Condensation Reactions in an Organically Modified Silica Sol-Gel," S. Prabakar, R. A. Assink, N. K. Raman, and C. J. Brinker, in Better Ceramics Through Chemistry VI, Mat. Res. Soc. Symp. Proc., Vol. 346, pp. 979 - 984 (1994).
16. "Formation, Structure, and Material Properties from the Reaction Product of $M(OCHMe_2)$ ($M = Ti, Zr$) and $HOAc$," T. M. Alam, T. J. Boyle, C. D. Buchheit, R. W. Schwartz, and J. W. Ziller, in Better Ceramics Through Chemistry VI, Mat. Res. Soc. Symp. Proc., Vol. 346, pp. 35 - 40 (1994).

Work Performed Jointly with other Programs

17. "X-Ray Scattering of Smectic Ordering in a Silica Aerogel", T. Bellini, N. A. Clark, R. M. Malzbender, B. N. Thomas, A. G. Rappaport, C. D. Muzny, And D. W. Schaefer, Phys. Rev. Lett. 71, 3505-3508 (1993).
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21. "Sol-Gel Processing of PZT Thin Films: A Review of the State-of-The-Art and Process Optimization Strategies," R. W. Schwartz, T. J. Boyle, S. J. Lockwood, M. B. Sinclair, D. Dimos, and C. D. Buchheit, Integrated Ferroelectrics (1995) in press (invited).
22. "Effects of Acetylacetone Additions on PZT Thin Film Processing," in Ferroelectric Thin Films IV, R. W. Schwartz, R. A. Assink, D. Dimos, M. B. Sinclair, T. J. Boyle, and C. D. Buchheit, Mat. Res. Soc. Symp. Proc., (1995) in press (invited).

Atomic Level Science of Adhesion

KC 02 01 02

Principal Investigators: T. A. Michalske, J. E. Houston, N. D. Shinn, and P. J. Feibelman

Goal: To understand in atomic detail the nature of the physical and chemical interactions that control interfacial binding and to use this understanding to: 1) develop predictive models for adhesive bond stability and 2) tailor material surfaces and interfaces for optimized adhesion and lubrication properties.

Recent Highlights

- **Molecular-Scale Adhesion** - We have used the interfacial force microscope (IFM) to make the first quantitative measurements of the force vs. separation between controlled surfaces consisting of self-assembling monolayer films on Au surfaces. Using various combinations of methyl ($-CH_3$), amine ($-NH_2$) and carboxyl ($-COOH$) end groups, we were able to identify the adhesive-force components resulting from van der Waals, hydrogen and acid/base interactions. By using the peak adhesive force, and established adhesion models, we obtained quantitative values for the bonding energies per molecular end group. The methyl/methyl interaction is purely van der Waals and our surface energy values closely agree with previous contact-angle measurements. Amine/amine and carboxyl/carboxyl interactions involve predominantly hydrogen bonding and the carboxyl/amine represents an acid/base interaction. Our measured values for the bond energies for these chemically active combinations scale as expected on the basis of previous gas-phase studies for molecular bonding involving similar groups in smaller molecules. These measurements characterize bonding at the molecular level providing the understanding that is necessary for the development of predictive models for adhesive-bond strength.
- **Nanomechanical Properties** - We have made the first measurements of the shear-stress threshold for plasticity for single-crystal Au surfaces as a function of probe radius down to radii of only 50 nm. The threshold stress is expected (based on continuum elasticity) to be constant. However, our measurements show that for tip radii under about 400 nm the threshold stress actually increases with decreasing radius. Measurements in this size range are accomplished virtually in the absence of existing dislocations and our data indicates that nucleating dislocations requires larger stresses when only a small number of Au-Au bonds are being stressed. This result demonstrates the clear divergence from continuum elasticity at nanoscale dimensions.
- **Technology Transfer** - We are in our final year of CRADA agreements involving Sandia, Digital Instruments, AT&T Bell Laboratories and the University of New Mexico, which has as its goal the development of a commercial IFM. Several sensor designs have been researched and a Si micromachining process has been developed. Efforts are presently directed toward finding a commercial vendor capable of fabricating sensors according to this process.
- **Adhesion of Metals on Oxides** - The chemical bonding of transition metals to oxide substrates need not involve interdiffusion or ionic bonding. Soft X-ray photoelectron spectroscopy shows that an iron monolayer on a titanium oxide substrate remains metallic. Interfacial bonding is attributed to hybridized Fe-3d and Ti-3d electronic states in the oxide band gap. Measurements of this kind will be invaluable in elucidating the electronic origins of the adhesive bonding studied with the new UHV/Surface Science IFM instrument.

Future Directions

The program will continue to focus on nanometer-scale measurements of interfacial adhesion, the development of theoretical models to address the chemical stability of the adhesive interface, and microscopic measurements to test macroscopic predictions. The probe tips and substrate surfaces will be tailored with self-assembled monolayer films to controllably examine the role of surface chemical groups on the formation and stability of the adhesive bond. A full UHV/surface science IFM will be brought into operation so that adhesion events can be examined on clean and adsorbate covered surfaces and the results compared with first principles atomistic simulations. We will also use the IFM to probe the mechanical response of small-scale structures so that we can better understand the behavior of materials near stress singularities and of nanoscale composite materials.

Interactions with DOE Technologies

Our fundamental studies of interfacial adhesion increase the reliability of composite materials interfaces that are important to DP- and EE-funded R&D and the Materials Joining Project of the DOE Synthesis and Processing Center.

Program Quality

The breadth of application of the IFM (biomedical, tribology, metrology, and adhesion) and the number of researchers already interested in applying this unique scanning force technique has been recognized this year by R&D Magazine with one of its prestigious R&D100 Awards.

9 publications, 4 invited presentations (Gordon Conf., Natick STM/AFM Conf., APS, ASME)

Atomic Level Science of Adhesion

KC 02 01 02

Publications

1. "Substrate Effects on the Nanometer-Scale Mechanics of Gold Films," P. Tangyonyong, R. C. Thomas, J. E. Houston, T. A. Michalske, R. M. Crooks and A. J. Howard, *J. Adhesion Sci. and Technol.* **8**, 897 (1994).
2. "Chemically-Sensitive Interfacial Force Microscopy: Contact Potential Measurements of Self-Assembling Monolayer Films," R. C. Thomas, P. Tangyonyong, J. E. Houston, T. A. Michalske and R. M. Crooks, *J. Phys. Chem.* **98**, 4493 (1994).
3. "The Role of Structural Relaxations in the Fracture of Vitreous Silica," T. A. Michalske, W. L. Smith, J. E. Houston, *J. Appl. Phys.* **76**, 2109 (1994).
4. "Oxidation of W(110): Valence-Band and Core-Level Spectroscopy," C. H. F. Peden and N. D. Shinn, *Surf. Sci.* **312**, 151 (1994).
5. "Electronic structure of ultrathin Fe films on TiO₂(110) studied with soft X-ray photoelectron spectroscopy and resonant photoemission," U. Diebold, H.-S. Tao, N. D. Shinn and T. E. Madey, *Phys. Rev.* **B50**, 14474 (1994).
6. "Probing Adhesion Forces at the Molecular Scale," R. C. Thomas, J. E. Houston, R. M. Crooks, T. Kim and T. A. Michalske, *J. Amer. Chem. Soc.* (In Press).
7. "Oxidation of W(110): Valence-Band and W(4f) Core-level Spectroscopy," N. D. Shinn, *Surface Science* (In Press).
8. "Acid-site characterization of water oxidized alumina films by near-edge X-ray absorption and soft X-ray photoemission," P. J. O'Hagan, R. P. Merrill, T. N. Rhodin, S. C. Woronick, N. D. Shinn, G. L. Woolery and A. W. Chester, in Applications of Synchrotron Radiation Techniques to Materials Science, L. J. Terminello, N. D. Shinn, G. Ice, K. L. D'Amico, and D. L. Perry, eds., Materials Research Society Proceedings, 1994, (in press).
9. "Growth and oxidation of ultra-thin Al films on Ru(0001)," Y. Wu, H.-S. Tao, E. Garfunkel, T. E. Madey and N. D. Shinn, *Surf. Sci.*, (in press)

Wetting and Flow of Liquid Metals and Amorphous Ceramics At Solid Interfaces

KC 02 01 02

Principal Investigators: T. A. Michalske, N. D. Shinn, F. G. Yost, R. Rye, R. Cannon (LBL), U. Landman (Georgia Tech.)

Goal: To experimentally measure and theoretically model the atomic-scale processes that control fluid flow at solid interfaces and use these understandings to develop predictive models for macroscopic wetting and flow behavior.

Recent Highlights

Funding for this program began in FY95. The following accomplishments were supported by partial redirection of FY94 funding from the BES Tailored Surfaces and Interfaces for Materials Applications Program:

- **Acoustic Wave Damping Technique** - Commercial acoustic wave sensors in contact with a solid film or fluid droplet are sensitive only to the incremental mass of the added material mechanically coupled to the oscillating device. Sandia is pioneering a new technology that is sensitive to acoustic wave damping (AWD) in the adsorbed material, enabling quantitative measurements of viscoelastic parameters. This technology will allow us to determine the effective viscosity or shear modulus of nanometer-thick liquid films.
- **Viscoelastic Response of Molecular Films** - In order to explore the sensitivity of our AWD technique, we have measured the shear moduli of nanometer-scale diacetylene-based Langmuir-Blodgett films and self-assembled monolayers on gold substrates. By varying the functional groups that anchor the films to the substrate, we are able to distinguish interfacial and intralayer contributions to the measured response. The complex shear moduli of these films were found to vary significantly with film thickness. These results show that interfacial bonding can alter the dynamic response of molecular films and therefore their physical properties as model lubricants.
- **Metal Film Melting** - Acoustic wave damping was used to monitor the melting, dewetting, and solidification of a micron-thick indium film on a polycrystalline tantalum substrate under vacuum conditions. This is the first application of AWD to elevated temperature phase transitions and demonstrates the feasibility of this approach for studying liquid metals.
- **Macroscopic Flow Behavior of Liquids** - Real-time video imaging has been used to make the first quantitative kinetic measurements of liquid spreading in well-defined surface grooves. The data are in good agreement with theoretical models based on traditional hydrodynamics with "no slip boundary" conditions. Surprisingly, the kinetics of non-reactive organic alcohols and tin-lead solders in copper grooves all scale with the ratio of surface tension to viscosity. This suggests that rate-limiting kinetic processes, such as intermetallic formation at the solder wetting front, may be overcome by substrate surface modification.

Future Directions

This program will combine AWD viscoelastic measurements, spectroscopic characterization, molecular dynamics simulations, and macroscopic flow measurements. Our nanoscale studies will begin with atomically sharp liquid-metal/solid interfacial structures, followed by chemically reactive and atomically diffuse interfaces, including their temporal evolution. We will use the microscopic results to derive new models to predict complex macroscopic spreading and creep behavior. This approach will be extended to amorphous ceramic films. This systematic progression through increasingly complex but well-defined interfacial structures will enable us to evaluate the role of various energy dissipation mechanisms, interface morphology, impurities, surfactants, and chemical reactions in determining macroscopically observed wetting, spreading, and creep behavior.

Interactions with DOE Technologies

Improving the wetting behavior of liquid metal alloys will greatly increase the reliability of widely used joining technologies such as soldering and brazing. This BES work has provided an accurate, broadly applicable kinetic model that will lead to more reliable predictions of solder wetting and flow for high-reliability defense microelectronics applications. This program will establish interactions with DP-funded R&D and with the Materials Joining Project of the DOE Synthesis and Processing Center.

Program Quality: 2 Patent disclosures pending; 3 publications.

Wetting and Flow of Liquid Metals and Amorphous Ceramics At Solid Interfaces
KC 02 01 02

Publications

Supported by redirected FY94 BES funds:

1. "The Flow of Simple Liquids in Narrow Surface Grooves," J. A. Mann, Jr., L. Romero, R. R. Rye, and F. G. Yost, Physical Review Letters (submitted).
2. "The Flow of Liquids in Surface Grooves," R. R. Rye, J. A. Mann, Jr. and F. G. Yost, Langmuir (submitted).

Joint with NCMS CRADA #1030B funded by DOE-DP:

3. "Flow in an Open Channel Capillary," L. Romero and F. G. Yost, J. Fluid Mechanics (submitted).

Energetic-Particle Synthesis and Science of Materials

KC 02 01 03

Principal Investigators: J.C. Barbour, M.T. Dugger, D.M. Follstaedt, J.A. Knapp, S.M. Myers, C.H. Seager, and W.R. Wampler

Goals: Use energetic beams and plasmas to create superior new materials and achieve fundamental understanding of the atomic processes, defects, and microstructures that govern materials processing and properties.

Research Highlights

- **Metal-atom gettering in Si:** We are identifying superior new implantation-based gettering processes and developing new mechanistic understanding of metal-atom trapping pursuant to impurity control in next-generation Si microelectronics. The strong trapping of Cu and Ni by He-implantation-induced nanocavities previously discovered in this program was shown to extend to Co, Fe, and Au solutes. Separately, recently reported gettering of Fe by high concentrations of ion-implanted B was mechanistically investigated and concluded to involve reversible trapping that scales with B concentration and promotes subsequent nucleation of Fe silicide (collaboration with AT&T Bell Labs). Nanocavities were shown to capture Fe atoms from B layers, further demonstrating the effectiveness of cavity gettering. (patent application filed on cavity gettering)
- **ECR-plasma synthesis of hard and optical Al-O materials:** Electron-beam evaporation of Al in electron-cyclotron-resonance (ECR) O₂ plasmas was shown to produce high-quality Al-Al₂O₃ layers with effective control over microstructure and composition for oxide volume fractions from 0 to 100 %. At the composition Al_{0.8}O_{0.2}, a homogeneous dispersion of nanometer-size oxide particles produced gigapascal flow strengths, consistent with hardening theory and with results from our earlier experiments on O-implanted Al. At the composition Al₂O₃, energetic-particle-enhanced crystallization led to formation of cubic γ -Al₂O₃ rather than amorphous oxide at only 400°C, greatly reducing optical loss within the material. (patent disclosure)
- **Nanocavity formation in GaAs:** The fragility of GaAs that prevents cavity synthesis by He ion implantation and subsequent annealing has been overcome through a new approach with two key features: first, the He is implanted at elevated temperatures where defect mobility is high and lattice recovery rapid; and, second, bubble nucleation in the low-defect matrix is stimulated by prior implantation of a low dose of Ar ions. This advance should make it possible to extend to compound semiconductors the cavity-related beneficial effects and mechanistic studies that we previously pursued in Si, including impurity gettering, characterization of surface energies and H-surface interactions, and cavity charging leading to electrical isolation. (patent caution)
- **Center for Synthesis and Processing - Project on Processing for Surface Hardness:** Our formation of high-strength Al-O layers by ECR-plasma deposition and ion implantation provides the basis for future large-scale synthesis of these materials by plasma-source ion-implantation being developed at LANL. Our advanced capabilities for elastic-recoil-detection (ERD) analysis were used to determine the compositions of cubic BN films grown by pulsed laser deposition (PLD) at SNL-CA; these measurements revealed that loss of the cubic phase observed at lower growth temperatures does not arise from N deficiency as previously suspected.

Future Directions

- Beam synthesis of superior new materials using energetic beams and plasmas
 - Nanocavities in Si and compound semiconductors for gettering, dislocation trapping, and electrical isolation.
 - High-strength Al- and Fe-based nanostructures synthesized by ion implantation, PLD, and ECR plasmas.
 - Low-temperature oxides and nitrides grown from ECR plasmas for surface passivation and optical structures.
- Ion-beam studies of fundamental atomic processes, defects, and microstructures
 - Trapping mechanisms for detrimental impurities and dislocations in semiconductors.
 - Injection and bonding of H in semiconductors as related to passivation of defects, surfaces, and impurities.
 - Hardening and dislocation motion in Al- and Fe-based nanostructures.

Interactions with DOE Technologies

This BES/Materials Sciences program provides scientific underpinning and new materials concepts for DP R&D programs on hard-layer synthesis and plasma-processing of electronic materials.

Other Interactions

- Collaborative programs with AT&T Bell Labs and UC-Berkeley on impurity gettering mechanisms in Si.
- Collaboration with U. Maine and Vanderbilt U. on ECR-plasma synthesis of materials.
- Participation in Center for Synthesis and Processing: Interlaboratory Project on Processing for Surface Hardness.

Program Quality

- Patent application and two patent disclosures.
- Five invited papers including 2 at Inter. Conf. on Ion-Beam Modif. of Mater., the premier forum of the field.
- 14 publications.

Energetic-Particle Synthesis and Science of Materials

KC 02 01 03

Publications

Work Performed under Present BES Program

1. "Chemical, Structural, and Electrical Properties of Cavities in Silicon and Germanium" (invited), S. M. Myers, D. M. Follstaedt, H. J. Stein, C. H. Seager, W. R. Wampler, and G. A. Petersen, in Proc. 9th Inter. Conf on Ion-Beam Modification of Materials, Canberra, Australia, Feb. 5-10, 1995 (submitted).
2. "Gettering of Metal Impurities by Cavities in He-Implanted Si" (invited), D. M. Follstaedt, S. M. Myers, and J. W. Medernach, in Proc. TMS Symp. on Ion-Beam and Laser Processing of Materials, Las Vegas, Feb. 12-16, 1995 (submitted).
3. "Gettering of Metal Impurities by Cavities in Silicon," S. M. Myers, D. M. Follstaedt, D. M. Bishop, and J. W. Medernach, in Semiconductor Silicon / 1994, edited by H. R. Huff, W. Bergholtz, and K. Sumino (ECS, 1994), pp. 808-819.
4. "Hydrogen Interactions with Cavities in Helium-Implanted Germanium," S. M. Myers, H. J. Stein, and D. M. Follstaedt, Phys. Rev. B (in press).
5. "Silicon Nitride and Oxynitride Film Formation Using Electron Cyclotron Resonance Plasmas" (invited), J. C. Barbour, in Silicon Nitride and Silicon Dioxide Thin Insulating Films, edited by V. J. Kapoor and W. D. Brown, Electrochem. Soc. Proc. 94-16, 505 (1994).
6. "ECR-Plasma-Assisted Deposition of AlOx and Al₂O₃" (invited), J. C. Barbour, D. M. Follstaedt, R. J. Bourcier, S. M. Myers, B. G. Potter, M. B. Sinclair, and J. S. Custer, in Proc. 9th Inter. Conf. on Ion-Beam Modification of Materials, Canberra, Australia, Feb. 5-10, 1995 (in press).
7. "ECR-Plasma-Assisted Deposition of Al₂O₃ with In-Situ Er Doping," J. C. Barbour, J. S. Custer, D. M. Follstaedt, B. G. Potter, and M. B. Sinclair, J. Vac. Sci. Technol. (in press).
8. "Elastic Recoil Detection" (invited), J. C. Barbour and B. L. Doyle, in Handbook of Modern Ion Beam Materials Analysis, edited by J. R. Tesmer, M. Nastasi, J. C. Barbour, C. J. Maggiore, and J. W. Mayer (MRS, 1995), Chapter 5.
9. "The Location of Deuterium on The Silicon (100) Monohydride Surface Determined by Transmission Channeling," W. R. Wampler, Phys. Rev. B (in press).
10. "Comment on 'Electron Paramagnetic Resonance of Molecular Hydrogen in Silicon,'" K. L. Brower, S. M. Myers, A. H. Edwards, N. M. Johnson, C. G. Van de Walle, and E. H. Poindexter, Phys. Rev. Lett. 73, 1456 (1994).

Work Performed Jointly with Other Programs

11. "Passivation of Compound Semiconductors: Improvement of the Dielectric/Sulfur/Semiconductor Interface," C. I. H. Ashby, K. R. Zavadil, J. C. Barbour, M. L. Lovejoy, R. J. Shul, and M. J. Hafich, J. Vac. Sci. Technol. (in press).
12. "Growth of Cubic BN Films on β -SiC by Ion-Assisted Pulsed Laser Deposition," P. B. Mirkarimi, D. L. Medlin, K. F. McCarty, and J. C. Barbour, Appl. Phys. Lett. (submitted).
13. "Materials Analysis Using Combined Elastic-Recoil Detection, High-Energy Backscattering, and Rutherford-Backscattering Spectrometry," J. H. Burkhart and J. C. Barbour, in Proc. Inter. Conf. on the Application of Accelerators in Research and Industry (in press).
14. "Photoluminescence and Passivation of Silicon Nanostructures," D. A. Redman, D. M. Follstaedt, T. R. Guilinger, and M. J. Kelley, Appl. Phys. Lett. 65, 2386 (1994).

Advanced Growth Techniques and the Science of Epitaxy

KC 02 01 03

Principal Investigators: E. Chason, J.Y. Tsao, J.A. Floro, B.S. Swartzentruber, E. Heller, B.K. Kellerman and S.T. Picraux

Goal: To advance our understanding of epitaxial crystal growth and the fundamental processes governing it. Advances will include the development of novel growth and energetic beam techniques, in situ diagnostics and models leading to an integrated understanding of the interactions among various surface processes which control growth.

Recent Highlights

- Temperature Dependence of Ion-Induced Surface Defect Yield - We have developed kinetic Monte Carlo simulations to understand the temperature-dependence of the surface defect yield during low-energy ion bombardment. We find that most of the defects created by the ions reach the surface. At low temperature the defects become immobile on the surface while at higher temperature they can diffuse and recombine. These results indicate that large numbers of defects are present transiently on the surface at growth temperatures, an important factor in understanding ion-assisted growth processes.
- Monte Carlo Simulations of CVD Processes - We have incorporated mobile precursor molecules into our Monte Carlo simulations of growth to simulate processes found in chemical vapor deposition. Comparison of these results with STM studies of cluster nucleation (joint with LDRD) will determine the importance of precursor mobility and preferential dissociation at clusters in the evolution of the growth morphology. These studies represent the first use of a kinetic Monte Carlo approach for the study of CVD growth.
- Saturation of the Single-A-Domain Si(001) Surface formed by Low-Energy Ion Bombardment - Using low-energy ions to bombard Si(001), we have studied the formation of a single domain surface comprised of a majority of A-type terraces. We find that the minority B domains persist regardless of ion dose due to the strain-induced repulsion of the steps. At high doses, the surface roughens due to stable step-kissing sites that form at anti-phase boundaries of the surface reconstruction.
- Group IV MBE capability - We have finished construction of our Group IV MBE system with 3 e-beam sources, RHEED and Auger diagnostics and ion-assisted growth capabilities. Optimal substrate preparation and growth conditions have been established and routine growth of heteroepitaxial SiGe alloys on Si has been achieved.
- Interface Roughness in CVD-grown SiGe/Si Heterostructures - The development of advanced heteroepitaxial SiGe/Si device structures requires thin SiGe layers with well-controlled interfacial roughness. We have used X-ray reflectivity to characterize SiGe heterolayers and related the interface quality to the CVD processing parameters. The presence of a graded interface was determined to be caused by the transient switching time of the gas flow.

Future Directions

The study of heteroepitaxial growth and the control of surface morphology will be major focuses of the advanced growth program. Heteroepitaxial structures in the group IV materials are becoming increasingly important as scaling limits are reached in Si production, so we will use our new MBE capability to study processes of roughening and strain relaxation in SiGe layers. In addition, we will explore the growth of novel SiGeC alloys in which the C compensates the Ge to produce layers lattice-matched to Si. In order to incorporate non-equilibrium concentrations of substitutional C into SiGe, we will use our expertise in beam-assisted growth to deposit energetic C from an ECR plasma source. X-ray reflectivity studies of roughening kinetics during strained SiGe growth on Si will be used to study the relationship between strain and surface roughness. Incorporation of an STM into a state-of-the-art III-V MBE growth chamber capable of producing device quality material will enable us to relate control of the surface structure to improvements in devices made from this material. The STM will also serve as an important diagnostic in studying the growth of nitrides (AlGa_{0.5}N, InGa_{0.5}N) for the development of blue and ultraviolet light emitting devices. STM studies of ion-induced single domain reconstructions will reveal information on fundamental surface kinetic processes and the elastic interactions between step edges.

Interactions with DOE Technologies

The development of advanced semiconductor characterization and in situ MBE growth-monitoring techniques provides underpinning for DP research and development programs. These efforts support our microelectronics and photonics manufacturing capabilities and are the foundation of a CRADA with Motorola.

Program Quality

BES Award for Sustained Outstanding Research in Metallurgy and Ceramics; 7 publications, 12 presentations (3 invited)

Advanced Growth Techniques and the Science of Epitaxy

KC 02 01 03

Publications

1. Growth pressure effects on Si/Si_{1-x}Ge_x Chemical Vapor Deposition, Z. Matutinovic Krstelj, J.C. Sturm and E. Chason, J. of Electronic Mater., submitted
2. Defect Production And Recombination During Low Energy Ion Processing, B.K. Kellerman, J.A. Floro, E. Chason, D.K. Brice, S.T. Picraux and J.M. White, J. Vac. Sci. Technol, submitted.
3. Temperature Programmed Evolution Of Low-energy Rare-gas Ions Implanted In Si(100), M.R. Tesauero, G. Underwood, B.K. Kellerman and A. Campion, Surf. Sci., submitted
4. Kinetics Of Atomic-scale Fluctuations Of Steps On Si(001) Measured With Variable Temperature STM, B.S. Swartzentruber and M. Schact, Surf. Sci., in press.
5. STM Measurements Of Step Flow Kinetics During Atom Removal By Low-energy Ion Bombardment Of Si(001), B.S. Swartzentruber, C.M. Matzke, D.L. Kendall and J.E. Houston, submitted

Work Performed Jointly with Other Programs

6. Initial Stages Of Fe Chemical Vapor Deposition Onto Si(100), D.P. Adams, T.M. Mayer, B.S. Swartzentruber and E. Chason, Appl. Phys. Lett, submitted (joint with LDRD).
7. Optical Measurements Of Bandgaps Of Si_{1-x}C_x/Si (0<X<0.14) Semiconductor Alloys, H. Lee, S.R. Kurtz, J.A. Floro, J. Strane, C.H. Seager, S.R. Lee, E.D. Jones, J.F. Nelson, T. Mayer and S.T. Picraux, Appl. Phys. Lett., submitted (joint with CRADA).

Artificially-Structured Semiconductor Materials Science

KC 02 01 05

Principal Investigators: P. L. Gourley, E. D. Jones, S. K. Lyo, J. S. Nelson, M. B. Sinclair, and J. R. Wendt

Goals: Investigate fundamental structural, optical, and electronic properties of artificially layered and/or surface-structured semiconductors produced by molecular beam epitaxy or metal-organic vapor phase epitaxy and/or electron beam lithography. Identify new artificial material and structures with potential for high scientific and technological impact.

Recent Highlights:

- **Carrier Dynamics in Multialloy InAlGaP Semiconductor Structures** - Using ultrafast laser spectroscopy we have measured the electron-hole recombination and photo-induced absorption changes in carrier distribution in multilayers of InAlGaP alloys. These multilayer structures are designed for broadband spectral emission in the visible and are under consideration for illumination sources. The measurements show that relaxation of carriers can be controlled from picosecond to nanoseconds by adjusting the layer thicknesses from 50 to 400 Å. At the same time the minority carrier lifetime was observed to increase 20 times due to decreases in interface recombination.
- **Energy Band Structure of AlAs/AlSb Short-Period Superlattices** - We have performed first-principles pseudopotential calculations to determine the electronic properties of [001] short-period superlattices (AlAs)_n/(AlSb)_n lattice-matched to InP for $n \leq 4$, including band mixing and zone folding effects. Compared to the indirect gap disordered alloy of AlAs_{0.5}Sb_{0.5}, the superlattices show "pseudodirect" transitions comparable to direct bandgap transitions. These transitions lie in the infrared for $n=1$ and in the visible for $n=2$ extending the range of emission wavelengths for semiconductors grown on InP.
- **Nanofabrication of Hexagonal Photonic Lattices** - We have developed a dry etch process for nanofabrication of two-dimensional photonic lattices in GaAs/AlGaAs designed for optical wavelengths near 1.5 μm. Hexagonal patterns of cylindrical posts with diameter of 0.45 μm and lattice constant of 0.9 μm were patterned into GaAs using an etch mask of SiO₂ covered with negative electron beam resist subjected to ultraviolet hardening. By varying the accelerating voltage of the reactive ion beam etch, we demonstrated how to control the post geometry. Posts were produced that varied from cylinders to tall tapered posts to short conical posts.
- **Effect of the Band-Nonparabolicity on the Magnetoexciton Binding Energy** - We have developed a numerical formalism to calculate the binding energy of excitons in magnetic fields by including the band-nonparabolicity in an arbitrary magnetic field. In the parabolic limit, our results yield excellent agreement with previous low-field and high-field results. Also, our results are valid for arbitrary fields. We have applied this formalism to recent magnetoluminescence data and have determined the nonparabolicity parameters in InAs/InAsSb strained-layer structures.
- **NREL Collaboration** - A new collaboration was initiated with National Renewable Energy Laboratory in FY 94 on compositional structuring and on alloy ordering to enhance the performance of semiconductor materials for photovoltaic and other optoelectronic applications.

Future Directions

Development of layered structures for visible and near infrared emission using molecular beam epitaxy and vapor phase epitaxy. Experimental studies of carrier relaxation and recombination in multialloy structures. Fabrication and study of semiconductor nanostructures synthesized with electron beam lithography. Explore implications of these new artificial structure for optical emission, detection, and photovoltaic properties.

Interactions with DOE Technologies

This project provides scientific underpinnings for Defense Programs R&D to develop photonic devices for high speed interconnects and communication applications. DP programs provide complimentary funding for these efforts.

Program Quality:

- 14 invited talks, 5 invited review articles
- Startup of new Advanced Energy Projects program on broadband light emitters as an outgrowth of this program.

Artificially-Structured Semiconductor Materials Science

KC 02 01 05

Publications

Work Performed under BES Program

1. Optical properties of 2-dimensional photonic lattices fabricated as honeycomb nanostructures in compound semiconductors, P. L. Gourley, J. R. Wendt, G. A. Vawter, T. M. Brennan, and B. E. Hammons, *Appl. Phys. Lett.* **64**, 687-689 (1994).
2. Microstructures of (In,Ga)P alloys grown on GaAs by MOVPE, D. M. Follstaedt, R. P. Schneider, Jr., and E. D. Jones, *J. Appl. Phys.* (1994).
3. Surface-emitting semiconductor structures fabricated by microlithography, P. L. Gourley and M. E. Warren, *International Journal of Nonlinear Optical Physics*, **4**, (to appear January, 1995). Invited Review.
4. Microstructured semiconductor lasers, P. L. Gourley, *Comments on Condensed Matter Physics*, **16**, 355-376, (1994). Invited Review.
5. Effect of exciton localization and delocalization on magnetic-field-dependent exciton photoluminescence line widths in semiconductors, S. K. Lyo, E. D. Jones, and S. R. Kurtz, *J. Luminescence* **60 & 61** 409, (1994).
6. Magnetic-field dependent photoluminescence studies of InGaAs/GaAs strained-single-quantum wells, E. D. Jones, L. R. Dawson, J. F. Klem, S. K. Lyo, D. Heiman, and X. C. Liu, *The Applications of High Magnetic Fields in Semiconductor Physics* (SEMIMAG-94), August 8-12, 1994, Boston, MA, (World Scientific Publishing, 1994).

Work Performed Jointly with Other Programs

7. Fractal quantum well heterostructures for broadband light emitters, M. Hagerott-Crawford, P. L. Gourley, E. D. Jones, M. B. Sinclair, W. W. Chow, and R. P. Schneider, Jr. *SPIE Proceedings of Photonics West95*, **2399**, submitted (1/95).
8. Microstructured semiconductor lasers for high-speed information processing, P. L. Gourley, *Nature* **371**, 571 (1994). Invited Review.
9. The edge of a different mirror, P. L. Gourley, K. L. Lear, and R. P. Schneider, Jr. *IEEE Spectrum*, **31**, 31-37 (August 1994). Invited Review.
10. GaInP unicompositional disorder-order-disorder quantum wells, R. P. Schneider, Jr., E. D. Jones, and D. M. Follstaedt, *Appl. Phys. Letters* **65**, 587 (1994).

Physics and Chemistry of Novel Superconductors

KC 02 02 02

Principal Investigators: T. L. Aselage, N. A. Missert, B. Morosin, P. P. Newcomer, J. E. Schirber, M. P. Siegal, E. B. Stechel and E. L. Venturini

Goals: Develop a fundamental understanding of the physics and chemistry of novel superconductors, particularly TI-based, with emphasis on: phase equilibria; controlled, scalable synthesis; intrinsic superconducting properties; structure-based control of the transport and magnetic behavior; and investigation of prototype device configurations.

Research Highlights:

- **Phase equilibria and properties:** The T_c 's of TI superconductors are insensitive (± 1 K) to their equilibrium preparation conditions, yet unit cell dimensions show that their stoichiometries vary systematically with these conditions. Low-temperature anneals to independently reduce the oxygen content increase T_c by up to 40 K for TI-1212. We infer that T_c in our equilibrated samples is fixed by self-compensation.
- **TI-Ba-Ca-Cu-O thin films:** Processing thin films using a two-zone furnace has led to high-quality, single-phase films. TI-1212 films were produced with T_c of 100 K, comparable to that for TI-2212 films, but with stronger intrinsic vortex pinning and, hence, significantly higher J_c 's in moderate fields.
- **Single Crystal Studies:** We have improved the growth of TI-Ba-Ca-Cu-O single crystals, obtaining larger plates with optimum T_c 's and narrow transitions. Single crystals are essential in understanding the intrinsic, highly anisotropic superconducting properties such as interlayer coupling, vortex pinning and critical current density.
- **Ion Damage in Crystals:** We studied ion-irradiation effects on TI-Ba-Ca-Cu-O single crystals and identified an unusual temperature dependence for the microstructural modifications. Varying the irradiation temperature offers control of the specific defects created, thus allowing optimization of vortex pinning and critical current density.
- **New Materials:** We developed an alternate synthesis route for the Hg-Ba-Ca-Cu-O family of superconductors and determined phase stability and optimum doping. We achieved higher T_c 's by extending the new oxyfluoride superconductor $Sr_2CuO_2F_{2+\delta}$ to the corresponding alkaline earth alloys, $(Sr_{1-x}M_x)_2CuO_2F_{2+\delta}$, with $M = Ba, Ca$.
- **Fullerene-based superconductors:** We have demonstrated that the "universal" T_c versus lattice constant relation differs for simple cubic Na-based C_{60} and fcc alkali metal-based C_{60} . These data provide a stringent test of band structure calculations for electron-phonon coupling and density of states in these novel superconductors.
- **Liquidus surface in Y-Ba-Cu-O:** Discovered free CuO promotes low-temp liquid formation in $YBa_2Cu_3O_{7-\delta}$, reducing the melting/crystallization temp. by up to 65°C. CuO arises from most interactions with the environment.
- **Theory:** The Luttinger Liquid correlation exponent K_ρ for a 1D CuO model shows that the singlet (extended s-wave) superconductivity (SS) and charge-density wave (CDW) susceptibilities may simultaneously diverge as $T \rightarrow 0$. We also calculated the parameter phase space diagram for SS, CDW and phase separation.

Future Directions

We will continue the integrated study of phase equilibria, synthesis, processing, and physics of various high- T_c materials, emphasizing the TI-Ba-Ca-Cu-O system. Our goals are two-fold: to understand the intrinsic properties of single crystals and ceramics and to optimize the electronic properties of epitaxial thin films for device applications through control of microstructure. Synthesis and properties of new cuprates, superoxygenated cuprates, fullerene-based and organic materials will be studied to enhance our knowledge of novel superconductivity.

Interactions with DOE Technologies

Defense Programs: superconducting energy storage, switches and interconnects form basis for future superconducting enablement in surety component development. **Energy Efficiency and Renewable Energy:** our BES phase equilibria and two-zone furnace processing knowledge are used to develop TI-based thick films and tapes. Both programs provide complementary funding in applied areas.

Other Interactions

- **Universities:** research collaborations with Indiana, Maryland, New Mexico, Pennsylvania, Wisconsin, Norges Tekniske Høgskole and Université Paris-Sud. **Industry:** AT&T Bell Labs, DuPont CR&D and Conductus. **National labs:** intergrowths and microstructure (ANL); vortex motion in high quality crystals (ANL) and thin films (ORNL); our unique high pressure oxygen capabilities provide samples to study phase separation and microstructure (LANL, Ames).
- **Tech Transfer:** Research supported by this BES program prompted a Technology Transfer Initiative CRADA with DuPont on development of a new manufacturing process for TI-based high- T_c superconducting thin films. Recently completed CRADA with Conductus produced a commercial surface resistance analyzer based on a confocal resonator.

Program Quality and Impact:

- 5 invited presentations, 18 publications including one book chapter, co-chairman of 1994 MRS Fall Meeting symposium on high-temperature superconductivity.

Physics and Chemistry of Novel Superconductors

KC 02 02 02

Publications

Work Performed under BES Program

1. "Two-Zone Equilibria of Tl-Ca-Ba-Cu-O Superconductors," T. L. Aselage, E. L. Venturini and S. B. Van Deusen, *J. Appl. Phys.* **75** 1023 (1994).
2. "Annealing Studies of Hg-Containing Materials," B. Morosin, E. L. Venturini, J. E. Schirber and P. P. Newcomer, *Physica C* **226** 175 (1994).
3. "Pairing Fluctuations in a One-Dimensional Copper-Oxide Model," E. B. Stechel, A. Sudbø, T. Giamarchi and C. M. Varma, *Phys. Rev. B*, in press.
4. "Superconducting Properties of Strontium Copper Oxyfluoride," $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, B. Morosin, E. L. Venturini, J. E. Schirber, R. G. Dunn and P. P. Newcomer, *Physica C*, in press.
5. "Anomalous Pressure Dependence of the Superconducting Transition Temperature of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$," J. E. Schirber, B. Morosin, E. L. Venturini and W. R. Bayless, *Physica C*, in press.
6. "Occurrence of Free CuO in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ and its Effect on Melting and Solidification," T. L. Aselage, *Physica C* **233** 292 (1994).

Work Performed Jointly with Other Programs

7. "Effect of He Pressure on the Superconducting Transition Temperatures of $\text{Na}_2\text{CsC}_{60}$ and $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$," J. E. Schirber, W. R. Bayless, M. J. Rosseinsky, O. Z. Zhou, R. M. Fleming, D. Murphy and J. E. Fischer, *Mater. Res. Soc. Symp. Proc.*, Fall Meeting, 1994, in press.
8. "Pressure Studies of Alkali Alkaline Earth and Rare Earth Doped C_{60} superconductors," J. E. Schirber, W. R. Bayless, A. R. Kortan, M. J. Rosseinsky, E. Ozdas, O. Zhou, R. M. Fleming, D. Murphy and J. E. Fischer, *Proc. 185th Mtg. Electrochem. Soc.*, in press.
9. "The Isotope Effect for Superconductivity in High- T_c $\beta^*(\text{ET})_2\text{I}_3$ with ^{13}C Isotopic Substitution in the Ring and Central C=C Atoms of bis(ethylenedithio)tetrathiafulvalene (ET)," K. D. Carlson, A. M. Kini, J. A. Schlueter, H. H. Wang, J. D. B. Sutin, J. M. Williams, J. E. Schirber and E. L. Venturini, *Physica C* **227** 10 (1994).
10. "Preparation and Properties of High- T_c TiCaBaCuO Superconducting Thin Films," W. Y. Lee, E. L. Venturini and J. S. Martens, in *Studies of High Temperature Superconductors*, ed. by A. Narlikar (Nova Science, Commack, NY, 1994), Vol. 13, Ch. 2.
11. "Phase-Separation in Oxygen Rich Single Crystal $\text{La}_2\text{CuO}_{4+x}$: Magnetic and Structural Neutron Diffraction Studies," D. Vaknin, J. L. Zarestky, D. C. Johnston, J. E. Schirber and Z. Fisk, *Phys. Rev. B* **49** 9057 (1994).
12. "Di- and Tri-Carboxylic-Acid-Based Etches for Processing High-Temperature Superconducting Films," D. S. Ginley, L. Barr, C. I. H. Ashby, T. A. Plut, D. Urea, M. P. Siegal and J. S. Martens, *J. Mater. Res.*, **9** 1126 (1994).
13. "Phase Separation and Doped-Hole Segregation in $\text{La}_2\text{CuO}_{4+\delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$," D. C. Johnston, W. R. Bayless, F. Borsa, P. C. Canfield, S. W. Cheong, J. H. Cho, F. C. Chou, Z. Fisk, J. D. Jorgensen, L. L. Miller, P. G. Radaelli, J. E. Schirber, D. R. Torgeson, D. Vaknin, J. L. Wagner, J. Zarestky and J. Ziola, *Physica C*, in press.
14. "Synthesis, Structure, and Properties of the Organic Conductor $(\text{BEDT-TTF})_2\text{Br}_2\text{SeCn}$," U. Geiser, H. H. Wang, J. A. Schlueter, J. M. Williams, J. L. Smart, A. C. Cooper, S. K. Kumar, M. Caleca, J. D. Dudek, K. D. Carlson, J. Ren, M.-H. Whangbo, J. E. Schirber and W. R. Bayless, *Inorg. Chem.* **33** 5101 (1994).
15. "Superconductivity up to 11.1 K in Three Solvated Salts Composed of $[\text{Ag}(\text{CF}_3)_4]^-$ and the Organic Electron Donor Molecule bis(ethylenedithio)tetrathiafulvalene (ET)," J. A. Schlueter, K. D. Carlson, U. Geiser, H. H. Wang, J. M. Williams, W.-K. Kwok, J. A. Fendrich, U. Welp, P. M. Keane, J. D. Dudek, A. S. Komosa, D. Naumann, T. Roy, J. E. Schirber, W. R. Bayless and B. Dodrill, *Physica C* **233** 379 (1994).
16. "First Organic Cation-Radical Salt Superconductor ($T_c = 4$ K): Superconductivity, Synthesis, and Structure of $(\text{BEDT-TTF})_2\text{Cu}(\text{CF}_3)_4$ TCE," J. A. Schlueter, U. Geiser, J. M. Williams, H. H. Wang, W.-K. Kwok, J. A. Fendrich, K. D. Carlson, C. A. Achenbach, J. D. Dudek, D. Naumann, T. Roy, J. E. Schirber and W. R. Bayless, *J. Chem. Soc., Chem. Commun.*, No. 13, p. 1599 (7 July 1994).
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18. "A New 9 K Superconducting Organic Salt Composed of the BEDT Electron-Donor Molecule and the $[\text{Cu}(\text{CF}_3)_4]^-$ anion," J. A. Schlueter, K. D. Carlson, J. M. Williams, U. Geiser, H. H. Wang, U. Welp, W.-K. Kwok, J. A. Fendrich, J. D. Dudek, C. A. Achenbach, P. M. Keane, A. S. Komora, D. Naumann, T. Roy, J. E. Schirber and W. R. Bayless, *Physica C* **230** 378 (1994).

Tailored Surfaces and Interfaces for Materials Applications

KC 02 02 02

Principal Investigators: G. L. Kellogg, P. J. Feibelman, T. M. Mayer, B. S. Swartzentruber, N. D. Shinn

Goal: To understand the atomic-level processes that control the synthesis and processing of thin surface layers and to use this understanding to tailor the structural and electronic properties of surfaces and interfaces for advanced materials applications.

Recent Highlights

- Unexpected Oscillations in Cluster Mobility on Metal Surfaces - Direct observations of small Rh clusters on the Rh(100) terrace show that the mobility oscillates as a function of cluster size. Compact configurations (squares and rectangles) have a consistently higher activation energy of surface diffusion than clusters with extra atoms at the periphery. The correlation between cluster shape and mobility agrees with a model in which diffusion takes place by individual displacements of edge atoms, thus defining the diffusion mechanism. The measured activation energies also provide quantitative input required for realistic, microscopic growth-simulation models.
- Kinetically Stabilized Surface Structures - We have used the new variable temperature STM to observe surface vacancy annihilation and adatom detachment from Si(001) step edges. We show that controlling the rate of vacancy formation (ion flux) can shift the balance between competing atomic-level processes to achieve desired mesoscopic surface structures. These findings suggest new approaches that can be used to stabilize desired surface structures through externally controlled growth parameters.
- Calculations of Anisotropic Surface Stress - First-principles calculations show that on non-reconstructed Pd(110) and Pt(110) the stress is considerably higher along the direction of the close-packed atomic rows than transverse to it. This intuitive result is counter to that deduced from fits to Ni(110) surface phonon spectra. Surface stress is believed to play a key role in defining surface atomic structure, but it is difficult to measure experimentally. Our calculations suggest that surface stress determinations based on surface phonon spectra are not reliable. Additional calculations are in progress in order to establish the stress-structure relationship more definitively.
- Interfacial Alloying During Ultra-Thin Film Growth - Soft X-ray photoelectron spectroscopy and ion scattering show that interfacial alloying occurs during the growth of Ni films on W(001). The exchange diffusion mechanism is proposed to account for the interfacial alloying, which is thermodynamically unexpected. This study illustrates how a fundamental growth process can impose unforeseen limits on fabricating atomically sharp interfaces.
- Nucleation Phenomena in Chemical and Physical Vapor Deposition: The atomic-scale processes active during the initial stages of CVD nucleation and growth have been identified in STM studies of Fe on Si(100). Growth mechanisms are inferred from the density and size distribution of clusters observed in STM images. Differences between the morphology of films produced by CVD of Fe(CO)₅ molecules and physical vapor deposition of Fe atoms imply a site-selective chemical reactivity of the molecular precursor with existing islands and/or mobility of adsorbed precursor molecules.

Future Directions

Research under this program will continue to focus on understanding the microscopic mechanisms that control the growth of thin surface films and using this knowledge to develop predictive models for materials synthesis. Atomic-scale experimental and theoretical investigations will determine how surface defects such as clusters, vacancies, and steps affect fundamental growth processes and control the overall quality of epitaxial films. Comprehensive microscopic models of morphology development in CVD of metals on Si will be lead to nanometer-scale selective area CVD growth by chemical manipulation of nucleation processes. New capabilities in Low Energy Electron Microscopy (LEEM) and optical techniques to examine "macroscopic" diffusion behavior will be added to enhance our real-time analysis of dynamical surface processes and to test predictions based on our atomic-level understanding.

Interactions with DOE Technologies:

This BES-supported research is providing both fundamental understanding and quantitative input required to develop science-based models of materials growth and stability. Interactions with DP- and Energy-funded R&D programs addressing the long-term stability of materials will lead to more reliable predictions of component reliability and safety.

Program Quality

- 1994 DOE/BES/MS Award for Sustained Outstanding Research in Solid State Physics
- Program Chair for the 41st National American Vacuum Society Symposium
- 1994 MRS Symposium Organizer - *Appl. of Synchrotron Radiation Techniques to Materials Science*
- Invited Review Articles in Surface Science Reports, Surface Science, and CRC Critical Reviews
- 18 Publications, 9 Invited Presentations

Tailored Surfaces and Interfaces for Materials Applications

KC 02 02 02

Publications

Work Performed under BES Program

1. "Oscillatory Behavior in the Size Dependence of Cluster Mobility on Metal Surfaces: Rh on Rh (100)," G. L. Kellogg, Phys. Rev. Lett. **73**, 1833 (1994).
2. "Field Ion Microscope Studies of Single-Atom Surface Diffusion and Cluster Nucleation on Metal Surfaces (Invited Review)," G. L. Kellogg, Surface Science Reports **21**, 1 (1994).
3. "Field Ion Microscope Studies of Exchange-Mediated Atom-Displacement Processes on Metal Surfaces," G. L. Kellogg, Appl. Surface Science (in press).
4. "An Atomic View of Surface Diffusion on Metal Surfaces," G. L. Kellogg, Proceedings of the NATO Advanced Workshop on the Synergy between Dynamics and Reactivity at Clusters and Surfaces, NATO Book Series (in press).
5. "Calculation of Surface Stress in a Linear Combination of Atomic Orbitals Representation," P. J. Feibelman, Phys. Rev. B **50**, 1908 (1994).
6. "Diffusion Barrier for a Ag Adatom on Pt(111)," P. J. Feibelman, Surface Science **313**, L801 (1994).
7. "Surmounting the Barriers," P. J. Feibelman and J. Harris, Nature **372**, 135 (1994).
8. "Kinetics of Atomic-Scale Fluctuations of Steps on Si(001) Measured with Variable-Temperature STM," B. S. Swartzentruber and M. Schacht, Surface Science (in press).
9. "STM Measurements of Step-Flow Kinetics During Atom Removal by Low-Energy Ion Bombardment of Si(100)," B. S. Swartzentruber, C. M. Matzke, D. L. Kendall, and J. E. Houston, Surface Science (in press).
10. "The Radiation-Induced PF₃ Decomposition on Ru(0001)," H. Tao, U. Diebold, V. Chakarian, D. K. Shuh, J. A. Yarmoff, N. D. Shinn and T. E. Madey, J. Vac. Sci. Technol. A (in press).
11. "Comment on 'Contrasted Behavior of Si(001) and Si(111) Surfaces with Respect to NH₃ Adsorption and Thermal Nitridation: A N(1s) and Si(2p) Core-Level Study with Synchrotron Radiation'," C. H. F. Peden, J. W. Rogers, Jr. and N. D. Shinn, Surface Science (in press).
12. "Surface Core-Level Shifts and Atomic Coordination at a Stepped W(110) Surface," D. M. Riffe, B. Kim, J. L. Erskine and N. D. Shinn, Phys. Rev. B **50**, 14481 (1994).
13. "Core-Level Photoemission and Alkali Ion Scattering Structure Analysis of Ni Adsorption and Surface Alloying on W(001)," S. H. Overbury, P. F. Lyman, D. R. Mullins and N. D. Shinn, Surface Science (submitted).
14. "Initial Stages of Fe Chemical Vapor Deposition on Si (100)," D. P. Adams, L. L. Tedder, T. M. Mayer, B. S. Swartzentruber, E. Chason, Appl. Phys. Lett. (submitted).

Work Performed jointly with other programs

15. "Physics of the Be(0001) Core Level Spectrum," P. J. Feibelman and R. Stumpf, Phys. Rev. B (in press).
16. "The Unusual Properties of Beryllium Surfaces," R. Stumpf, J. B. Hannon, P. J. Feibelman, and E. W. Plummer, Proc. Bad Hannof Conference on Surface States and Surface Bonding (in press).
17. "The Interaction of H with the Be(0001) Surface," R. Stumpf and P. J. Feibelman, Phys. Rev. B (submitted).
18. "X-Ray Specular Reflectivity for Surface and Interface Studies (Invited Review)," E. Chason, T. M. Mayer, CRC Critical Reviews, (in press).

Boron-Rich Solids

KC 02 02 05

Principal Investigators: T. L. Aselage, D. Emin, B. Morosin and D. R. Tallant

Goals: To understand the novel properties of boron-based materials, to assess their potential for unusual applications and to apply insights gained to the study of solids generally.

Highlights

- Damage from irradiating boron-rich solids with different structures and conductivities with energetic electrons was observed with TEM. Radiation-induced boron vacancies and interstitials spontaneously recombine only in icosahedral borides. This extraordinary self-healing arises from the unusual stability of icosahedral fragments.
- Neutron diffraction of boron carbides at pressures to 11 GPa confirms that the icosahedral units compress more than the intericosahedral bonds. These findings justify our interpretations of vibrational spectra and transport.
- Raman spectra of $B_{12}P_2$, $B_{12}As_2$ and $B_{12}O_2$ were studied with samples enriched in ^{10}B and ^{11}B . Small boron isotope dependences of P-P and As-As chain vibrations show these chains to be strongly bonded. By contrast, the large isotope dependence of the oxygen Raman band is consistent with negligible bonding of these widely separated oxygen atoms. Similarly, the large boron isotope effect of boron carbides' chain motion signifies its weak bonding.
- Our neutron diffraction of ^{11}B enriched boron carbides find very easy displacement of chains' central atom.
- Seebeck coefficients of boron carbides (10-1000 K) were measured with two apparatus. The temperature dependences are very distinctive. They rise slowly at low temperatures, swoop up toward a large value ($\approx 200 \mu V/K$) near 300 K and remain nearly constant at higher temperature. The Seebeck coefficients vary nonmonotonically with carrier concentration, having their lowest values when the carrier density is highest.
- Boron carbides' Seebeck coefficients were explained by a model in which the polarizabilities of multi-site bipolarons soften the structure in their vicinity. The reductions of the vibrational frequencies that are thereby produced give rise to an extra (nonstandard) contribution to Seebeck coefficients. The temperature dependence and magnitude of this effect are consistent with bipolarons confined to boron carbides' icosahedra.
- The energetically favorable way for bipolarons to hop is for the pair to break and then reform rather than stay together. If the carriers' spins thermalize while the pair is separated, these spins will act as paramagnets. This theory explains why measurements of boron carbides' magnetic susceptibilities above room temperature show a thermally activated contribution having the same activation energy as that of the measured mobility.

Future Directions

Boron carbides: Measuring the magnetic field dependence of Seebeck coefficients will determine carriers' magnetic moments ascertaining whether they are singlet bipolarons. Low-temperature Hall mobility and low- and high-field conductance measurements will be used to probe the effects of disorder, trapping and correlation on hopping transport. ^{13}C NMR will be performed to determine the charge states of icosahedral carbons and the rates of intericosahedral charge transfer. Studies of disorder-induced polaron formation in covalent borides will continue. β -Rhombohedral boron: Although β -boron has a metal-like carrier density, its dc conductivity is semiconductor-like. We conjecture that most of β -boron's carriers are confined within disconnected regions. The low-frequency ac conductivity will be measured to test this conjecture. In addition, our theory of low-temperature small-disorder low-frequency hopping conductivity of polaronic carriers must be extended to apply at high temperatures and large disorder energies. Other borides: Crystals of $B_{12}P_2$ and $B_{12}As_2$ grown at high temperatures tend to lose P and As due to their high vapor pressures. Films will be grown by low-temperature deposition. Combined electronic transport measurements will be used to resolve whether diboride conductors are unconventional metals. Large bipolarons: Electronic and thermal transport arising from bipolarons collective motions will be calculated. The unusual (two-phonon) process by which phonons and large-bipolarons scatter one another is expected to result in unconventional transport. We will seek large bipolarons in highly ionic solids.

Relations to DOE Technologies

This program supports DP, ER and Nonproliferation interests in boron-based high-temperature thermoelectric energy conversion, radiation-hard semiconductors, boron-carbon first-wall MFE materials and neutron detectors.

Program Quality

- Invited to: write reviews for Rev. of Mod. Phys. and for Intl. J. of Mod. Phys., and edit book on Boron-rich Solids
- Two members of the "Int'l Scientific Committee on Boron, Borides and Related Compounds"
- 12 invited talks (4 meetings and 8 colloquia), 10 publications
- Consulting with Science and Engineering Associates (SEA) and High-Z Technologies.

Boron-Rich Solids

KC 02 02 05

Publications

1. "Disorder-Induced Small-Polaron Formation," D. Emin and M.-N. Bussac, *Physical Review B* 49, 14 290 (1994).
2. "Defect Clustering and Self-healing of Electron-Irradiated Boron-Rich Solids," M. Carrard, D. Emin and L. Zuppiroli, *Physical Review B* (in press)
3. "Observation of Inverted-Molecular Compression in Boron Carbide," R. J. Nelmes, J. S. Loveday, R. M. Wilson, W. G. Marshall, J. M. Besson, S. Klotz, G. Hamel, T. L. Aselage and S. Hull, *Physical Review Letters* (in press)
4. "Neutron Powder Diffraction Refinement of Boron Carbides: Nature of Intericosahedral Chains," B. Morosin, G.H Kwei, A.C. Lawson, T.L. Aselage and D. Emin, *Journal of Alloys and Compounds* (submitted)
5. "The Diboride Compounds Of Molybdenum," MoB_{2-x} and $\text{Mo}_2\text{B}_{5-y}$, H. Klesnar, T. L. Aselage, G. H. Kwei, A. C. Lawson and B. Morosin, *Journal of Alloys and Compounds* (submitted)
6. "Synthesis And Cell Refinement For Icosahedral Boron Phosphide B_{12}P_2 ," P. Yang and T. L. Aselage, *Powder Diffraction* (submitted)
7. "Formation, Phase Separation and Superconductivity of Large Bipolarons," D. Emin in Polarons and Bipolarons in High- T_c Superconductors and Related Materials, W.Y. Liang, E. S. H. Salje and A. S. Alexandrov eds., (Cambridge University Press, 1995) (in press).
8. "Large Bipolarons and Superconductivity," D. Emin, *Journal of Superconductivity* (in press).
9. "Large Bipolarons And Superconductivity," D. Emin *Molecular Physics Reports* (in press).
10. "High Mobility N-type Charge Carriers In Large Single Crystals Of Anatase (TiO_2)," L. Forro, D. Emin, O. Chauvet, L. Zuppiroli, H. Berger and F. Levy, *Journal of Applied Physics* 75, 633 (1994).

CVD Sciences KC 02 03 03

Principal Investigators: P. Esherick, M. E. Bartram, W. G. Breiland, M. E. Coltrin, J. R. Creighton, P. Ho, K. P. Killeen, H. K. Moffat, J. E. Parmeter, R. J. Kee, F. Rupley

Goals: To advance the understanding of the basic physics and chemistry of thin-film synthesis by chemical vapor deposition (CVD), including metal organic CVD, and plasma assisted CVD. This includes the development of new measurement techniques and theoretical tools that can be used both for fundamental scientific studies and for improvements of CVD processes and equipment that can be transferred to industry.

Recent Highlights

- *In situ* growth rate monitors: A new method has been developed and implemented in a commercial CVD reactor to extract growth rates and optical constants from a thin film using *in situ* reflectance during chemical vapor deposition. This provides the first practical pre-growth calibration tool for chemical vapor deposition applications that serves the same function as reflection high energy electron diffraction (RHEED) does for molecular beam epitaxy. The method can be used on an arbitrarily complicated multi-layer substrate.
- *In-situ* Determination of the Surface Composition of InP Surfaces Treated in H₂/CH₄/Ar Plasmas: We have demonstrated that rf hydrogen plasmas can completely remove surface carbon and native oxides from InP surfaces. In addition, variation of the process parameters can be used to control the surface composition (stoichiometry) of the resultant surface from phosphorous depleted InP_{0.1} to phosphorous rich InP_{0.7}.
- New Insight into the Chemistry of SiO₂ Deposition from TEOS: We have combined quantum chemistry calculations with molecular beam experiments to show that in the deposition of SiO₂ from TEOS, TEOS decomposes via the beta-hydride elimination of ethylene, forming a reactive gas-phase intermediate that can have deleterious effects on deposition uniformity and step-coverage in CVD of thin dielectric films.
- Measurement of TEOS Surface Reaction Kinetics on SiO₂ at CVD Temperatures and Pressures: We have shown with FTIR and isotopic labeling that silanols play a pivotal role in SiO₂ deposition by participating directly in TEOS surface reactions on SiO₂ at CVD temperatures. TEOS reacts with Si-OH and Si-OD with equal rates, suggesting that the rate-determining step in chemisorption may not involve proton transfer.
- AlGaAs Surface Chemistry Explored: We have investigated and compared the surface chemistry of TMGa and TMAI on GaAs and AlAs(100). For TMAI on AlAs, the stronger Al-C bond manifests itself with higher CH₃ desorption temperature and significantly more CH₃ dehydrogenation (i.e. carbon doping). We have also shown that surface structure strongly affects the chemistry of TMGa on GaAs by comparing the decomposition of TMGa on the polar (100) and (111)A surfaces relative to the ideally terminated non-polar (110) surface.
- Enhancements to Chemkin software: We have expanded the capabilities of our Chemkin and Surface Chemkin software to include features needed in plasma modeling. Enhancements include specification of separate electron and gas temperatures if desired, multiple material types, non-integer stoichiometric coefficients or reaction orders for use with phenomenological reaction mechanisms.
- Development of Massively Parallel (MP) computer codes: BES CVD Science Project staff have collaborated with Sandia staff in High-Performance Computing to develop a massively parallel implementation of our finite element CVD codes. This work was recognized as a finalist in the 1994 Gordon Bell Prize competition.

Future Directions

We will pursue the development of new diagnostic tools to probe the details of deposition chemistry relevant to CVD, with our emphasis on *in situ* techniques to study molecular species reacting at surfaces. We will expand our knowledge base of chemical systems, including investigations of materials systems important for solar control coatings and photovoltaics. Applications of new diagnostic and computational tools will serve as the basis for developing first-principles models of the complex chemically reacting flows typical of CVD.

Interactions with DOE Technologies

In a collaboration with DP sponsored projects, we have implemented our BES-developed MOCVD rotating disk reactor technology on a production Aixtron MOCVD system and have demonstrated an order of magnitude improvement in film uniformity by growing AlAs/AlGaAs 650 nm distributed Bragg reflector (DBR) optoelectronics structures that were uniform to within $\pm 0.1\%$ over a two inch wafer. The Optical sensors developed in this program are being implemented on DP-funded growth chambers for producing devices.

Program Quality

- 1994 BES Award for DOE Related Technologies in Materials Chemistry
- 14 publications, 3 reports, 27 presentations, including 10 invited talks at national or international symposia.
- This work has led to 8 DP funded CRADAs and 2 ARPA funded program with industry.

**CVD Sciences
KC 02 03 03**

Publications

Work performed under BES Program

1. "The Surface Chemistry and Kinetics of Tungsten CVD and Selectivity Loss", J. R. Creighton, Thin Solid Films, 241,310, (1994).
2. "Accounting for Stoichiometry Changes on Compound Semiconductor Surfaces", J. R. Creighton, J. Crystal Growth, (in press).
3. "Surface Stoichiometry and the Role of Adsorbates During GaAs Atomic Layer Epitaxy," J. R. Creighton, Applied Surface Science, (in press).
4. "Theoretical Study of the Thermochemistry of Molecules in the Si-O-H-C System", P. Ho, and C. F. Melius, Journal of Physical Chemistry, (accepted).
5. "Comparison of BOH and SiOH Reactivities in Boron-Doped SiO₂ Chemical Vapor Deposition from Trimethyl Borate and Tetraethyl Orthosilicate", M. E. Bartram and H. K. Moffat, 40th National Symposium of the AVS, 11/15-19/93, Orlando, FL.
6. "Heterogeneous Reaction Mechanisms and Kinetics Relevant to the CVD of Semiconductor Materials", J. R. Creighton and M. E. Coltrin, SAND94-0033, 1/1994.
7. "SURFTHERM: A Program to Analyze Thermochemical and Kinetic Data in Gas-Phase and Surface Chemical Reaction Mechanisms," M. E. Coltrin and H. K. Moffat, SAND94-0219, 1/1994.

Work performed jointly with other programs, including DP/TTI supported CRADAs

8. "Spectral Reflectance as an In Situ Monitor for MOCVD", W. G. Breiland and K. P. Killeen, Material Research Symposium Proc. V. 324, (1994), p99.
9. "Kinetics of TEOS Surface Reactions on SiO₂ Between 765 K and 1200 K Studied with FTIR", M. E. Bartram and H. K. Moffat, Electrochemical Society Proceedings, Spring ECS Symposia, San Francisco, CA, May 1994, (in press).
10. "Experimental Measurements and Numerical Simulations of the Gas Composition in a Hot Filament-Assisted Diamond Chemical Vapor Deposition Reactor", M. C. McMaster, W. L. Hsu, M. E. Coltrin, and D. S. Dandy, Journal of Applied Physics, 76, 7567 (1994).
11. "Dependence of the Gas Composition in a Microwave Plasma-Assisted Diamond Chemical Vapor Deposition Reactor on the Inlet Carbon Source: CH₄ and C₂H₂," M. C. McMaster, W. L. Hsu, M. E. Coltrin and D. S. Dandy, Diamond and Related Materials, submitted for publication.
12. "Relationship Between Diamond Growth Rate and Hydrocarbon Injector Location in Direct-Current Arcjet Reactors", D. S. Dandy and M. E. Coltrin, Appl. Phys. Lett., scheduled to appear Jan. 21, 1995.
13. "Enhanced Chemical Vapor Deposition of Copper from (hfac)Cu(TMVS) using Liquid Coinjection of TMVS", G. A. Petersen, J. E. Parmeter, C. A. Applebitt, M. F. Gonzales, T. R. Omstead, J. A. T. Norman, and P. M. Smith, J. Electrochem. Soc., (accepted).
14. "Characterization of Thin Copper Films Grown via Chemical Vapor Deposition using Liquid Coinjection of TMVS and (hfac)Cu(TMVS)", J. E. Parmeter, G. A. Petersen, P. M. Smith, C. A. Applebitt, J. S. Reid, J. A. T. Norman, A. K. Hochberg, D. A. Roberts, and T. R. Omstead, J. Vac. Sci. Technol. B, (accepted).
15. "Chemical Additives for Improved Copper CVD Processing", J. A. T. Norman, D. A. Roberts, A. K. Hochberg, P. M. Smith, G. A. Petersen, J. E. Parmeter, C. A. Applebitt, and T. R. Omstead, Thin Solid Films, (submitted).
16. "Copper CVD using Liquid Coinjection of (hfac)Cu(TMVS) and TMVS", J. S. Custer, G. A. Petersen, Paul M. Smith, J. E. Parmeter, C. A. Applebitt, J. A. T. Norman, A. K. Hochberg, and D. A. Roberts, Advanced Metallization for ULSI Applications 1994, Materials Research Society, (accepted).
17. Final Technical Report for "Application of IRIS to Semiconductor Plasma Processing", (CRADA # 1031), SAND 94-2439, P. Ho, K. P. Killeen, C. F. Melius and R. J. Buss, 11/1994.

Synthesis and Processing of Nanoclusters for Energy Applications

KC 02 03 03

Principal Investigators: J. P. Wilcoxon, J. E. Martin, D. Bliss, P. P. Newcomer, E. Venturini, G. A. Samara and T. R. Thurston (BNL).

Goal: Develop synthetic and processing methods for producing chemically pure, highly crystalline metal and semiconductor nanoclusters with controlled sizes. Investigate the physical properties of these nanoclusters of importance to energy applications such as catalysis.

Recent Highlights:

BES funding for this work started in mid FY94. The following results were obtained jointly with LDRD-funded research which terminated at the end of FY 95.

- The inverse micellar synthetic process was used to produce size-selected clusters of Fe, Pd and metal sulfides of Pb, Fe and Mo.
- The first core-shell nanoclusters of semiconductors coated with metals of were synthesized (PbS/Au and FeS₂/Pd). Enhancements of visible absorbance were observed well beyond the intrinsic bandgap of the semiconductor core while the excitonic features of the semiconductor were maintained, but blue shifted slightly. Coating of FeS₂ with Pd removed its oxygen sensitivity for the first time opening a range of new applications for this inexpensive, non-toxic semiconductor material. Dramatic changes of the photoluminescence properties of PbS/Au compared to PbS of the same size were observed, showing our ability to adjust the electronic properties of these new materials at the molecular level.
- Novel characterization and processing methods based upon chromatographic separation of the clusters from the byproducts of the chemical synthesis were developed and used to examine the inherent absorbance and photoemission properties of MoS₂ and Pd clusters. Size-exclusion chromatography was used to examine the cluster size and size distribution and to obtain purified cluster samples suitable for other physical measurements such as light scattering.
- It was discovered that the chemical type of surfactant micelle used to grow iron clusters could be used to control the crystallographic structure of the nanocluster and both nanosize γ and α -Fe clusters could be produced. Nanosize γ -Fe had not been produced previously. High resolution microscopy was used to demonstrate complete crystallinity in both types of iron with no annealing above room temperature required.
- The magnetic properties of α -Fe clusters with sizes between 1.4 and 15 nm in diameter were studied in a SQUID magnetometer as a function of cluster size, temperature and applied magnetic field. The blocking temperature, coercive field and remanent moment of 12.5 nm Fe clusters in inverse micelles were found to be significantly lower than those reported for clusters of similar α -Fe core size but with a surface oxide, while 3.7 nm clusters had a significantly larger blocking temperature than predicted theoretically. The first studies of the magnetic behavior γ -Fe demonstrated qualitatively different behavior compared to α -Fe of the same size.
- The size-dependent bandgaps of nanosize MoS₂ and FeS₂ were investigated and a clear transition from solid-like to molecular-like behavior was observed and analyzed in terms of the features observed in the bulk.

Future Directions:

Now that the synthetic, processing and characterization methods for a number of interesting nanocluster materials have been developed, we will perform dielectric, magnetic, optical and catalytic measurements on purified nanoclusters to determine the inherent properties of the clusters and the effect of the embedding medium and passivating agents on their properties. Particular emphasis will be placed on the photocatalytic and catalytic properties of MoS₂, FeS₂ and Fe nanoclusters since this is the area we believe will have the greatest impact on DOE interests.

Interactions with DOE Technologies

This program interacts with Fossil Energy's coal catalysis program (PETC). Defense Programs supports complementary efforts related to potential device applications and on potential use of inverse micelles for environmental remediation.

Program Quality/Interactions

- 6 publications, 9 presentations
- Collaborative Research with Colorado State University and with BNL on hydrogen storage in nanoclusters.
- Program participates in S&P Center Project on Nanoscale Materials for Energy Applications.

Synthesis and Processing of Nanoclusters for Energy Applications

KC 02 03 03

Publications

Performed Jointly with LDRD Funding

1. "Optical Properties of Lead Sulfide Nanoclusters: Effects of Size, Stoichiometry and Surface Alloying", D.E. Bliss, J.P. Wilcoxon, and G. Samara, Proceedings of Symposium F, meeting of the MRS Society, Boston, MA., (1994).
2. "Optical Features of Nanosize Iron and Molybdenum Sulfide Clusters", J.P. Wilcoxon, G. Samara, and P. Newcomer Proceedings of Symposium F, meeting of the MRS Society, Boston, MA., (1994).
3. "Strong Quantum-Size Effects in a Layered Semiconductor: MoS₂ Nanoclusters", J.P. Wilcoxon and G.A. Samara, Physical Rev, Rapid Comm., accepted, (1994).

Performed Jointly with Fossil Energy and LDRD Funding

4. "Magnetic Properties of Nanosize Iron Clusters", Venturini E.L., Wilcoxon J.P., and Newcomer P.P., Symposium V, Proceedings of the Spring Meeting of the Materials Research Soc., San Francisco, CA. (1994).
5. "Synthesis and Characterization of Fe and FeS₂ (Pyrite) Coal Liquefaction Catalysts in Inverse Micelles", A. Martino, J.P. Wilcoxon, and J. Kawola, Energy and Fuels, in press (1994).
6. "Synthesis and Catalytic Properties of Metal and Semiconductor Nanoclusters", Wilcoxon J.P., Martino T., E. Klavetter, and Sylwester A.P., in Nanophase Materials, ed. G. Hadjipanayis and D. Siegel, Kluwer Acad. Pub., 770-780, 1994.

Distribution

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Internal

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0360	1000	A.R.C. Westwood
0320	1010	P.L. Mattern
0336	1100	R.J. Eagan (5)
0349	1102	S.T. Picraux
0346	1103	G.A. Samara (8)
1056	1111	B.L. Doyle
0350	1112	S.M. Myers
0350	1112	E. Chason
0344	1114	T.A. Michalske
0344	1114	G. Kellogg
0601	1126	P. Esherick
0601	1128	G.N. Hays
0345	1153	D. Emin
0345	1153	E.L. Venturini
0350	1155	G.C. Osbourn
1079	1300	P.S. Peercy
0603	1311	J.Y. Tsao
0609	1841	A. Hurd
1349	1708	R.E. Loehman
0337	1800	A.D. Romig
0339	1802	G.E. Pike
0724	6000	D.L. Hartley
0725	6908	J.S. Binkley
0100	7613-2	Document Processing (10) for DOE/OSTI
9163	8302	W. Bauer
9161	8341	W.G. Wolfer
9056	8355	G.A. Fisk
9018	8523-2	Central Technical Files
0619	12613	Print Media (1)
0899	13414	Technical Library (5)