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PROGRESS REPORT FOR FY 1993 and RESEARCH PROPOSAL FOR FY 1994

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Materials Research Laboratory
University of Illinois at Urbana-Champaign

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B. GENERAL PROGRAMMATIC AND INSTITUTIONAL ISSUES

B.1 LABORATORY MANAGEMENT STRUCTURE

General Description

The Materials Research Laboratory at the University of Illinois is an interdisciplinary laboratory operated in the College of Engineering. Faculty associated with the Materials Research Laboratory are members of the Departments of Physics, Materials Science and Engineering, Chemistry, Chemical Engineering, Electrical Engineering, Mechanical Engineering, and Nuclear Engineering. Support for the intellectual program of the Materials Research Laboratory is obtained from Grant DEFG02-91ER45439 with the Department of Energy, from Cooperative Agreement DMR-89-20538 with the National Science Foundation, from a National Science Foundation Science and Technology Cooperative Agreement in Superconductivity, and from supplementary funds from the University of Illinois.

Howard Birnbaum acts as the Director of the Materials Research Laboratory and has the status of a Department Head in the Engineering College. In this position he has oversight responsibility for both the DOE and the NSF programs and supervises the Central Facilities of the MRL. The programs of the MRL are under the technical leadership of H. K. Birnbaum for the DOE Metals and Ceramics Program, T.-C. Chiang for the DOE Solid State Sciences and Materials Chemistry Program, J. Wolfe for the NSF/ MRL Program and M. Klein for the University of Illinois part of the NSF S&T Center Program. The Executive Committee of the laboratory consists of H. Birnbaum, T.-C. Chiang, J. Wolfe, and M. Klein and has the responsibility for advising the Director of the MRL on the general policies and needs of the Laboratory. The Director of the MRL coordinates its needs and opportunities with the relevant Department Heads; D. Campbell of Physics, J. Jonas of Chemistry, J. Economy of Materials Science and Eng., T. Trick of Electrical Eng., T. Addy of Mechanical Eng., H. Aref of Theoretical and Applied Mechanics, and B. Jones of Nuclear Eng. An external advisory committee of prominent scientists is being appointed to evaluate the DOE programs and to advise the Director on the overall function of the MRL.

B.2 PROGRAM REVIEW ACTIVITIES

The MRL/DOE program information meeting was held in the spring of 1992 at Oak Ridge National Laboratory in conjunction with that of Argonne National Laboratory, Ames National Laboratory, and Oak Ridge National Laboratory.

The individual programs are in the process of being reviewed by the DOE Office of Program Analysis. To date no unresolved issues or difficulties have arisen as a result of these reviews.

In addition to the laboratory review, each program is periodically reviewed by selected external reviewers. The Principal Investigators are asked to prepare a program statement, a publication list with the DOE supported publications marked, copies of five publications from the past five years which they considered to be most significant, a list of graduate students who received degrees while supported by the DoE, and a statement of the important directions of the program, its significance, and new directions being undertaken. The responses from the reviewers, the evaluations of the External Review Committee, and the assessment of the program by the Program Head and by the Director are used to form an evaluation of the program.

B.3 OVERALL GOALS OF THE D.M.S. PROGRAM

The goals of the Department of Energy, Division of Materials Sciences program at the Illinois Materials Research Laboratory can be succinctly stated as:

a. Development of the highest quality research program in the areas of science and engineering which underlie the energy systems of the U.S.

b. Education of scientists and engineers at the Ph.D. and Post-doctoral level who are skilled in the areas of science and engineering essential to the development and maintenance of the energy systems of the U.S.

c. Mutually supportive interactions with US industry in the areas of technology transfer and continuing education.

The Department of Energy program at the MRL has many of the best aspects of the DOE Laboratory Program and the DOE University Program. DOE support allows development of a unique combination of creative University faculty directed programs interfaced with Central Facilities. Central Facilities allow development and maintenance of major, expensive equipment to be combined with an excellent group of professional scientists who maintain, operate, and develop these instruments, as well as teach their use and the science associated with them. The flexible support of the DOE program allows best utilization of the available funding through local management which can recognize and optimize scientific opportunities.

The MRL program is about 30% of the total Materials Science and Engineering effort on the University of Illinois campus. It can choose the best of the available programs, support them at an effective level, and focus their efforts on problems of great importance to the Department of Energy. In recent years, we have attempted to balance the excellent single investigator programs with programs requiring a grouping of research efforts, each of which complements the others in a correlated investigation of complex problems.

Coordinated efforts are being carried out in the areas of Structural Ceramics, Grain Boundaries, Field Responsive Polymeric and Organic Materials, The Molecular Structure of Solid-Liquid Interfaces and Its Relation to Corrosion, and X-ray Scattering Science. These coordinated efforts bring together the research programs of individual faculty groups which have a common theme and interest and foster the interactions between them.

B.4 PROGRAM DIRECTIONS AND CHANGES IN DIRECTIONS

Program and Staff Changes

Despite the very severe financial constraints placed on the MRL / DOE program by the constant dollar budgets of recent years, it is absolutely imperative that new scientific directions be initiated. In FY 1992 we have been able to begin some of the exciting new programs which have been made available to the MRL by the addition of new faculty to various departments of the University. In a number of cases the MRL, using non-DoE funds, has played a leading role in attracting these faculty to the University of Illinois. We have been able to begin to support some of these programs, but at a level which is not adequate to the opportunities. This has been possible <u>only</u> by limiting the development of other programs.

In FY 1992, the MRL managed to make several significant additions to its DOE program. Ian Robinson, who joined the Physics Department from Bell Laboratories in the fall of 1992, began a program using synchrotron radiation to study surface phenomena. Petros Sofronis who joined the faculty of the Theoretical and Applied Mechanics Department began a program which is modeling the mechanics of deformation and fracture of a variety of systems. David Cahill, who joined the Department of Materials Science and Engineering, began a program which studies the microscopic aspects of crystal growth. S. Lance Cooper, who joined the Physics Department, has begin a program which studies the properties of magnetic semiconductor epilayers and heterostructures.

The MRL began a small program on Radiation Effects in Solids using funds obtained from non-DoE sources in FY 1992. Funds for the continuance of this program have now been obtained from the DOE and we look forward to the flourishing of this program.

We have added a new engineer, Doug Jeffers, who is skilled in the maintenance and operation of MBE. equipment and who will assist in the operation of the EpiCenter.

Helen Farrell has joined the staff of the Center for the Microanalysis of Materials to provide leadership for the Surface Analysis / Microchemistry group.

Proposed New Programs

In the next year, our highest priority new program is the New Initiative On Understanding Fuel Cell Catalysis Using Surface NMR-Electrochemistry, Vibrational Spectroscopies, scanning Probe Microscopies, and Synthetic Methods. (Section C.1).

An interesting development of the program on the Molecular Properties of the Solid-Liquid Interface and Their Relation to Corrosion is proposed in Section C.2.a. The proposed expansion of this program is strongly supported by the MRL.

We received the funding for the construction of the APS beam lines beginning in FY 1993 and the design and construction program is underway. A part of the proposed program was for funding of the underlying synchrotron based research on new and novel materials and characterization techniques. Funding for these efforts was not available. Some of the core efforts have been supported by discretionary funds available to the MRL but this source of funding is not able to sustain an effective effort. We are requesting funding for the program on Synchrotron Based Science of New Materials to allow us to develop the science as well as the instrumentation for the APS effort (Section C.2.b).

In response to the national interest in Synthesis and Processing and New Materials, we have re-developed our proposal to study the synthesis and processing of nanophase metallic and ceramic systems and the properties of these systems. This proposal is outlined in Section C.2.c. This program has the strong support of the MRL. Nanophase solids is the area we have chosen to develop within the Sandia managed Center for Synthesis and Processing and is one which we would like to expand our efforts in.

Additional exciting new individual investigator research opportunities have been presented to the MRL by several new, young faculty additions (Section C.3). These have been reviewed and selected from a much larger number of proposals received by the MRL during the past year. All are considered to be of high quality.

Since many dynamic systems are limited by lubrication of moving parts, it is critical that we understand the major issues of tribology. These are basically issues of surface chemistry and physics. Granick proposes to study the tribology of complex liquids and additives at the molecular level. The systems chosen are relevant to lubrication at high pressures (Section C.3.a).

Professor A. Hubler is proposing to study the behavior of complex materials and material systems using a nonlinear science approach. this program (Section C.3.b) proposes to apply both an experimental and a theoretical approach to these very complex but important problems.

Professor D. Campbell is proposing a theoretical study of the "Field-Responsive Effects in Conducting Polymers and Organic Charge Transfer Solids".

Professor I. Masel of the Chemical Engineering Department has developed new methods for the understanding of how the surface chemistry determines the film properties during CVD growth of advanced materials and would like to begin a DOE program in this subject (Section C.3.d).

Professor D. Viehland of the Materials Science and Engineering Department is interested in new ferroelectric relaxor materials and in their processing to optimize their utility as sensors, actuators and "smart" materials (Section C.3.e).

C. STATEMENT OF CAPITAL EQUIPMENT NEEDS

Central Facilities play a very important part in the function of the Materials Research Laboratory. The Materials Research Laboratory spends about 30% of its total budget for development and maintenance of its Central Facilities, with the financial responsibilities divided between the DOE, NSF, and STC programs in proportion to use. Due to the importance of these Central Facilities to the DOE program, our Mid-year Request for FY 1993 is for an equipment item for the Center for the Microanalysis of Materials. During FY 1992 we received partial funding for the purchase of a Field Emission Scanning Transmission Electron Microscope. Funds to complete the purchase of this microscope remains the highest priority request for Mid-year 1993.

The MRL has operated an HB-5 STEM for the past 16 years, during which period it has proven to be invaluable for many of the DOE research programs. It allows microanalysis with a spatial resolution of the order of 2 nm as well as microdiffraction over similar volumes. This instrument no longer functions at a level compatible with first class research and needs replacement with a modern instrument; several of which have recently become available.

The new instrument would have a 300 keV field emission source and the capability for microanalysis, microdiffraction and high resolution imaging. The vacuum capabilities in the specimen chamber region will be in the 10^{-10} torr range, thus allowing analysis without contamination from gas adsorption and film growth. Parallel EELS and windowless EDX analytic capabilities will be required. A wide angle detector for "Z contrast imaging" will be required, as will the capabilities for carrying out holographic electron imaging and electron diffraction correlation spectroscopy, both of which will utilize the coherence of the electron source.

The estimated cost of this instrument is $2,500,000 in FY 1992 dollars.

C.1. MAJOR EQUIPMENT NEEDS

In the following sections we outline our needs for major capital equipment items for the next few years. These needs are not possible to meet by use of the normal project funds. The following section describes the needs of the Central Facilities; principally the Center for the Microanalysis of Materials (CMM). The costs specified are the proportionate share for the DOE based on anticipated usage. The MRL/NSF, MRL/S&T, and University of Illinois contributions will be used to complete the purchases.

FY 1994

300 kV STEM

The 300 kV STEM electron microscope described above would be purchased in this fiscal year if the funds are available.

The total funds needed from all sources is $2,500,000.

Center for the Microanalysis of Materials

EpiSEM

The extensive capabilities of the MRL EpiCenter for the growth of new and novel materials and combinations of materials have given rise to a very exciting set of questions concerning the structure and chemistry of the interfaces in layered material. We propose to develop an instrument, the EpiSEM, based on a UHV scanning electron microscope, to investigate some of these issues. This instrument will involve design concepts developed in the CMM and will incorporate capabilities not yet available in commercial instruments. The scanning electron microscope beam will be used in a surface reflection mode to allow imaging of surface atomic steps as well as the structure below the surface. Bulk specimens as well as thin films could be studied. The UHV capabilities of the instrument will make it compatible with the growth chambers of the EpiCenter thereby allowing the EpiSEM to be installed on one of the transfer tubes. This would allow real time studies of crystal growth under conditions where the chemistry of the interfaces can be controlled. If this instrument is developed it is expected that it will have significant commercial potential.

The cost for developing this instrument will be $600,000.

FY 1995

Center for the Microanalysis of Materials

Computerization of Data Acquisition and Analysis

The next major advance in the development of instrumentation for electron microscopy is the quantification of data acquisition and analysis. This will require data acquisition in a high resolution digitized manner. During the period of FY 1995 we need to develop the instrumentation and techniques to acquire TEM images and analyze them in a digital mode. Instrumentation for doing so will be available in this time frame.

The estimated cost for carrying out this program will be $ 350,000.

Center for Computation

We will require a significant upgrade of the computational facility of the MRL in this time period. The MRL has developed a highly effective, decentralized system which utilizes RISC workstations and integrated access to programming and file handlers. The next step in our orderly program will be to upgrade the quality of our workstations and the central file storage and management systems.

The estimated cost (DOE share) for this upgrade is $ 400,000.

Molecular Beam Epitaxy Center - EpiCenter and the Center for the Microanalysis of Materials

Ion Accelerator

An increasing amount of microanalytic and microstructural studies is being carried out in the CMM using ion beam methods. The specimens for these studies are often grown in the EpiCenter using MBE, MOCVD, and other vapor phase methods. Analysis of these specimens can yield quantitative information about the structure and chemistry of surfaces, interfaces, and the bulk. In may cases the analysis requires that the specimens be examined *in situ* during growth and without exposing the specimens to ambient. At present we utilize a modified Van de Graff accelerator which was installed in the CMM in 1965. This precludes *in situ* analysis during growth and requires that the specimens be exposed to ambient for transport to the CMM from the EpiCenter.

A new, modern ion accelerator is badly needed to allow continuation of these studies and to allow an expansion of technique development in this area. It will be located in the new MRL space below the EpiCenter and will allow ion beams to be directed to the growth chambers for *in situ* studies. In addition to its use for analytic studies, this instrument will be extensively used for radiation effects studies with specimens prepared by the Molecular Beam Epitaxy Center. Operation of this instrument will be a joint effort between the CMM and the EpiCenter staff.

The estimated cost for purchasing this instrument is $ 600,000.

C.2 ISSUES

The major budgetary issues arise because of the significant opportunities presented to the MRL DOE program by new faculty additions, by the continued development of the Center for the Microanalysis of Materials as a premier research instrumentation facility, and by the opportunity to engage in the development of the Advanced Photon Source Facility at Argonne National Laboratory.

Our highest priority new program is the New Initiative On Understanding Fuel Cell Catalysis Using Surface NMR-Electrochemistry, Vibrational Spectroscopies, Scanning Probe Microscopy and Synthetic Methods. This is discussed in Section C.1.

We have begun the development of the UNICAT APS beamline program in cooperation with ORNL, Allied-Signal Corp. and UOP Corp. as described in our previous executive summary and in discussions with the DOE. The DoE funding which began in FY 93 is critical to this effort. Funding for the underlying program of Synchrotron Based Science of New Materials is still problematical as we have not located the funds to provide this program with ample ongoing research support. Most of the effort is being funded with MRL discretionary funds which are in increasingly short supply. A proposal for support of this research areas is included in Section C.2.b.

We also discuss additional individual P.I. program possibilities in Section C.3. The programs described have been pre-selected from a considerably larger number and are all considered to be of very high quality.

In a somewhat different category, we offer an expansion of our present program on Solid-Liquid Interfaces to a more comprehensive study of corrosion at solid-liquid interfaces on a molecular level (Section C.2.a)

Program Additions

In FY 1992, the MRL managed to make several significant additions to its DoE program. Ian Robinson, who joined the Physics Department from Bell Laboratories in the fall of 1992, began a program using synchrotron radiation to study surface phenomena. Petros Sofronis who joined the faculty of the Theoretical and Applied Mechanics Department began a program which is modeling the mechanics of deformation and fracture of a variety of systems. David Cahill, who joined the Department of Materials Science and Engineering, began a program which studies the microscopic aspects of crystal growth. S. Lance Cooper, who joined the Physics Department, has begun a program which studies the properties of magnetic semiconductor epilayers and heterostructures.

Central Facility Needs

Central Facilities play a major role in the functioning of the Materials Research Laboratory. They provide a focus for many of our research programs, allow flexibility in the programs' abilities to respond to changing research needs, educate a very large number of graduate students and Research Associates in the application and use of modern research tools, and make a very efficient use of research funds for support of instrument intensive modern research endeavors. The plans for development of the Center for the Microanalysis of Materials have been presented to the DoE and these remain of primary interest to us.

Building Construction

The MRL has obtained State of Illinois funds to construct a three story building between the present MRL building and the Coordinated Science Laboratory Building which lies to the north. The CSL Building has become available to the MRL for its research activities. This will greatly enhance our programs, as it will allow almost all of the MRL activities to be housed in contiguous space; thus increasing the interactions between research groups.

The MRL has obtained a grant from the Department of Education which will provide the funds for renovation of the added space in the present CSL building and which will allow completion of the basement of the interpass to suit the needs of the Center for the Microanalysis of Materials.

FUEL CELL CATALYSIS BY SURFACE NMR-ELECTROCHEMISTRY, VIBRATIONAL SPECTROSCOPIES, SCANNING PROBE MICROSCOPIES AND SYNTHETIC METHODS

A.A. Gewirth, R.J. Kirkpatrick, R. Nuzzo, E. Oldfield, M. Weaver, and A. Wieckowski

I. Work Package Description

The focus of research in this proposal is to study the structural , molecular, and dynamic features of fuel cell catalysis. The scope of research includes: microscopic chemical characterization of catalysts that are currently considered for automotive fuel cell applications, characterization of solid-state and molten electrolytes used in fuel cells, synthesis of new electrode catalyst materials for fuel cell applications, and correlation of structure with dynamic events on these materials. The initial research will utilize an array of powerful techniques of surface characterization including *in situ* NMR-electrochemical, vibrational and AFM (STM) techniques. These methods will provide detailed information on the structure of bare and poisoned catalysts, and on surface diffusion of adsorbates. Electrokinetic measurements will augment the above, in order to examine reactivity on these electrodes. Solid and molten electrolytes, which are important in real fuel cells, will be characterized by advanced NMR techniques in order to understand dynamics of ion transport in these systems. The insights from the characterization studies will be used to synthesize new catalyst and electrolyte materials.

II. PURPOSE

The purpose of this program is to improve our understanding of the basic sciences which underlie the performance of fuel cells. Specific issues to be addressed are: electrocatalyst structure, small molecule binding, catalyst poisoning and degradation, synthesis and processing of new catalyst materials, solid and molten electrolyte structure, H_2 and O_2 oxidation/reduction mechanisms, and reformer catalyst characterization. Improved understanding of these phenomena will contribute strongly to the development of new practical fuel cell materials.

Fuel cells offer considerable promise for future use in energy applications, both space and terrestrial, since they operate efficiently, are capable of running on a wide range of non-petroleum fuels, and have almost no NO_x, S, or particle emissions. Because they are more efficient, they have the potential of greatly reducing CO_2 emissions and other greenhouse gasses.

Despite this promise, there are several aspects of fuel cell catalysis which lead to less than optimal performance. Only H_2 has been used as a fuel. Other potential fuels, such as methanol and ethanol, must be reformed to H_2 before use, which requires installation of heavy, expensive equipment. If methanol or ethanol are used directly, the fuel cell catalyst is quickly poisoned and reactivity stops. This precludes utilizing these more easily transportable liquids for automotive applications. There is also a relatively poor understanding of the events occurring on fuel cell electrode surfaces and in the electrolyte around the catalyst. Finally, real catalysts use substantial quantities of precious metals which can make fuel cell costs prohibitive. More fundamentally, there is relatively little information about the primary molecular processes involved in fuel cell catalysis.

While many of the questions surrounding fuel cell catalysts have been intensively studied for many years, recent dramatic advances in characterization techniques are making complicated problems tractable. Previous work in fuel cell science has utilized classical techniques which provide an overview of surface structure and reactivity, but relatively little *in situ* detail at the molecular level. This lack of detail has greatly hindered subsequent efforts at understanding processes occurring on fuel cell electrode surfaces. New techniques utilized in this work include: Surface NMR-Electrochemical spectroscopy, Electrochemical AFM (and STM) imaging techniques, vibrational and ultra-high vacuum spectroscopies and electrochemistry. Together, these methods enable a comprehensive, detailed picture of the primary events in fuel cell electrocatalysis.

The insight derived from catalyst and system characterization will be used as a guide to prepare new alloy- and chemically-modified electrode materials. We focus specifically on preparation of novel Cu-oxide and silicate materials and on formation of well-defined mixed-metal materials.

In the first portion of the program we will characterize at a fundamental level materials currently used in fuel cells. Catalyst materials which show the highest promise in automotive fuel cells applications include: Pt, Rh, Ir, Ru, Sn, Cu composites, alloys of Pt, and Ru and Ir oxides. Gewirth will study the atomic structures of bare and alloy-modified electrocatalyst surfaces by using electrochemical AFM (and STM). Utilizing electrochemical NMR, Wieckowski and Oldfield will examine the structure of small catalytically active particles as well as catalyst-support interactions. They will also invesitgate the effects of catalytic promoters on the metallic/catalytic properties of platinum and rhodium microparticles. Regarding fuel cell electrolytes, Kirkpatrick has considerable expertise investigating carbonate materials, and will study carbonate melts and molten oxide materials. Oldfield will use NMR methods to study of *solid electrolyte* fuel cells with particular focus on mechanisms of ionic conduction in the solid oxide crystal lattice. There are many advantages associated with use of solid electrolyte fuel cells - for example, since there are no liquids present, maintenance of stable 3 phase interfaces and pore flooding problems are absent, and moreover, this type of cell appears particularly promising for use in coal gasification. Oldfield will also study the heterogeneous catalysts used in reforming reactions for commercial production of hydrogen for fuel cells.

A crucial component of the proposed thrust involves the identification and characterization of adsorbed species present under working electrocatalytic conditions that can partake in the reactions of interest either as intermediates and/or poisons. Wieckowski has recently demonstrated, for the first time, that ^{13}C nuclei of the adsorbates on fuel cell catalysts can be observed directly, and that the electrode potential inside the cell can be controlled from an external power source during NMR measurements. In addition to studying fuel cell catalysts Wieckowski, Oldfield and Kirkpatrick will study surface diffusion, small molecule binding sites and surface chemical bonds using the surface NMR-electrochemical approach. Wieckowski will also use electrochemical techniques to obtain rate data in order to dynamically characterize the reacting fuel cell systems. Gewirth will use AFM and STM to characterize of the initial molecular events in small molecule oxidation and reduction on fuel cell materials. The probe microscopy will be used to elucidate the initial sites of poison formation on electrode surfaces and to monitor the progress of poison growth. Weaver will apply surface Raman and infrared spectroscopies to the *in situ* vibrational characterization of adsorbates on working electrocatalytic surfaces, along with evaluation of the electrochemical kinetics. These studies will enable us to derive relationships between the structure of the fuel cell catalyst-small molecule complex and the reactivity of this system. That is, they will provide, for the first time, a crucial link between rates, electrolytic environment and the substrate geometry in the type of catalysis concerned in this proposal. The quantitative identification of this link is anticipated to be of primary importance.

In the second portion of the program, the insight obtained from electrode and electrode process characterization will be utilized to aid in synthesis of advanced catalytic materials. Nuzzo will emphasize two specific areas: the development of improved electrode materials for methanol fuel cells and study of the electrocatalysis of oxygen reduction. He will focus on new classes of materials which have been only minimally studied for fuel cell applications. One emphasis will be copper oxides catalysts which might be expected to show interesting and perhaps useful properties towards the electroreduction of dioxygen. Gewirth and Nuzzo will synthesize new alloy materials based on the insight derived from the characterization effort.

A cohesive mutidisciplinary research base is essential for fundamental studies of the fuel cell catalyst systems. The various interactions and perspectives outlined in this proposal show promise for creating new interconnections in the study of fuel cell catalysis. A rich harvest of imaginative new technological advances can be expected as a consequence.

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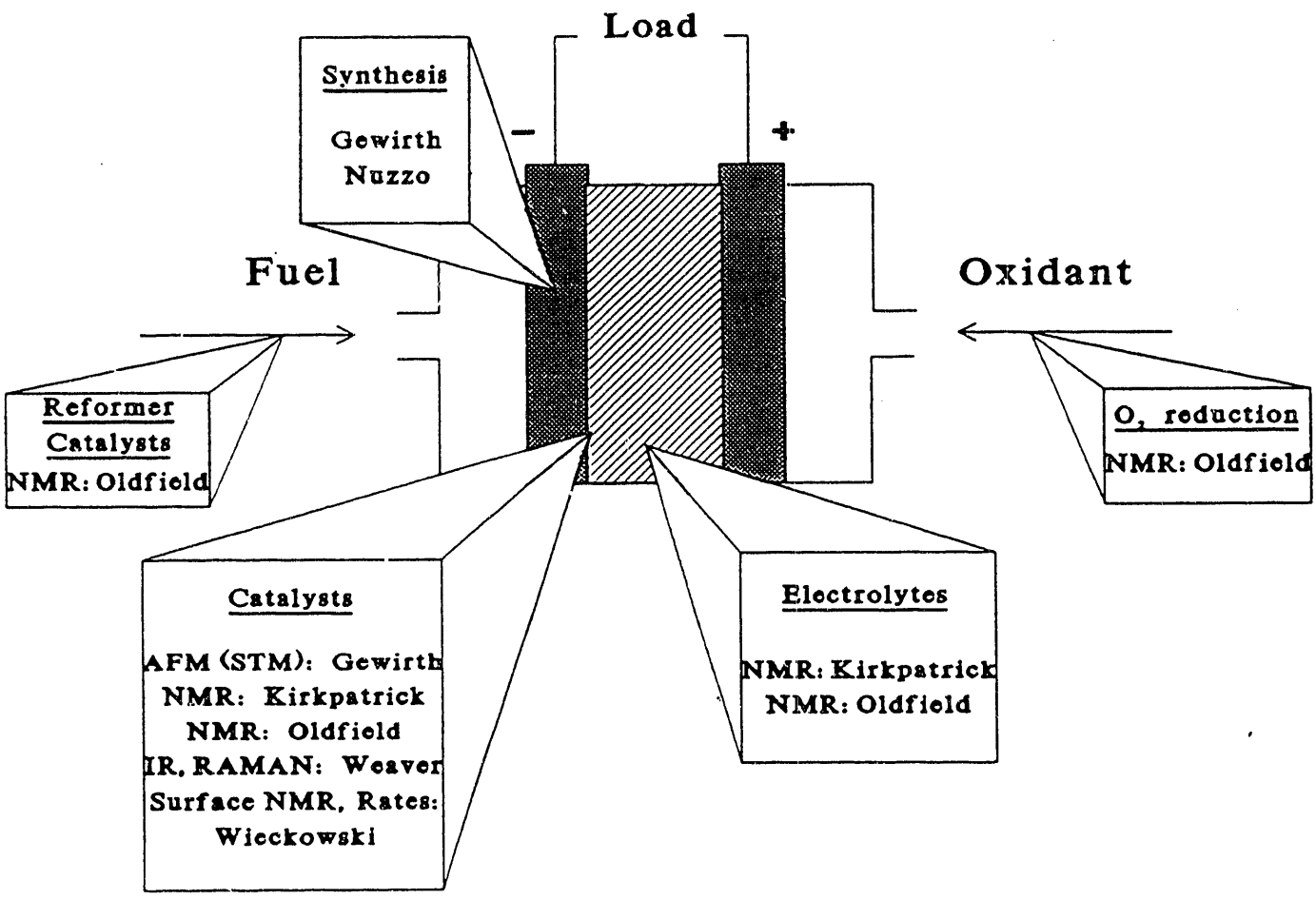
A Fuel Cell and Fuel Cell Catalysis Thrust



III. INDIVIDUAL CONTRIBUTIONS

Catalyst Structure and Reactivity

Andrew A. Gewirth

The focus of proposed research is to utilize advanced microscopic techniques to study processes occurring on materials and surfaces relevant to fuel cells. We have demonstrated that significant insight into structure and reactivity of electrode surfaces can be obtained by using the Atomic Force Microscope (AFM) and Scanning Tunneling Microscope (STM) [1]. We focus here, on the development and characterization of alloy materials utilized as advanced fuel cell catalysts, on obtaining insight into the structure and defects existent on highly dispersed catalytic microparticles, and on the characterization of the initial molecular events in small molecule oxidation and reduction on fuel cell materials.

In the first area, we propose to examine, at the atomic level, structural consequences of methanol and formate oxidation on bare and alloy-modified electrode surfaces. We will examine changes occurring on the surface as reactivity proceeds by using the STM and AFM in the electrochemical environment. Oxidation of CH_3OH and HCOOH on pure, bare Pt surfaces proceeds with the formation of a strongly bound intermediate which poisons subsequent reactivity. There is also a substantial (700 mV) overpotential required for reactivity to occur. Alloying of an oxophilic element with Pt considerably improves the resistance of the catalyst to this poisoning and decreases the overpotential, presumably because the oxophilic element provides additional oxidation equivalents. However, the role of the alloying element in Pt , the uniqueness of the Pt based alloys, and the necessity for Pt is really not understood. In addition, it is not known how the poisoning species grows on the electrode surface. An understanding of this mechanism, and of how and where the poison initiates on the surface could provide insight into ways of preventing its formation. The poison also exhibits substantial structural sensitivity on the low Miller index faces of Pt, which suggests that specific sites are required to nucleate the poisoning process. In particular, the (111) surface exhibits greatest resistance toward poisoning, while the (110) and (100) surfaces are substantially more sensitive. This may mean the poisoning on the (111) surface initiates at steps and defects which show the atomic stacking of the other faces.

We propose experiments to investigate poison growth on electrode surfaces. We will oxidize formate and methanol on Pt(hkl) surfaces in acid environments. The growth of the poison should proceed differently on the different Pt faces. This should provide a direct correlation of atomic structure with reactivity, a necessity in understanding the oxidation processes that occurs in fuel cells. The intermediate should be readily observable by both STM and AFM. With the AFM, it is reasonable to expect atomic resolution on clean Pt surfaces, because this is what has been observed on every other metal we've studied. The poisoned surface may exhibit a disordered amorphous texture, but the distinction between this and bare Pt should be clear. The growth of the deposit may perhaps be better monitored by STM, because the STM is sensitive to defects which may be the poison nucleation sites. While atomic resolution may not be available with the STM on these surfaces, monitoring the effective barrier height to tunneling, di/ds, while scanning should provide information about the defects which are the initial nucleation sites. We have used this detection method previously to investigate the growth of amorphous oxides on graphite [2].

Alloy modified surfaces exhibit substantially increased resistance to poisoning, ostensibly because the oxophilic alloy enhances oxidation of poisons. We will use the STM and AFM to examine the microstructure of Rh-Pt and Ir-Pt alloys. These materials will be synthesized in collaboration with Nuzzo. In particular, we will ascertain whether these surfaces are significantly more defected than surfaces fabricated from the pure elements. We will quantify the types of terraces, steps, and kinks existent on these materials and determine if surface segregation of the alloy occurs. Because the alloy is likely to be highly oxided, conductivity on this surface may be somewhat diminished relative to bare metals, and AFM measurements, which do not rely on current flow, will be utilized. We have shown previously that the AFM can distinguish structural differences on catalyst surfaces. In Fig. 1, we show AFM images of a bare and Bi monolayer-modified Au(111) electrode [3]. The

modified surface -- a (2x2)-Bi overlayer -- acts as a catalyst for electroreduction of H_2O_2 to H_2O. Our direct, *in situ* observation of this catalyst structure represents the first time this has been accomplished in the electrochemical environment. We also have shown that the AFM can image kinks and monatomic steps [4]. Because the alloy-modified surface is more resistant to poisoning, growth of this inhibitor should be different from what occurs on unmodified surfaces, and we will compare poison growth between the two. Growth of the poison species, monitored by the probe microscopy, will be compared with results obtained by *in situ* NMR measurements to be performed by Wieckowski. These experiments should provide insight into synthetic directions necessary to make stable fuel cell electrode materials.

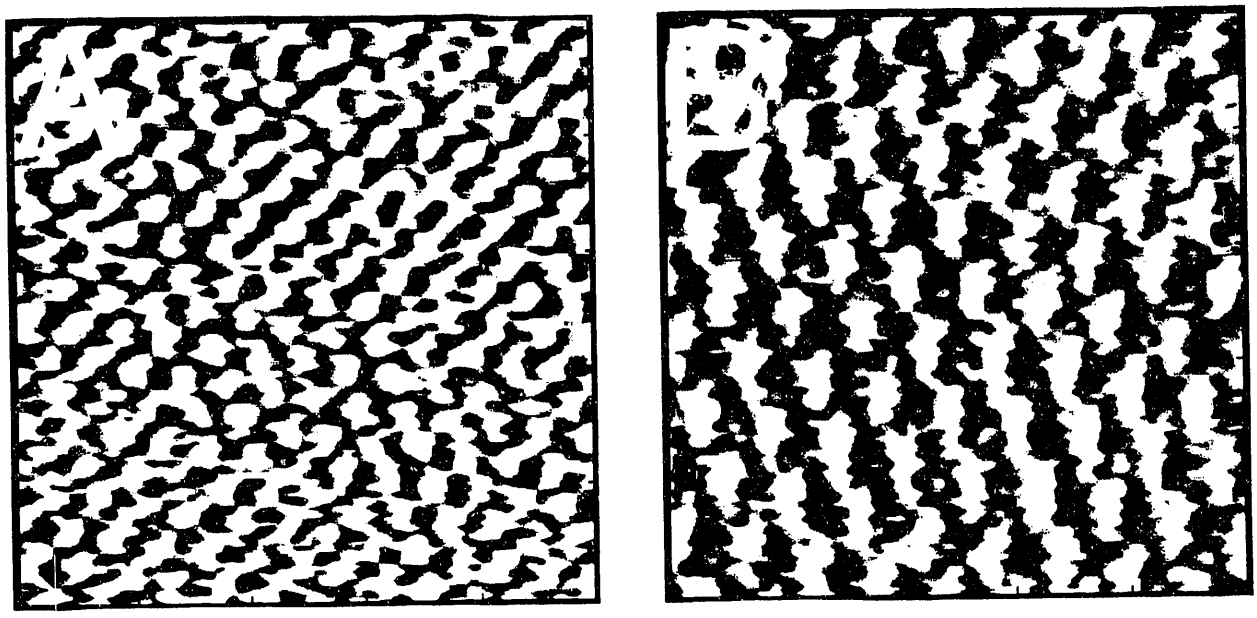


Figure 1: 5 x 5 nm AFM images obtained in 0.1 M $HClO_4$ + 1 mM Bi^{3+}. A) Image of bare Au(111) showing a 0.29 nm atom-atom spacing and hexagonal structure. B) (2x2)-Bi overlayer which acts as a catalyst for the electroreduction of H_2O_2 to H_2O. The adlattice exhibits open Au and Bi atoms which are likely the site of catalytic activity.

A second aspect of research will be to examine the structure of Pt microparticles supported on carbon and other surfaces. The shape and defect density of these particles are expected to strongly affect their reactivity. In particular, steps and defects on terraces existing on facets of these particles may provide initial binding sites for MeOH oxidation. Characterization of these microparticles by STM and AFM should enable correlation of these larger scale structural features with reactivity monitored by standard electrochemical means. The microparticles will be supported on flat carbon and oxide surfaces. The density and types of defects detected by probe microscopy will be compared with that determined by NMR and standard electrochemical measurement in collaboration with Wieckowski and Oldfield.

The final aspect of proposed research will be to examine modes of binding of small molecules to bare and alloy-modified electrode surfaces. This area is important, not only because the small molecule binding event is central to electrocatalytic phenomena, but also because of the intrinsic interest in thin films and organic materials of use in microelectronics, optical, and corrosion processes. The proposed research examines several model small molecule binding events at the solid-liquid interface, with the goal of discerning how different surface structural features affect the organic adherent. In collaboration with Nuzzo and Wieckowski, we will examine how changing from the UHV to the electrochemical environment influences the structure, binding, and reactivity of candidate small molecules. The direct structural information obtained by AFM and STM will be compared with the insights obtained by Weaver using IR spectroscopic means. We have already shown that phenol forms a close-packed, interdigitated monolayer on Au(111) electrode

surfaces at positive potentials [5] while much more open overlayers are observed in UHV. We will correlate the structures observed by AFM with those inferred by standard electrochemical methods Specific molecules to be studied include candidate fuels such as short-chain alcohols and organic acids.

Relationship to other projects

The detailed structural and reactive insight available from *in situ* STM and AFM will significantly augment the other projects in this proposal. The catalyst materials synthesized by Nuzzo will be examined and their surface structure characterized by probe microscopy. Small molecule binding – and poison formation -- studied by Oldfield, Weaver, and Wieckowski using NMR and IR techniques will be correlated with the real space structures available with the STM and AFM. We will correlate the phosphate binding studies of Kirkpatrick with detailed structural information on oxide materials. Small Pt particles characterized by NMR and electrochemical techniques by Wieckowski, will also be examined by STM and AFM. The correspondence of the direct structural measurement with other techniques will particularly enhance our understanding of processes and surfaces related to fuel cell catalysis.

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NMR Investigation of Molten Electrolytes and Adsorbed Species

R. James Kirkpatrick

NMR spectroscopy is a powerful probe of the structure and dynamic behavior of molten materials and adsorbed species. The objectives of the present program are to use these capabilities to investigate potential molten catalysts (initially alkali carbonates) and adsorbed species (initially phosphate) relevant to fuel cell technology.

Molten Electrolytes

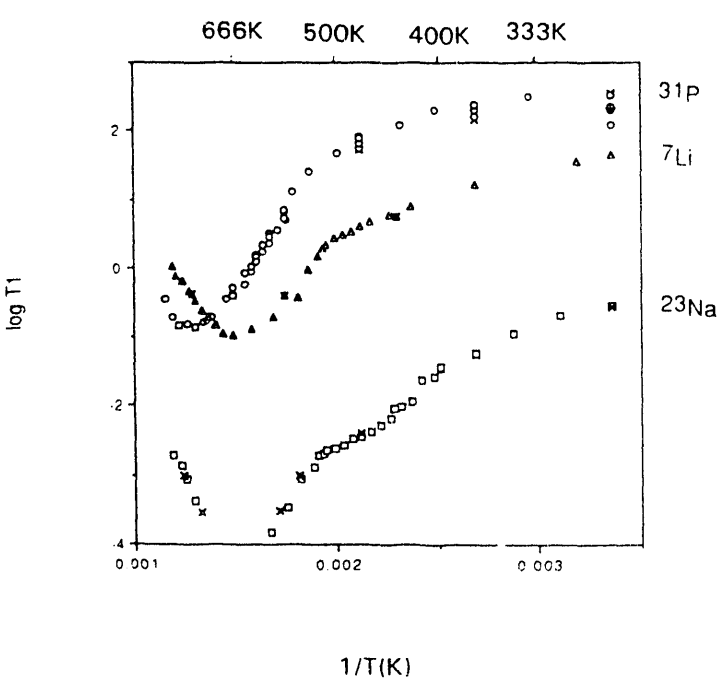
Fuel cells based on molten carbonate electrolytes have several advantages over those based on acids, but little is known about the structure or dynamic behavior of molten carbonates. Kirkpatrick has considerable experience investigating molten oxide materials using NMR spectroscopy and will use those capabilities here.

Fuel cells based on molten carbonates have higher power densities at higher voltages than traditional fuel cells. In addition, the fuel processor is simpler, because the cell can tolerate the presence of carbon dioxide. Thus, the reforming process can occur in the fuel cell and a reformer and shift converter are not required. Internal reforming is likely to be quite efficient. Because water is removed only at the anode, smaller and lower-cost condensers can be used.

We propose to use *in situ* high-temperature NMR methods to probe the structure and dynamical behavior of potential molten alkali carbonate electrolytes. These systems are particularly amenable to investigation be NMR methods, because all the elements present can be observed: ^{7}Li, ^{13}C, ^{17}O, ^{23}Na, ^{39}K, and even ^{87}Rb and ^{133}Cs. Thus, information about the structural environments and dynamical behavior of both the anionic and cationic species can be obtained. The primary data to be obtained are the temperature and composition dependencies of the chemical shifts, chemical shift anisotropies, peak widths, and NMR relaxation rates. These data will be interpreted in terms of local structural environments and atomic motion and will be used to understand the role of the various components in the

current transport and to assist in developing and optimizing molten carbonate electrolytes.

With the advent of high-field superconducting magnets in the early 1980's, NMR investigation of glasses and other amorphous materials expanded rapidly, and Kirkpatrick was a leader in the investigation of aluminosilicate, phosphate, and aluminophosphate materials (1,2). More recently, this work has expanded to include *in situ* investigation of molten materials. Work on silicate and aluminate materials has been published (e.g., 3,4).



Recent work by Kirkpatrick has demonstrated the capabilities of using these methods for understanding the behavior of alkali phosphate melts, which like carbonate melts, are oxide materials with relatively low viscosities and melting points. This work has been done using our sample probe capable of operating to 900K, well within the range of interest for alkali carbonate melts. As for the proposed work on molten carbonates, this work has focused on determining NMR chemical shifts, chemical shift anisotropies, peak widths, and relaxation rates to provide dynamical and local structural information. For instance, the temperature dependencies of the T_1 relaxation rates for ^{7}Li, ^{23}Na, and ^{31}P (Figure 1) show that rapid alkali motion occurs at lower temperatures than phosphate motion (even below the glass transition). Li and Na have multiple relaxation mechanisms with the relaxation being controlled by interaction of the quadrupole moment of the nuclei with varying electric field gradients at the nuclei. One of these mechanisms probably involves hopping between sites, and the other readjustments of the alkali environments. P in the melt, on the other hand, relaxes by its chemical shift anisotropy and rapid motion. The isotropic chemical shift for ^{31}P does not change with temperature, indicating that the average nearest-neighbor and next nearest-neighbor structural environments do not change. For ^{23}Na, on the other hand, the chemical shift becomes more shielded with increasing temperature, indicating an increase in its nearest-neighbor coordination. Thus, the expansion of the melt is due primarily to changes in the alkali environments.

For the molten carbonates, we expect to be able to obtain similar information about the relative mobilities of the various species, how their structural environments vary with temperature and composition, and how their behavior affects the transport properties.

Figure 1. T_1 relaxation times for ^{7}LI, ^{23}Na, and ^{31}P in a mixed alkali phosphate melt/glass.

In addition to the direct work on molten carbonates, it will be necessary to investigate the NMR properties of crystalline model compounds. Kirkpatrick has experience with the investigation of alkaline earth carbonate systems (5).

Later in the project, we will expand our investigations to nitrate and mixed carbonate/nitrate and carbonate/phosphate systems, which may also have potential as molten electrolytes.

Phosphate Adsorption

Phosphoric acid and polymer electrolytes are commonly used in fuel cells, but little is known about the interaction of the phosphate and the catalyst materials. Kirkpatrick and Weaver will use ^{31}P NMR to investigate the structural environments and dynamical behavior of surface phosphate species on relevant catalysts.

^{31}P is an especially useful NMR nuclide, because it is 100% abundant, very sensitive, and does not suffer from unaveraged second-order quadrupole broadening under magic-angle spinning conditions. Kirkpatrick has considerable experience using ^{31}P NMR and is presently investigating phosphate species adsorbed on clay and alumina surfaces. As many as five surface phosphate species can be observed in these systems, with the chemical shifts being controlled by the polymerization and next-nearest structural environments of the various species and the protonation of the phosphate groups at different pH's (Figure 2). Similar changes may occur on metal and metal oxide surfaces.

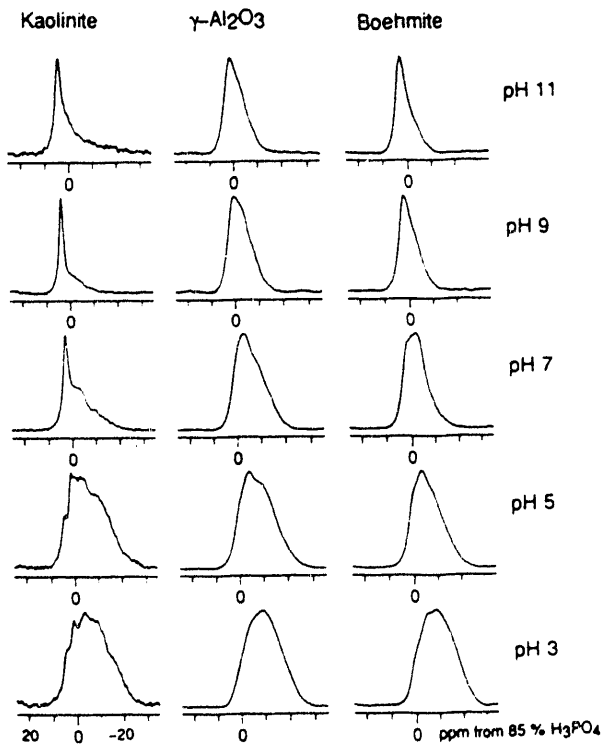


Figure 2. ^{31}P MAS NMR spectra of surface phosphate species on kaolinite and aluminum oxide materials.

Surface alkali species (especially Cs) are known to promote catalysis of gas-phase reactions, and the possibility of similar effects on fuel cell electrodes will be investigated. If the effects are significant, the surface species will be investigated using NMR (e.g., ^{133}Cs). Kirkpatrick has considerable experience with adsorbed alkali cations (e.g., 6).

Relationship to Other Projects

Kirkpatrick and Oldfield have jointly run an NMR laboratory for the past 10 years and have collaborated on many projects (e.g., 7).

The laboratory is equipped with five NMR spectrometers (two at 11.7T and three at 8.45T) and a wide range of sample probes. Of particular importance here is the capability of obtaining NMR spectra under static and magic angle spinning conditions to temperatures as high as 900K. This capability is essential for investigation of the molten electrolytes. The work on solid and molten electrolytes and various adsorbed species will be done in this laboratory, and there will be considerable cross fertilization between the investigators, post-docs and students. The work on adsorbed phosphate will be done in collaboration with Weaver and Gewirth. There will also be collaboration with Nuzzo on surface speciation of transition metal oxide catalysts. Interaction with Gewirth will also be necessary to provide NMR characterization of his surface species and microscopic characterization of adsorbed species studied here.

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New Catalytic Materials

R. Nuzzo

It is proposed that a directed study be undertaken to identify new catalyst materials which will resist poisoning by adsorbates such as CO in Direct Methanol Oxidation (DMO) fuel cells. We propose to examine intermetallic compounds and surface modified phases as potential catalyst materials for these applications. Nuzzo has shown that the adsorptive properties of metals such as Pt can be extensively altered by surface modification. PtSi, for example, forms readily on a platinum surface when it is exposed to silane at modest temperatures. We have prepared a variety of intermetallic compound phases in this way by substituting other gaseous metal hydrides for silane. Methanol is readily activated on many of these surface phases. There are other compound phases which may prove to be of interest in this application however. Ce ions are well known promoters of methanol oxidation. Ce also forms a number of well defined stable phases with metals such as Pt, Pd, Rh, and Ru. We propose to examine how various compound phases of this sort perform as a methanol oxidation catalyst and further explore their reactivity towards adsorbates such as water and CO. As an example, it will be most interesting to examine a range of stoichiometries (such as CeM, CeM_2, CeM_3 etc.). The compound metal phases we prepare will be completely characterized by diffraction and a variety of spectroscopies including x-ray photoelectron and Auger electron spectroscopies. Their chemisorption and fundamental surface chemistries will be explored in detail (see below). Another interesting approach to the modification of the DMO catalyst phases comes from analogies found in organic transformations involving these same metals as catalysts. It is possible, for example, that the catalyst particles can be modified with selective poisons which protect the metal centers against ligands such as CO and still leave them active in the anodic processes. Platinum surfaces modified by the coadsorption of $BaSO_4$ provides one specific example of an attractive candidate for study in this regard.

The basic chemistries of multimetallic catalysts also are of great interest to this program. There has been very little systematic study of the fundamental surface chemistries of the important ternary (Pd/Pt/Cu, Rh/Pt/Cu) systems which may be employed as catalysts. We propose to examine the surface reactivity of such materials towards adsorbates such as CO, water, and methanol using a wide variety of UHV techniques including XPS, AES, HREELS, Reflection Infrared spectroscopy, reactive

molecular beam-surface scattering, and temperature programmed desorption spectroscopy. From these studies, we will unravel the structural sensitivities of the thermal reaction channels and directly measure the relevant heats of adsorption of the adsorbates which might compete for surface sites on the catalyst.

It is well appreciated that adsorbates which can strongly mediate the electron transfer reactions involved in the reduction of O_2 to water will greatly influence both fuel cell and battery technologies. There are interesting classes of materials which we wish to explore towards this end. Copper oxides are well known to be efficient activators of dioxygen. Indeed the success of the well known Wacker catalysts requires the very efficient redox recycling of the palladium constituent to avoid its precipitation as colloidal metal. We propose to examine the ability of copper oxide phases, such as small particles of the perovskite phases for example, and discrete Cu compounds which are readily activated on palladium to function as redox promoters. An example of the latter is provided by the compound bis(hexafluoroacetylacetone) copper(II). We have extensively characterized the redox chemistry of this compound on palladium surfaces and have noticed that oxidants can effect the desorption of the compound in a highly facile process. In principle, any highly efficient ligand assisted reaction involving the type of redox equilibria of the sort involved here ($M(0)/Cu(II)L_2$ --> $M/Cu(I)L + L + O_2$ --> $M/Cu(II)L_2$) might serve as a highly effective catalyst for oxygen reduction. We have preliminary evidence that the aforementioned system might function in this way.

DMO and other fuel cells are also limited by the performance of the ionomer membranes that are part of these systems. It has been suggested, although it has not been unequivocally demonstrated, that the varying interfaces formed with these materials (such as with the carbon base electrodes or the catalyst particles) can strongly influence performance (by effecting proton transport for example). It is proposed that fundamental studies be undertaken to explore the structural properties of these interfaces. We propose to employ quantitative infrared analyses to explore the phase behaviors which occur at these interfaces. We have an extensive background in the determination of molecular orientations at surfaces using infrared spectroscopy and these techniques seem ideally suited to the needs of this portion of the program.

Relationship to other projects

The materials synthesized in Nuzzo's program will be characterized by using the techniques provided by others in this thrust. Specific surface structures of ternary catalyst materials will be examined by Gewirth using *in situ* AFM and STM. NMR characterization of oxide phases will be carried out in collaboration with Kirkpatrick. Small molecule adsorption will be quantified using NMR in collaboration with Wieckowski and Oldfield and by using *in situ* vibrational spectroscopy in collaboration with Weaver. The electrochemical vibrational work will be compared with analogous measurements in Nuzzo's laboratory in the UHV environment.

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Solid-State NMR in Fuel Cell Chemistry

E. Oldfield

Introduction

While catalysts play a role in many energy related processes, the need to improve the efficiency of such processes, combined with the ability to deal with their environmental effects, calls for an increased understanding of the detailed mechanisms of catalytic reactions. Two topics of major current interest are the electrocatalytic oxidation of organic fuels (such as MeOH), and the direct fuel cell conversion of hydrogen (from reformer reactions). In this research we propose to use several different nuclear magnetic resonance (NMR) approaches to investigate three different fuel-cell related topics:

- Solid electrolytes
- H_2/O_2 oxidation/reduction reactions
- Reformer Catalysts

Solid electrolytes

We will first begin an exploratory study of *solid electrolyte* fuel cells. In these systems, the mechanism of ionic conduction is oxygen ion transport via anion defects in the solid oxide crystal lattice. There are many advantages associated with use of solid electrolyte fuel cells - for example, since there are no liquids present, maintenance of stable three phase interfaces and pore flooding problems are absent. This type of cell appears particularly promising for use in coal gasification.

We have shown previously that the vast majority of metal oxides can be isotopically enriched in ^{17}O simply by $^{17}O_2$ gas exchange at elevated temperatures. We will use a novel closed-system circulator:

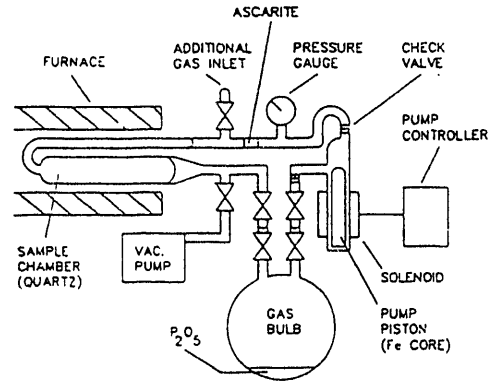

Figure 1: Schematic diagram of $^{17}O_2$ gas circulator.

to isotopically (^{17}O) label a number of ceramic electrolytes, and then use our very high temperature probe to investigate the dynamics of the ^{17}O nuclei in the labeled system. For ^{17}O, spin-spin and spin-lattice relaxation in mobile systems is generally overwhelmingly quadrupolar, thus useful correlation time and activation energy information can be deduced from relaxation time measurements. In addition, of course, other nuclei present (e.g. Zr, Y) provide additional information on spin dynamics, and they will be investigated as well.

A system of some current interest is the ZrO_2-Y_2O_3 solid electrolyte. In previous work, Oldfield investigated the system $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ by ^{89}Y NMR spectroscopy and showed that the Y^{3+} ions in cubic, fluorite-like $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ were associated with a pair of vacancies along <111>. Like ZrO_2-Y_2O_3, interest in this solid solution stems from its exceptionally high oxide ion conductivity. Neutron scattering studies have revealed a cubic fluorite-related structure with an exceptionally high concentration of vacancies on the anion sublattice. Diffuse scattering measurements indicate that vacancy ordering occurs along both the <111> and <110> directions, and it has been postulated that the Y^{3+} ion may prefer the centrosymmetric site created by a <111> vacancy pair as shown below :

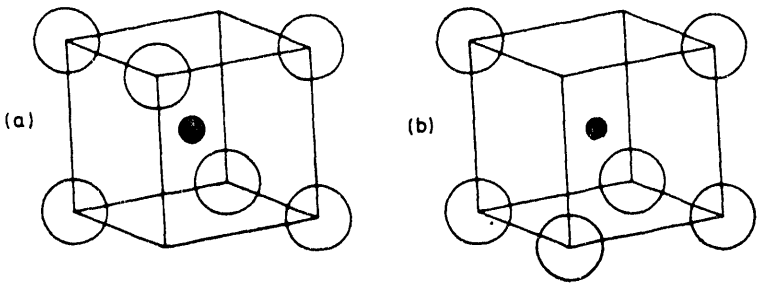

Figure 2: The cation site in the fluorite structure surrounded by six anions and (a) a <111> vacancy pair or (b) a <110> vacancy pair.

whereas the non-centrosymmetric site between a pair of <110> vacancies will be more suitable for Bi^{3+} ions, which are known to take irregular co-ordination geometries. Although a subsequent EXAFS study was consistent with this hypothesis, it remained the result of intuition rather than experiment. However, using the technique of ^{89}Y MAS NMR spectroscopy, we were able to obtain direct verification of the model, and the techniques developed should never be applicable to commercial materials.

The following Figure shows ^{89}Y MAS NMR spectra of Y_2O_3 and $(Bi_2O_3)_{0.6}(Y_2O_3)_{0.4}$:

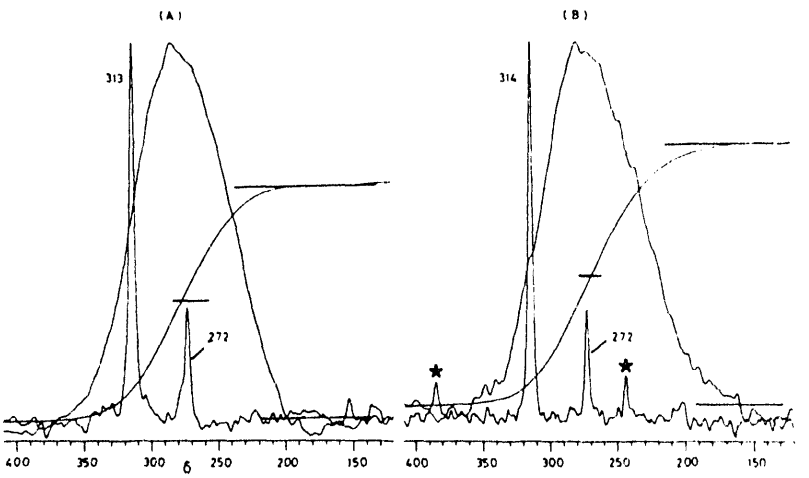

Figure 3: (A) 17.6 MHz and (B) 24.5 MHz ^{89}Y MAS NMR spectra of Y_2O_3 (sharp line spectra) and $(Bi_2O_3)_{0.6}(Y_2O_3)_{0.4}$ at 24 ± 2°C (d in p.p.m. from 1M YCl_3 in H_2O). The mean center of gravity of the broad peak (from the half height of the integral) is at 275 ± 2 p.p.m., close to the 272 p.p.m. value found for Y in the <111> site of Y_2O_3. The peaks marked * arise from spinning side bands.

In spectra of Y_2O_3 at 17.6 and 24.5 MHz, two resonances are clearly present, at 314 ± 1 and 272 ± 1 ppm. The crystal structure of this compound can be thought of as an ordered, anion-deficient fluorite such that there are two environments for Y^{3+} cations, i.e., they may be surrounded by either a <110> anion vacancy pair or by a <111> vacancy pair, the former type of cation site occurring three times as frequently as the latter. We therefore assign the stronger resonance at ca. 314 ppm to the <110> site and the weaker resonance at ca. 272 ppm to the <111> site. The spectra of $(Bi_2O_3)_{0.6}(2O_3)_{0.4}$ at 17.6 and 24.5 MHz are also shown in Figure 3. At both field strengths there is a single broad resonance, centered at ca. 275 ± 2 ppm. Spectra of the 27 and 34% Y-doped materials are very similar in appearance, with the maximum always occurring at ca. 275 ppm. The large field-independent (in ppm) linewidth of the Bi-containing sample is expected in a solid solution where a range of local environments (bond angles and bond lengths) will inevitably be present. We therefore concluded that the Y^{3+} ions in this solid solution are predominantly surrounded by <111> vacancy pairs, the Bi^{3+} ions must then be surrounded by the <110> vacancy pairs detected in the neutron scattering experiments.

We believe these experiments clearly demonstrate the potential of MAS NMR in oxide defect chemistry. The ability to investigate ^{89}Y, ^{17}O and ^{91}Zr (using spin-echo techniques) over a very large range of temperature should, in future work, give a wealth of information on the static and dynamic structure of such complex solid electrolytes.

H_2/O_2 oxidation/reduction reactions

Oxygen-17 NMR also has the potential of being a useful probe of the oxygen reduction reaction. In previous work, we have shown that many solid oxides exchange O atoms with $^{17}O_2$ gas on heating:

$$MO + 1/2\ ^{17}O_2\ [MO^*O]\ M^*O + 1/2 O^*O \quad (1)$$

The mechanism(s) of this apparently ubiquitous reaction are not known, although in the case of BaO, a well characterized peroxide forms:

$$BaO + 1/2\ ^*O_2\ BaO^*O\ Ba^*O + 1/2\ O^*O \quad (2)$$

this reaction being the basis of the Brin process for O_2 production. We believe that it may be possible to detect similar peroxy - intermediates on our electrocalatysts - since the chemical shift of oxygen (and its quadrupole coupling constant) are characteristic signatures of peroxy-species, and very low T operation yields very large S/N gains. We will also attempt investigation of O_2 species adsorbed onto metal electrodes, again attempting to identify intermediates in the oxygen reduction process.

Similarly, we will investigate the hydrogen oxidation reaction in our electrocatalysts. Here, both ^1H and ^2H NMR will be investigated. For H_2 and D_2 gas, signals can be greatly attenuated because of their long relaxation times, while H_2O can be edited by using selective excitation. For H or D-bonded metals, relaxation rates will be rapid (due to interaction with conduction electron spins), and we can currently examine samples over a 900K range in temperature, which will give a considerable change in relaxation behavior. In most ^1H-containing solids, H-H dipolar interactions give rise to very large (80 kHz) powder pattern widths. However, by using isotopic ($^1H/^2H$) dilution, this dipolar broadening is greatly reduced, and with ^2H double-quantum decoupling, or with MAS, it is almost completely removed. We believe that ^1H MAS NMR (using the glass powder/rod technique of Duncan to remove Eddy current/spinning problems) could be a powerful probe of the hydrogen-reduction reaction, and we will pursue its investigation using the isotope dilution technique, as well as with the CRAMPS approach (see below) with researchers at Mobil Corp.

For investigation of ^1H NMR of H_2 adsorbed onto supported metal particles, we have recently developed a solid-state MAS NMR probe along the lines of that used previously by Ian Gay [1-3], which permits investigation of sealed samples using conventional sealed 5 mm sample tubes. ^1H MAS NMR resonances show extremely unusual 50-80 ppm shielded resonances, and promise to be a very powerful probe of electrocatalyst materials, including bimetallic electrocatalysts (e.g. Pt-Sn).

Also of considerable interest will be the nature of the interactions of H_2 and organic species with the graphite support surfaces. Recent work with perdeuteroneopentane ($C(CD_3)_4$) [4] has demonstrated an exceptionally large magnetic shift anisotropy for ^2H - rather than a quadrupole interaction, due to the large "ring-currents" generated in the graphite surface, and such unusual behavior needs to be studied in detail in graphite supported electrocatalysts, in order to dissect out the specific metal-adsorbate interactions.

Reforming catalysts

We also wish to investigate some of the heterogeneous catalysts used in the reforming reactions likely to be used in the commercial production of H_2 for fuel cell use. At present it appears that indirect/reformer routes offer considerable promise, with immobilized phosphoric acid fuel cells being particularly attractive. We plan to use solid-state NMR techniques to investigate reforming catalysts, which are typically metal loaded aluminas or zeolites. Hydrogen is a high-value product in refineries, and there is considerable interest in its production. Oldfield plans to continue his collaborative work with the catalysis group at Mobil Corp., focusing on the characterization of reformer catalysts, their regeneration and supports, as well as the topics of metal-support and metal-hydrogen interactions, using ^1H MAS

and ^{1}H CRAMPS (multiple-pulse) experiments. Of particular interest is the characterization of zeolite based materials which contain various metals. Solid state ^{27}Al NMR has recently been shown to be a very useful technique for investigation of aluminas, silica-aluminas and zeolites, since 4, 5 and 6-coordinate Al and framework vs. non-framework Al species can also be detected and quantified. In commercial reformer catalysts, such chlorided-alumina and metal-zeolite catalysts, there are many questions as to structure, and structure changes which occur during processing or regeneration. ^{27}Al and ^{1}H MAS NMR techniques should play an important role in catalyst characterization.

A second approach to investigating reformer reactions will be to use be of other ^{13}C MAS NMR. 13C MAS NMR has been shown to be an important way to characterize the MeOH gasoline (Mobil MTG) process, and we believe that it should be possible to similarly use ^{13}C NMR (of labeled MeOH or EtOH) to investigate the formation of H_2 in reformer catalysts.

Relationship to other projects

Oldfield has already worked with Kirkpatrick for over 10 years, investigating the structures of inorganic solids using solid-state NMR techniques [5], and continued collaboration in the oxide-electrolyte fuel cell area are anticipated. Oldfield and Wieckowski have collaborated together over the past three years in surface NMR-electrochemistry, and are currently working together on the Pt-HCN system described below. Oldfield provides some expertise in solid-state NMR, and has a well-equipped NMR laboratory, and continued strong interactions with Wieckowski in the area of low-temperature NMR, and surface NMR, are anticipated. Oldfield will also work closely with Nuzzo, who will provide novel catalyst materials for NMR characterization. For example, novel Pd/Pt/Cu or Rh/Pt/Cu interactions (in bulk) with CO, H_2O, MeOH, H_2, will all be investigated using the ^{1}H, ^{13}C and ^{2}H NMR techniques outlined above, in many cases with Wieckowski providing electrochemically prepared samples.

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Vibrational Spectroscopic Characterization of Electrocatalytic Materials

M. Weaver

A crucial component of the proposed thrust involves the identification and characterization of adsorbed species present under working electrocatalytic conditions that can partake in the reactions of interest either as intermediates and/or poisons. Both in-situ infrared and Raman spectroscopies can provide such information, but with markedly differing spheres of applicability. Infrared reflectance-absorption spectroscopy (IRAS) is capable of providing vibrational spectra for electrochemical adsorbates with moderate or high sensitivity by employing potential-difference tactics along with thin-layer cells to extract the desired potential-dependent surface spectral components. The application of such tactics to the mechanistic examination of irreversible electrocatalytic processes, especially organic oxidations, is a hallmark of recent Weaver group contributions on this topic[1]. A major virtue of IRAS is its applicability to a wide range of surface morphologies, from ordered monocrystals to the rougher polycrystalline materials that are of particular interest in practical electrocatalysis.

By comparison, Raman spectroscopy has received much less attention as a vibrational probe in heterogeneous catalytic systems, primarily due to the perceived low sensitivity of the technique. A pair of advances made in the Weaver group, however, allow the technique to be endowed with remarkably high sensitivity for in-situ electrocatalytic applications. First, an

electrochemical pretreatment procedure yielding stable as well as intense surface-enhanced Raman (SER) activity for gold electrodes was developed[2]. Second, the desired SER effect can be extended to a wide range of surface materials, including Pt-group transition metals and metal oxides, by depositing them as ultrathin films on gold[3]. This tactic enables vibrational spectra to be obtained for a diverse range of adsorbates in electrochemical and other environments (e.g. high gas pressures) with remarkable sensitivity and freedom from bulk-phase interferences[4]. Moreover, the recent advent of CCD detectors now enables us to obtain individual spectra sufficiently rapidly (0.1-2 s) so to allow spectral sequences to be acquired during reactive electrochemical perturbations such as cyclic voltammograms[5]. This tactic is of primary importance in correlating the potential-dependent spectral and electrochemical responses, and thereby assessing the role of specific adspecies, detected vibrationally, in the electrocatalysis.

In the specific context of the proposed thrust, we propose to target several electrocatalytic molecule/interface systems for vibrational scrutiny by infrared and/or Raman spectroscopy where appropriate. One type of reactant system of particular interest will be small organic molecules used as fuel-cell anodes, that it is anticipated will be characterized by ^{13}C NMR spectroscopy by Wieckowski. Some issues are:

- What are the molecular/atomic fragments formed by reactant surface decomposition?
- How are they bound to the substrate?
- What role do the chemisorbates play in the electrocatalysis?
- Most importantly, how may we control or modify the surface chemistry/electrochemistry so to optimize electrocatalytic rates and stability?

Information on such issues requires a combined effort involving the diverse techniques provided by the thrust members. The vibrational methods will be particularly useful in identifying the adsorbates and probing the surface bonding.

One reactant system earmarked for detailed scrutiny by Raman (SER) spectroscopy will be oxygen reduction on transition-metal electrocatalysts. Very recent work in the Weaver group has demonstrated the excellent suitability of our thin-film SERS technique for following surface oxidation, including metal oxide formation. This exploit the high sensitivity of the technique in the low-frequency region (200-900 cm $^{-1}$) where metal-oxygen vibrations are located[6]. It will be of particular importance to assess the presence of adsorbed oxygen and metal oxides formed under reactive conditions, and their role in the reaction mechanism(s). An example of the information garnered for adsorbed oxygen and oxide formation by SERS is shown in Figure 1. The spectral sequences in the left- and right-hand columns were obtained on a rutheniumfilm electrode in 0.1 M $HClO_4$ and 0.1 M KOH, respectively, during a cyclic voltammogram run at 50 mV s^{-1}. Several spectral features are seen, identified with Ru-O vibrations characteristic of specific states (Ru^{II}, Ru^{IV}, Ru^{VI}) of surface oxidation, formed under transient electrochemical conditions. The ability to identify and characterize, by in-situ vibrational spectroscopic means these (and many other) adsorbed species partaking in electrocatalytic processes is a crucial virtue of this technique for the present Thrust.

The expertise of Weaver in the area of electrochemical kinetics should also prove valuable to this thrust, not only in relating the vibrational data to electrocatalytic activity, but also in undertaking kinetic and mechanistic rate analyses from data obtained more generally in the thrust research.

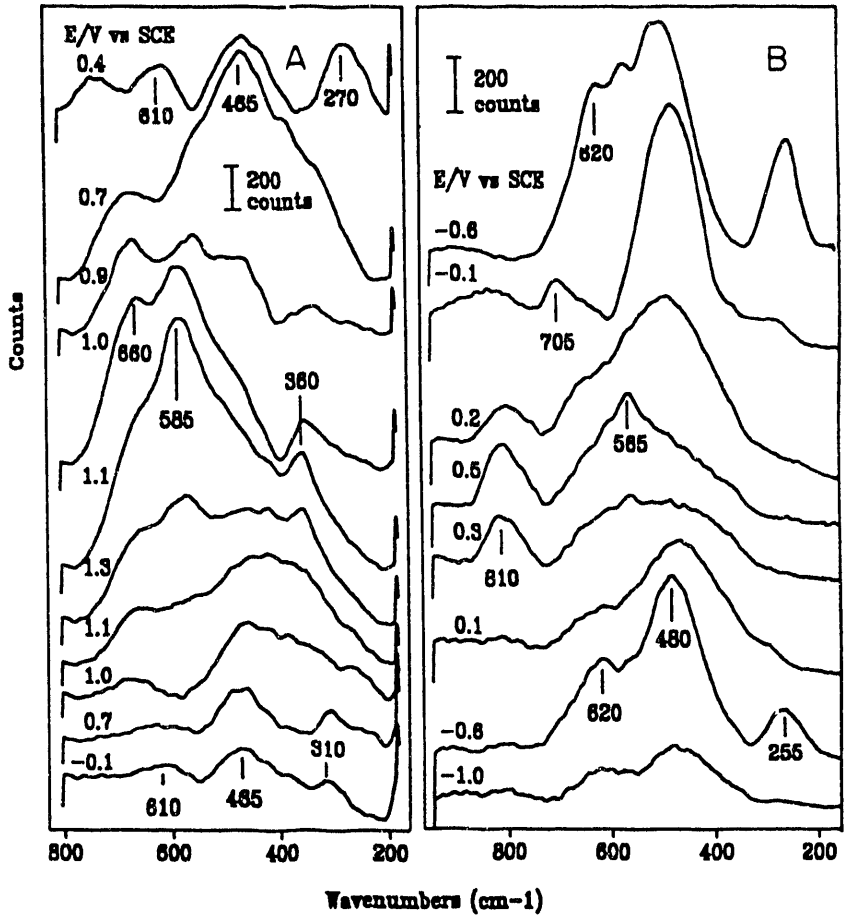

Figure 1. Identification of oxide formation processes on a ruthenium film electrode by *in situ* Raman spectroscopy.

Relationship to other projects

A major on-going focus of attention in the Weaver group concerns the development and application of vibrational spectroscopic and other *in-situ* microscopic-level techniques to the elucidation of structure and bonding at electrochemical interfaces, and especially the impact of such insight to electrochemical kinetics and mechanisms. This expertise is naturally complementary to the other proposed Thrust members. In particular, the research activities of Wieckowski in electrochemical surface science, including NMR and radiotracer assay of adsorbed species and single-crystal metal electrochemistry provide a powerful combination with the Weaver expertise. Indeed, Wieckowski and Weaver have collaborated extensively, and co-authored several research paper together, in the recent past. The contributions of Gewirth and Oldfield in electrochemical probe microscopic characterization of the electrocatalysts and in NMR, close interplay with the corresponding spectroscopic data from Weaver. In addition, the spectroscopic facilities of the Weaver group will be invaluable for the further examination of new electrode materials prepared and characterized by Nuzzo.

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Fuel Cell Catalysts and Poisons by Surface NMR-Electrochemistry and Reaction Rates

A. Wieckowski

Introduction

We have recently demonstrated that NMR spectra for adsorbed species on metal surfaces in solution and under potential control can be obtained.[1,2] This opens up the possibilities of *in situ* examination of electrocatalytic materials and accessing molecular structure of adsorbed catalytic poisons, or reacting species, at high surface area, fuel cell catalysts. The electrochemical NMR technique is now poised to make the same contributions to our understanding of the surface chemical bond *in situ* as surface NMR operating in gas phase has made to structure and bonding in this environment, through the seminal work of Vaughan, Slichter, Duncan, Mastikhin, Zlim and coworkers [3-5]. Of particular recent interest has been the very detailed characterization of gas phase CO and ethylidene bonding to supported metal catalysts. Taken together, these new techniques allow us to obtain insight into fuel cell electrode processes with unprecedented detail.

In order to identify surface properties that account for fuel cell poisoning, we propose to study small molecule binding sites and surface chemical bonds by electrochemical NMR. We will use platinum and rhodium as main catalytic metals and Ru, Sn, Pd and Cu as catalytic promoters. The target molecules as related to particular fuel cells [6], are listed in Table 1.

The bond characterization will involve knowledge of surface coordination, bond lengths and molecular surface geometries through NMR and, in collaboration with other thrust members, through vibrational techniques, AFM and STM. An understanding of the nature of surface chemical bonds involved in the poisoning processes is an important prelude to a rational design of catalytic surfaces selective for poison-free current generation. Some issues are:

Table 1: Molecules in binding sites/surface chemical bonds studies.

Fuel cell	Critical bond	Molecules
Methanol	M-C	CO, CH_3OH, C_2H_5OH
Hydrogen	M-H	H_2, H_2O
Nitrogenous Compounds	M-N	Urea, HCN, NO_x, hydrazine

- What is the electronic structure of the target molecules when bound to the surface?
- What is the extent of electron donation to the catalysts?
- What is the scientific rationale for heterogeneous catalysis by metals and alloys?
- What catalyst design guidelines can be developed from the results to be obtained in this project?

In Situ NMR Structural Studies

The NMR work proposed falls into three broad areas: NMR characterization of fuel cell materials, detection and NMR characterization of adsorbed small molecule species, and studies of surface diffusion.

We will begin with fuel cell grade platinum and rhodium black (AESAR) as the electrocatalysts. We also use Pt and Rh catalysts dispersed on conducting carbon and oxide supports (RuO_x, IrO_2), separated by glass rods and on non-conducting substrates, to remove eddy current/spinning problems for MAS measurements (Duncan). The methodology for such catalyst preparation is well-known from surface gas-phase literature. The focus here will be on the support-catalyst interaction throughout measurements of chemical shift of ^{195}Pt and ^{103}Rh depending on the type of support, metal dispersion and catalyst promoters. Samples will be characterized by scanning and transmission electron microscopies located in the Molecular Research Laboratory at the University of Illinois at Champaign-Urbana.

As a general example of the NMR approach to investigating adsorbed species, we have recently been able to observe the binding of CN^- a prototypical electrocatalyst poison (like CO [1,2]) onto high surface area Pt. The following Figure shows a typical 360 MHz (1H) 13C NMR spectrum of Pt (13CN):

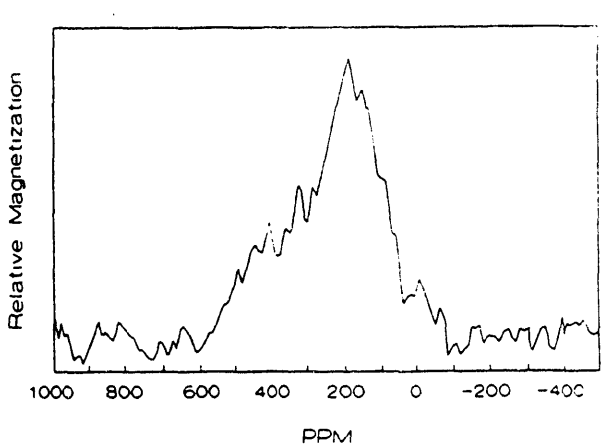

Figure 1: 90.5 MHz 13C NMR spectrum of electrosorbed CN on Pt.

The lineshape is axially symmetric and has an anisotropy,, of ~500 ppm. We plan to follow up this initial observation -- obtained using the spin-echo technique – on a static sample, by using the magic-angle spinning (MAS). This technique permits a more accurate determination of the components of the 13C shielding tensor and allows us to extend our observations to 15N NMR. We will correlate our results with infra-red measurements obtained in collaboration with Weaver on these same NMR samples. Double resonance experiments, which should permit very accurate determinations of C-N, C-O and N-O bond lengths of the small molecules identified in Table 1, and adsorbed onto electrocatalyst materials will be carried out. Relaxation experiments as a function of temperature on frozen samples will allow us to probe the electronic density of states at 13C, 15N (via the Korringa relation). The very low temperature equipment (pumped LHe, ~3 K) essential for these experiments is currently available.

We anticipate that MAS NMR will give a considerable increase in spectral resolution, so that end-bound, bridge-bound, and planar CN species may all be observable. We will examine the bonding of these species as a function of catalyst preparation and electrochemical potential. With MAS NMR, higher magnetic field strengths, and a wide range of temperatures available, we should be able to make very detailed analyses of CO, NO and CN bonding to Pt, Rh and other metal surfaces and composites.

In addition to providing structural information, NMR has the ability to perform *in situ* experiments on a time scale of microseconds to hundreds of seconds, which is unattainable by other spectroscopic techniques. This allows for the study of motions, such as surface diffusion. It is generally known that surface diffusion contributes significantly to rates in heterogeneous catalysis. The surface dynamic measurements of the small organic molecules given in Table 1 will follow Duncan's spin-population labeling scheme [8], and will be carried out at variable temperature. The labels will be created by narrow bandwidth pulses which selectively invert ^{13}C (^{15}N) nuclear spins. The selective labeling utilizes chemical shift anisotropy of molecules adsorbed at specific angle relative to external magnetic field. Models for diffusion on multi-faceted metal particles will be developed to fit to the time-dependence of the spectral hole.

Progress in surface and solid-state NMR is such that surface-NMR-electrochemistry is poised to become a main research tool in broadening the molecular-level base of electrochemical surface science and electrocatalysis. A major impact of this new technique on materials and surface chemistry in electric fields seems only a matter of consistent

research, such as that proposed here, and further technical advancements in NMR technology. Further work will utilize methods of increasing NMR surface sensitivity, such as photon pumping options or using signal enchanters implanted in the electrode materials. We anticipate that further progress in the NMR science will establish long-range ordered interfaces as an ultimate target for basic surface-electrochemistry and materials investigations.

Catalytic Reaction Rates

We have recently developed a fast chronoamperometric method for measurements of instantaneous currents involved in catalytic oxidation of organic molecules. (The instantaneous current is the initial net oxidation current obtained by extrapolation of the potentiostatic transients to zero time.) The oxidation current was measured on a millisecond time scale, Figure 2. For methanol, in view of practically unlimited diffusion delivery of the fuel to the surface, and of a relatively small current measured, the drop in the electric current is exclusively accounted for by the surface poison formation, most likely chemisorbed CO:

$$CH_3OH \rightarrow CO + 4H^+ + 4e^- \quad (1)$$

which competes with the oxidation of methanol to CO_2:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (2)$$

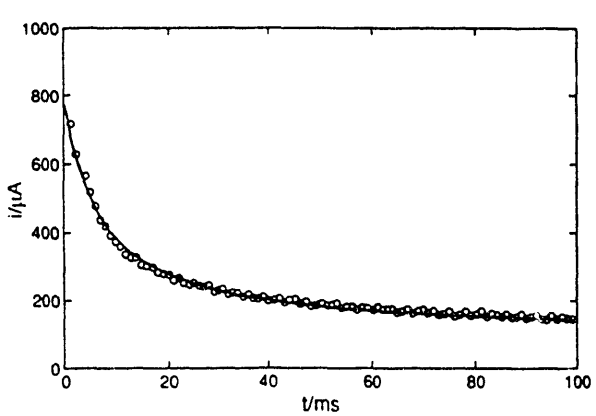

Figure 2. Current-time plot for oxidation of methanol on the Pt(110) electrode in 0.2 M solution of CH_3OH in 0.1 M H_2SO_4 at E = 0.400 V. Shown is the background corrected current and the fitting least-squares line.

The potentiostatic, current-time relationship was derived to have the following form:

$$i = i_{t=0}[1-\theta_{max}{}^2 k_{ad} t(1+\theta_{max} k_{ad} t)^{-1}] + $$
$$+ 4k_{ad} e N_{Pt} m^{-1} (\theta_{max})^3 \cdot$$
$$[1-\theta_{max} k_{ad} t(1+\theta_{max} k_{ad} t)^{-1}]^2 \quad (3)$$

where $i_{t=0}$ is the instantaneous, net oxidation current, θ is the fraction of the electrode covered by surface CO, 4 is the number of electrons produced in the CO formation process, e is the elementary charge, N_{Pt} is the total number of surface Pt sites, θ_{max} the maximum coverage of the surface CO, m is the number of surface sites occupied by one CO molecule, and k_{ad} is the rate constant for the site blocking process. Four quantities shown in equation 3, $i_{t=0}$, k_{ad}, θ_{max} and m, have been treated as adjustable parameters and determined from the experimental i-t data by using the least-squares method (Simplex algorithm, typically 300 data points per fitting procedure).

Calculations have shown that the adsorption current contribution to the instantaneous current is not essential. Significantly, through the work with Pt(111) and Pt(110) electrodes in sulfuric acid with the light and heavy methanol, Wieckowski et al. have proven [8] that the elementary step in the methanol oxidation sequence is:

$$CH_3OH \rightarrow (CH_2OH)_{ads} + H^+ + e^- \quad (4)$$

Through equation 3, and via the application the computerized pulse method for potential programming, we have, for the first time, the correct instantaneous values of methanol oxidation current. This has already led to several interesting observations. For instance, with the Pt(110) electrode, the methanol oxidation current taken at 0.2 V, vs. Ag/AgCl reference, is 156 $mA \cdot cm^{-2}$, which corresponds to a turnover of 162.5 molecules $(Pt\ site)^{-1} \cdot s^{-1}$. This is an extremely high turnover, in fact, much higher than previously believed.

Using this method, we propose to reveal intimate details of the structure-function relationship in the oxidation of methanol, ethanol and hydrazine on test catalysts examined in this research. Since the number of

uncertainties concerning the catalyst structure and poisoning processes will considerably be reduced in this proposed research, we would provide, for the first time, a crucial link between rates, electrolytic environment and the substrate geometry in the type of catalysis concerned in this proposal. The quantitative identification of this link is anticipated to be the main product of the proposed research.

Catalytic oxidation rates will be also measured with a small-size, high surface area electrocatalysts. The interest would be to learn how the macroscopic roughness, measured by the roughness factor, R, affects the oxidation rates and, perhaps, mechanisms. The data obtained with the test molecules will be available for generalization to other systems that belong to the category of oxidative catalysis on metal electrodes. Via our work with macroroughened surfaces, an understanding of the connection between model-single-crystal electrodes and microparticle platinum catalysts should be considerably advanced. Therefore, this work could contribute to the accelerated development of both fundamental and applied aspects of catalytic electrochemistry, and would bring this area to a new molecular-level understanding. It will constitute an important prelude to the rational design of metal particle catalysts in electrochemistry. At the end of the project, we expect to have better control on how heterogeneous electrocatalysis functions.

Relationship to other projects

The proposed *in situ* measurements will allow us to build detailed structural models for the relevant catalyst and surface species. We plan to interact strongly with Oldfield and Kirkpatrick to use progressively advanced methods of Solid NMR. Oldfield's and our group have already a great deal of direct contacts owing to our mutual interests in NMR. We will carefully correlate the information we will obtain from NMR with vibrational measurements from Weaver ,and our structural NMR spectroscopy data with the AFM and STM results of Gewirth. Indeed, we, Weaver and Gewirth have collaborated extensively, and co-authored several research papers together.

Information on fuel cell reactivity and surface two-dimensional motions will be obtained by the electrokinetic methods and solid NMR. Coupling the dynamic and structural information requires a combined effort involving the diverse techniques provided by all thrust members. Due to the collaborative spirit of this proposal, obtaining the crucial quantitative connections between rates and structures will be possible. Reporting on multifaceted structure/function relationships relevant to fuel cell technologies will be the main product of this joint research effort.

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D.2 FOCUSED AREA PROGRAMS PROPOSED FOR EXPANDED FUNDING

D.2. a A MOLECULAR APPROACH TO THE UNDERSTANDING OF CORROSION AT THE SOLID-LIQUID INTERFACE

R. Alkire, P. Bohn, A. Gewirth, A. Wieckowski, I. Robinson, K. Suslick, and D. MacDonald

Work Package Description

This document outlines a proposal to expand an existing MRL-DoE program titled "Molecular Properties of the Solid-Liquid Interface and Their Relation to Corrosion." The expanded program focuses on the chemistry and physics of surface defects and their unique influence on corrosion phenomena. The expanded program includes the five original participants plus additional faculty. This increased effort will require funding in excess of the current budget for the Liquid-Solid Interface effort in the MRL. The proposed expansion of the program includes increased funding for collaborative research plus funds for shared equipment, and for promoting strong interaction with industrial and academic programs through a program of visitors and symposia.

Purpose

Our current program addresses molecular behavior that play a fundamental role in corrosion initiation at inclusions and in corrosion inhibition. The goal of the current program is to relate macroscopic corrosion behavior to molecular properties of the solid-liquid interface by understanding structure, function, and local surface chemistry. The proposed expanded program builds on this base by adding new expertise in methods for creating and characterizing defects at the solid-liquid interface, by broadening the range of materials of study, and by providing a residency program for visitors.

The creation and sustained growth of corrosion sites is influenced to a significant extent, at the molecular level, by the presence of flaws such as lattice defects on the metal surface or in the surface film, inclusions, and adsorbed organic and/or ionic species. The expanded program will support development of a variety of new methods for the controlled formation of surface defects and inclusions by ion bombardment, sonification, application of local fields manipulated by STM or surface force devices, coupling of chemical characterization of surfaces with atomic force microscopy, and adsorption of organic species.

The expanded program will also add new methods of characterization such an synchrotron radiation, vibrational spectroscopy of water at solid surfaces and surface films, and surface force measurements on complex metal-electrolyte interfaces that include surface films and adsorbed organic species. The new program will provide a strong new research component in the area of cavitation and erosion/corrosion, and will add to existing strengths in corrosion inhibition of adsorbed organic species and polymer films, and corrosion at inhomogeneities and inclusions.

A residency program for visiting scholars will be introduced to promote interaction with industrial and off-campus colleagues.

The University of Illinois is unusually, if not uniquely, qualified for such a program owing to exceptional strength in the chemical sciences and solid state physics, and to its outstanding facilities for shared use of equipment. The principal investigators are broadly educated in a variety of disciplines and are therefore in a position to visualize how to approach such a complex phenomenon as corrosion. In addition, they share a fundamental focus on understanding of molecular behavior and its relation to the macroscopic world. Each of the participants is currently active in research areas outside of corrosion and is thus in a position to bring fresh techniques and concepts into corrosion field.

Technical Program

The proposed expanded program focuses on the existence of defects in condensed phases and the role that such defects exert on the stability of the solid-liquid interface toward spontaneous corrosion reactions. The likely participants in

the effort include the four current Principal Investigators:

Richard Alkire	Chemical Engineering
Paul Bohn	Analytical Chemistry
Andrew Gewirth	Inorganic Chemistry
Andrzej Wieckowski	Analytical Chemistry

plus several new principal investigators. The following individuals would join the program at the higher funding level:

Digby MacDonald	Center for Advanced Materials at Penn. State Univ.
Kenneth Suslick	Inorganic Chemistry
Ian Robinson	Physics

Summaries of the proposed new research that would be developed with added funding are given below:

Incorporation of Molecular Properties of Surfaces In Macroscopic Models of Corrosion Phenomena

Richard Alkire

Cavitation/Erosion Phenomena

We have previously developed experimental methods for investigation of corrosion during cavitation created by spherical piezoelectric lenses. It was found on Fe specimens immersed in sulfuric acid that a critical intensity of ultrasonic illumination led to breakdown of passivity. Based on a model of transport and surface reaction phenomena in the presence of collapsing cavitation bubble, we have predicted critical conditions for passivity breakdown and for repassivation. In collaboration with Suslick, we propose to develop improved knowledge of the effect of cavitation on surface pressure in order to investigate whether there is a critical surface pressure that leads to passive film failure by electrostriction phenomena.

Mathematical models of solution agitation created by collapse of cavitation bubbles was found to predict conditions under which repassivation was possible. In collaboration with Suslick, we propose to incorporate refined understanding of cavitation phenomena in our macroscopic models. The predictions of the model will be tested on corrosion specimens under controlled conditions of cavitation.

Corrosion Inhibition by Organic Species

We have previously discovered that the effect of benzotriazole inhibition of Cu corrosion is accompanied by the formation of a thick polymer-like surface barrier film which has a dual structure. We are currently collaborating with Bohn and Wieckowski to investigate how the structure of adsorbed monolayers of simple organic species, characterized by HREELS and surface vibrational spectroscopy, is related to corrosion inhibition.

We propose to extend this work to thick organic films in collaboration with Nuzzo and Granick in order to investigate whether the dual structure exhibited by benzotriazole-like molecules is a property of the inhibitor film alone, or whether it occurs owing to formation of a metal salt film located between the organic film and the substrate metal. We plan to collaborate with Ian Robinson in the use of synchrotron radiation methods for determining the structure of such surface films.

In addition, we plan to investigate the adsorption of inhibitors on metal oxide surfaces for which preliminary studies have indicated that benzotriazole forms patches which obey a Langmuir isotherm. We proposed to collaborate with Gewirth and Nuzzo to use *in situ* atomic force measurements of how organic species self-assemble on metal oxides, and from this information to develop a model for inhibition efficiency.

Shape Evolution During Early Stages of Corrosion

In studies on metal etching and corrosion phenomena, we have developed a variety of mathematical models for predicting local reaction and convective transport phenomena using finite element methods. These methods are well-poised for the investigation of transient shape evolution. We are currently collaborating with Gewirth in the development of atomic force microscopy techniques for *in situ* measurement of shape during initial stages of

pitting corrosion near MnS inclusions in stainless steel. We propose to expand this program significantly in collaboration with Nuzzo to investigate pit formation at intermetallic inclusions on Al.

Corrosion Initiation at Ion-Implanted Sites

We have previously developed methods for initiation of corrosion at single sites on Al and stainless steel by seeding the surface locally with foreign atoms. We plan to use ion-bombardment techniques for creating individual defect sites of precisely controlled geometry for observing shape evolution during early stages of corrosion. In particular, we seek to test our theoretical predictions which indicate that only defect sites above a certain minimum critical size are effective for initiating pitting corrosion.

Corrosion Initiation at Sulfide and Intermetallic Inclusions

We have previously suggested that pit initiation of 304 stainless steel in NaCl solution occurs by the concerted action of thiosulfate, produced by dissolution of MnS inclusions, and chloride ions. We currently collaborate with Wieckowski in using radioactive species to measure the adsorption thermodynamics of these ions on stainless steel. We propose to expand this interaction in collaboration with Nuzzo and Ian Robertson in order to investigate the behavior of Al-alloys. In particular, we would seek to characterize the composition of the passive film adjacent to an intermetallic inclusion by surface NMR and synchrotron methods.

EXPANDED STUDY OF CORROSION AND OTHER SOLID-LIQUID PROCESSES

Andy Gewirth

We propose extending our research from well defined, low Miller index surfaces to other, more complicated, materials and systems. In our preliminary studies of stainless steel corrosion, carried out in collaboration with Alkire, we have observed pit formation and other evidence of anisotropic corrosion with the AFM. We propose to model this complicated behavior by controlled introduction of defects on simpler materials.

We have observed dissolution of bulk-deposited Cu(111) films using the AFM, and propose to study the effects of small impurity levels on the dissolution mechanism. Similar AFM studies of the corrosion of defected surfaces produced by sputter bombardment will be carried out under specific electrochemical conditions.

We propose to utilize techniques which provide chemical information complimentary to the structural information obtained from the AFM. On well defined surfaces, we will compare the structural information with that obtained from spectroscopic measurements such as optical reflection, capacitance, and XANES. Our observation of unusual surface structural behavior in solution makes it important to ascertain whether this behavior can be replicated in a more controlled environment. We thus propose UHV STM and AFM measurements on metal surfaces modified with adsorbates which mimic those studied in solution.

EROSION/CORROSION - MECHANICAL OR ELECTROCHEMICAL PHENOMENON?

Digby D. MacDonald

Erosion/corrosion (E/C) is one of the principal forms of corrosive attack in industrial systems, including power generating facilities, oil and gas systems, domestic and industrial water supplies, and in naval systems [1-3]. E/C is characterized by a sudden increase in corrosion rate at a critical flow velocity of the

corrosive medium relative to the metal surface. The attack may occur locally or over an extended area. From a hydrodynamic viewpoint, E/C occupies a position intermediate between mass transport enhanced corrosion at low flow velocities and cavitation attack at very high turbulence, where bubble formation and collapse become important.

Traditionally, E/C is explained in terms of shear rupture of the passive film on the metal surface thereby exposing the underlying metal to enhanced attack. However, on close examination this mechanism does not account for the experimental facts, nor is it realistic when one realizes that passivity is due to the barrier oxide layer that is generally less than 5 nm thick (at least for transition metals and alloys). Because this dimension is orders of magnitude less than the thickness of the hydrodynamic boundary layer at which E/C occurs, it is difficult to envisage shear forces on the film being of sufficient magnitude to strip a tightly adherent barrier layer from the surface. Thus, a purely "mechanical" explanation of E/C does not seem to be viable.

Alternatively, in the case of copper-nickel alloys, at least, increasing flow velocity shifts the corrosion potential of the substrate in the positive direction due to enhanced mass transport of oxygen to the surface. At a sufficiently high potential, enhanced ejection of cations from the barrier layer occurs resulting in a sudden increase in the cation vacancy flux from the film/solution interface to the metal/film interface where they may condense locally or over extended areas. The formation of cation vacancy condensate at the metal/film interface decreases the adhesion of the barrier layer to the substrate metal, thereby rendering the film more susceptible to the hydrodynamically-generated shear forces at the surface. This explanation of E/C is primarily "electrochemical" in nature and is supported by the fact that, for copper-nickel alloys, the corrosion potential at which erosion/corrosion occurs is close to that at which the passive film becomes unstable in the absence of flow. In many respects, the explanation offered above for E/C, which is based on the point defect model for the growth and breakdown of passive films, is analogous to that for the initiation of pitting corrosion except that attack occurs over a larger area than is characteristic for a single pit.

The proposed work will seek answers to the following important question related to the onset of erosion/corrosion in model systems and in industrially-important alloys:

1. What are the relative contributions of shear and electrochemistry to the onset of E/C?

2. What is the nature of the breakdown sites at the surface and how are these sites related to the metallurgical and microstructural properties of the substrate?

3. Is the point defect model for passivity breakdown capable of accounting for the susceptibility of metals and alloys to E/C?

4. Can passive films be modified chemically or electrochemically to render metals and alloys less susceptible to erosion/corrosion?

5. What is the role of alloying elements in determining the susceptibility of an alloy to E/C? Can the solute/vacancy interaction model[4-6], which successfully accounts for the effects of alloying elements on the nucleation of corrosion pits, also account for alloying effects in E/C?

6. Is it possible to design new, erosion/corrosion resistant alloys for specific applications?

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CHEMICAL STUDIES OF CAVITATION AND CORROSION

Kenneth S. Suslick

Many of the corrosion phenomena associated with turbulent flow systems are associated with cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. For the past twelve years we have been deeply involved in the exploration of the chemical effects of cavitation. Cavitation is produced whenever the local negative pressure in a liquid exceeds its tensile strength. This can occur during turbulent flow, as with propellers and high speed pipe lines, but also with high intensity ultrasound. Ultrasound represents a long-neglected method of causing chemical reactions through the process of cavitation.

We have demonstrated that enormous temperatures and pressures are obtainable during acoustic cavitation (> 5000 K and ~ 1 kBar), and the impressive heating and cooling rates (> 2×10^9 K/sec) bring chemical reactivity into energy regimes previously virtually unobtainable by other means. The use of ultrasound for the modification of chemical reactivity and for the synthesis of novel materials will have substantial effects on research in diverse areas of chemistry. Our recent discovery of a bench-top synthesis of pure amorphous iron, for example, reinforces this point.

Related phenomena occur with cavitation in liquid-solid systems. Near extended surfaces, cavitation induces an asymmetric bubble collapse that generates a high speed microjet of liquid directed at the surface. This can induce pitting of the surface and increase surface susceptibility to corrosion. In powder slurries, such microjet formation cannot occur. We have recently discovered, however, that cavitation and the shockwaves it creates can accelerate solid particles to extraordinary velocities (up to half the speed of sound!). The resultant interparticle collisions are capable of inducing dramatic changes in surface morphology, composition, and reactivity; they can even induce melting of refractory metals with peak temperatures on impact of ~ 3000 K. These events are perhaps closely related to the chemical effects of friction and other tribochemical (mechanochemical) reactions. In the area of heterogeneous sonochemistry, we have used ultrasound to make dramatic improvements in both catalytic and stoichiometric reactions and have developed a detailed understanding of the changes in surface morphology and composition that are responsible. We have found increases in the catalytic reactivity of nickel, for example, of nearly a million-fold!

Our interests as a participant in this program will focus on the chemical and physical effects on metal surfaces of cavitation, induced by ultrasound, by turbulent flow, or by high speed liquid jets. These three techniques of generating cavitation are all related, and of substantial technological importance. Our prior expertise with acoustic cavitation are well developed. In addition, we have recently begun a collaboration with Dean Technologies, Inc., to examine the chemical effects of high speed liquid jets.

We will be concerned with the mode of defect creation during such interactions as well as the change in surface reactivity. Special emphasis will be made on technologically important metals, especially iron or aluminum alloys. Our studies will embrace a three-fold methodology: the measurement of effects of cavitation on surface reactivity, the examination of surface morphology by SEM and Scanning Probe Microscopies, and the determination of surface composition by Auger and x-ray photoelectron spectroscopies. As in our prior studies, we expect to make heavy use of the Center for the Microanalysis of Materials in the UIUC Materials Research Laboratory. Further collaborations with the Gewirth group on STM and AFM characterization of cavitated surfaces are also expected.

RELATION OF SURFACE ADSORPTION TO CORROSION

A. Wieckowski

The present program would be expanded in the following specific areas.

1. Chloride co-adsorption with corrosion inhibitors.

According to many investigators, chloride adsorption is the major cause of pitting corrosion. Once on the surface, chloride coordinates metal sites, prevents passivation and accelerates metal dissolution. Corrosion inhibitors displace surface chloride and activate the protection mechanism. To test this theory, or to determine its applicability range, we propose to carry out detailed investigations of chloride co-adsorption with selected inorganic and organic corrosion inhibitors. The radioactive labeling method developed in my laboratory is the most direct, and probably the best *in situ* technique to study the corrosion-relevant, adsorption (co-adsorption) processes. Using ^{35}Cl-labeled chloride, we will collect information on the surface population by chloride as a function of the electrode potential, adsorption (desorption) time and solution/surface composition with respect to corrosion inhibitors. If films are formed on the metal surfaces, the film composition will be determined by the use of ultra-high vacuum (UHV) depth profiling procedures and Auger spectroscopy. The inorganic inhibitors proposed to be tested are chromate and phosphate. The organic inhibitors are pyridine, nicotinic acid, salicylic acid, HEDPA phosphonate. The data will be presented as isotherms: G vs. E and G vs. c, where G is the surface concentration, E is the electrode potential and c is the bulk concentration of the inhibitors. Surface concentration of the inhibitors will, or may, be known from the parallel or correlated radiochemical measurements. Thermodynamic parameters of adsorption will be derived from the isotherms.

2. Anodic oxide growth on stainless-steel single crystal electrodes by synchrotron X-ray.

Here, we propose to expand our research with single crystal stainless-steel samples to accommodate synchrotron X-ray analyses of reacting interfaces. Contrary to LEED, surface crystallography by synchrotron X-ray can be done *in situ* and as a function of the electrode potential. If single crystal phases are preserved upon early stages of electrooxidation, a full crystallographic analysis can be available which, when combined with the EXAFS data, will provide unique surface and subsurface information of outstanding corrosion relevance. The inverse space information will be correlated with Gewirth's AFM-type local information and may add to his XANES initiative.

3. Diffuse infrared (IR) work with powdered electrodes.

Using diffuse infrared (IR) to learn about molecular-level surface chemistry of adsorbed inhibitors at the reacting interfaces may prove simpler than using IRRAS. We propose to prepare powdered samples of 316 stainless steel and study surface interactions of the corrosion inhibitors specified above in collaboration with Paul Bohn.

SOLID-LIQUID INTERFACES

I. K. Robinson

The object of this program is to start to understand, at an atomic level, the formation of structures at interfaces between crystal faces and liquids or ions dissolved in liquids. This will include the possibilities of electrochemically-driven or stabilized processes, corrosion interfaces, interfaces during crystal growth, and interfaces generated during chemical modification. The plan is to examine these systems *in-situ*, in contact with macroscopic quantities of the liquid. The principal attraction of the APS undulator is that it offers large flux at higher energies, above 20 keV, where several mm of liquid can be penetrated without drastic attenuation.

The development of techniques to explore the liquid-solid interface using x-rays will open an entirely new field of study of extremely important scientific and engineering issues. Illustrative of those which we will focus our attention on are the following.

Corrosion

The natural extension of the study of oxygen adsorbates on single crystal metal surfaces is to understand the various stages of oxidation. The later stages can be followed by a continuation to high oxygen pressures. Corrosion of metal crystals by liquid electrolytes will be studied *in situ* in an analogous way to chemically modified surfaces by variation of ionic strength, pH and applied potential. The first systems to be studied will be Cu, as an example of a near noble metal, and Al which is very reactive and whose passivation is an important technological process.

It is expected that single crystals will be employed as much as possible because the most specific information about structure and bonding would then be available. It is likely for some systems that no memory of crystal orientation will be retained; here, polycrystalline substrates would be satisfactory, and x-ray reflectivity measurements would be the most valuable. X-ray reflectivity is the surface diffraction analog of small-angle scattering and is likely to become a widely used technique for interface problems where atomic-level information is unimportant or irrelevant.

These studies are closely linked to other activities of the program on Molecular Properties of the Solid-Liquid Interface and Their Relation to Corrosion and active interactions will be developed to make use of the complementary techniques.

Electrochemical Interface

X-ray diffraction experiments on electrochemical interfaces under potential control have recently been demonstrated by the groups of Toney (IBM) and Ocko (BNL). Reversible structural changes both in the crystal electrode surface and in the electrolyte have been resolved. A number of the difficulties encountered in these early experiments were associated with the thin layer geometry and containment membrane used by both groups: the small electrolyte volume was prone to impurity or gas contamination, and limited diffusion of ions can lead to resistance problems. By using harder 20 keV x-rays and a cell of 3-5mm thickness, we will be able to avoid these problems.

We plan to carry out fundamental studies of low index crystals of Pt, Au and Ag in simple electrolytes to understand their structures and how they change with applied potential. Morphological rearrangements analogous to roughening and faceting can be followed by the x-ray crystal truncation rod method. By introducing heavy ions into the electrolyte and enhancing the contrast by anomalous scattering methods, we will investigate their height distribution above the electrode to verify the structure of the Helmholtz doublelayer that is believed to form. Electrodeposition in the single layer (UPD) and bulk regimes can then be studied as well.

Collaboration with the Corrosion Community

Several of the PIs are internationally prominent in corrosion and its underlying electrochemical science and engineering. These individuals will play a key role in guiding the scientific impact of this program toward significant applied corrosion problems. The participation of these experts should also serve as a beacon for attracting additional new corrosion talent to the program through faculty recruiting.

In order to network the program with the corrosion community at large, we propose to set aside funds for support of visiting scholars from industrial, governmental and educational laboratories. The funds will cover research costs associated with visits to the University of Illinois of about 3-6 months duration. The purpose of the exchange is for visiting scholars to develop proficiency with the methods of study developed by the PIs in this program so that they can return to their home institution with increased skill.

Since the late 1970s, the DOE Corrosion Contractors have met annually at a site of one of the contractors in order to present recent advances and discuss how the DOE corrosion program could be tuned. We propose to offer to host a meeting of DOE Corrosion Contractors on the UI campus as soon as possible.

Some but not all of the PIs attend corrosion conferences on a regular basis. To encourage an increased visibility in the corrosion community, we plan to set aside funds for the purpose of travel to scientific meetings where corrosion research is discussed. While the details of distribution of such funds is yet to be agreed upon, we plan to give highest priority to situations where the PI is taking a lead in organizing a corrosion conference or symposium.

D.2.b SYNCHROTRON BASED SCIENCE OF NEW MATERIALS

The Materials Research Laboratory at the University of Illinois recognizes the great scientific and engineering opportunities presented by the ability to apply the techniques of synchrotron to materials. We would like to expand our programs in the area of Synchrotron Based Science of New Materials and Novel Characterization Techniques. The proposed research is based on science which has been initially undertaken at the NSLS X-14 beamline, which the Materials Research Laboratory shares with Oak Ridge National Laboratory. Development of the proposed themes will require the higher brilliance and the timing structure of the Advanced Photon Source. Much of the present research program is being supported by discretionary funds of the MRL and require a more stable funding base for its full development.

In the following section brief research summaries are given for the MRL/DOE supported investigators.

H. Chen will pursue studies of the local atomic structure of alloys and the properties of defects in solids using diffuse scattering and small angle scattering. The high brilliance of the APS allows a major advance in determining the contributions due to inelastic scattering and the timing structure allows the dynamics of phase transitions to be determined. T.-C. Chiang and H. Chen will study phase transitions at surfaces, the structure of surfaces and interfaces in CVD and MBE grown structures using surface scattering techniques. Similar techniques will be applied to the study of corrosion and the electrochemical interface in a co-operative program with I. Robinson. T.-C. Chiang will focus his attention on surface scattering methods applied to interfaces and surfaces in semiconducting systems with particular attention paid to surface and interface reconstructions. In a complementary program I. Robinson will focus his attention on surface scattering techniques applied to surface crystallography of metallic systems, surface phase transitions, and the dynamics of gas mediated surface reactions. These methods will also be used to study the solid-liquid interfaces during crystal growth, chemical modification of surfaces and electrochemical reactions.

The magnetic structure of novel magnetic systems based on the rare earths and on multilayers will be studied by M. Salamon using polarized x-ray beams obtained from the high brilliance APS undulator. These magnetic measurements, which are only possible at the high intensity synchrotron sources will provide more complete information about the magnetic structure of alloys than is possible from neutron sources. Similarly, the high brilliance of the APS will allow development of milli-electron and micro-electron volt energy resolution x-ray scattering and enable the study of inelastic scattering from a variety of excitations in condensed systems.

High energy resolution scattering methods will be used by R. Simmons to study vibrational anharmonicities, the dynamics of liquids and defect dynamics.

Coupling effects in structural transformations will be studied by R. Simmons. These studies will interface with those of D. Viehland who will examine the concurrent ordering and phase decomposition in relaxor ferroelectrics and H. Birnbaum who will study phase transitions in interstitial alloy systems. Strain fluctuations will be studied in the relaxor ferroelectric systems by D. Viehland and in the interstitial alloy systems by H. Birnbaum as these very diverse and previously uncorrelated systems appear to exhibit closely related behaviors.

A number of the proposed programs will make use of the excellent coherence of the APS synchrotron beam to study dynamic fluctuations using the methods of Intensity Correlation Quasi-elastic X-ray Scattering, which is similar to laser speckle studies, albeit in the x-ray energy range. M. Weissman will focus his program on developing this method to study glass transitions and the dynamics of glass phases. These studies will have wide applicability as the dynamics of "two level system" transitions are of interest in large number of mesoscopic systems. These x-ray speckle techniques will be applied to the dynamics of surface processes by I. Robinson and to hydrogen density fluctuations by H. Birnbaum. Since this method is applicable to structural fluctuations characterized by a very wide range of energies, it is expected that it will achieve a wide range of applications as it becomes developed.

A different approach to the study of interfaces and surfaces will be taken by G. Girolami, and R. Nuzzo who will apply the methods of EXAFS, NEXAFS, and SEXAFS to studying and developing chemistry at the interfaces and surfaces. Ceramic film growth processes by hybrid CVD and MOCVD techniques will be studied *in situ* to understand and develop novel growth methods.

The proposed program is a very comprehensive effort to apply synchrotron science to develop an understanding of new and novel material systems and to develop new materials having a controlled structure and designed for particular properties. It is possible only because the opportunity to apply synchrotron science at the APS has excited the interest of a number of presently funded MRL/DOE scientists (Chen, Chiang, Simmons, Robinson, Birnbaum, Girolami, and Nuzzo) who will re-direct a part of their program to utilize this facility. They will receive some additional funding to enable them to extend their programs into these new areas. Additional funding will also enable DOE support to be extended to a number of new scientists (Salamon, Viehland, Weissman) who will receive sufficient funding to allow their programs to be developed into reasonable efforts.

The advent of the APS and other modern synchrotron sources has presented the DOE, the MRL, and the University of Illinois with an opportunity to revitalize the entire field of Scattering Science. The University has recognized this opportunity and has made a major appointment in the Department of Physics, Ian Robinson. Additional faculty in this area will be appointed in the Departments of Materials Science and Engineering and Physics. The MRL is making a major commitment of its discretionary funds in support of this area of science and for the construction of the APS UNI-CAT sector. We will be subsidizing the salaries of about four faculty in this area of research for two years to assist the departments in obtaining the funds necessary to hire the additional faculty.

The MRL will operate its share of the UNI-CAT sector as an integral part of its Central Facilities and hence the opportunity to utilize these methods will be made widely available. We also will be educating a new generation of scientists and engineers schooled in the very powerful techniques of Scattering Science.

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D.2.c STRUCTURE AND PROPERTIES OF NANOPHASE MATERIALS

OVERVIEW OF THE PROGRAM

Advances in materials science are often driven by discoveries of new methods to synthesize and process materials with unique structures and properties. In the past several years, an explosion of activity has occurred in research directed toward synthesizing and consolidating materials with nanoscale dimensions. Most of this work has been concerned with compositionally modulated thin-film structures because of their significance for electronic, optical, and magnetic devices. More recently, interest has developed for synthesizing nanoscale structures in three dimensions. This has resulted in a renewed interest in clusters and the new field of cluster assembled materials involving physical chemists, condensed matter physicists and materials scientists. In this initiative we propose a broad range of research on the properties and structures of consolidated materials with nanometer particle or grain sizes, denoted as "nanophase" materials. The tremendous growth of interest that has developed in these materials is motivated by the wide variety of research opportunities that they afford for advancements in science and engineering. These opportunities fall into four categories.

1. Nanophase materials are unique in that large fractions of their atoms, ≈ 5-30%, are located on grain or interphase boundaries. A detailed understanding of the short range order associated with this structure has remained somewhat elusive, but it must resemble, to some extent, that of high angle grain boundaries. Consequently, the density of nanophase materials, particularly in the grain boundary region, must be less than their bulk counterparts. The short range order at the boundaries, correspondingly differs from that in the bulk, or for that matter, from that in amorphous materials where the density is generally reduced by only a few percent. Consequently the properties of these materials are expected to be different from those of their bulk counterparts. Indeed, this has been shown to be true in several cases. Thus, nanophase science offers opportunities for developing new materials with unique and potentially useful properties.

2. Nanophase materials are of interest because of their small grain size, per se, as many properties of materials depend strongly on grain size. Among mechanical properties, the yield strength depends on grain size as $d^{-1/2}$ (Hall-Petch relationship), the creep strain rate as d^{-3} (Coble creep), and densification rates during sintering as d^{-4}, where d is the grain diameter. Whether these relationships can be extrapolated to nanometer sized grains, however, is unknown. Small grain sizes are also important for reaction kinetics, since diffusion distances are short and chemical activities high. These properties are important for non-equilibrium processing of metastable phases, as processing temperatures can be kept low.

3. Nanophase materials can be used to study properties that are not readily accessible by other means. Owing to the large fractional volume of grain boundaries, they are particularly suited for studying grain boundary properties. Calorimetry and neutron scattering, for example, can be employed to probe vibrational and other thermodynamic properties of the boundaries. X-ray diffraction can be used to observe interfacial reactions between particles or grains of different phases. These techniques, which yield volume averages, are not useful for studying boundaries in larger- grained materials.

4. Nanophase processing can be employed to synthesize new composite structures on a nanometer length scale. Moreover, as the fraction of atoms in grain boundaries is large, "pseudo" alloys can be formed where atoms on one grain are nearest neighbors of atoms on another. Since the individual particles are separately formed and then consolidated by mechanical means, many of the thermodynamic and kinetic constraints encountered during standard processing of alloys are relieved. These new structures can also be utilized for investigating fundamental properties of materials, much in the way that thin film structures and superlattices are employed for studies in two dimensions.

A number of methods are now available to synthesize nano-sized materials, with the choice

being dictated by the specific applications and materials of interest. Sol-gel methods, for example, are promising for synthesizing ultra-fine grained ceramics, particularly in forming electronic films, since the use of nanophase precursors eliminates the need for high temperature calcination. Other methods, such as high energy ball milling, laser ablation, and hydrothermal pyrolysis are also being explored as outlined below.

For our research, we will employ the method of inert gas condensation combined with *in situ* powder compaction, a method originally developed by Gleiter and co-workers at Universität der Saarlandes. Inert gas condensation has several advantages for the basic research program proposed here. First, the synthesis of the ultra-fine particles and their compaction can be performed in an ultra-high vacuum system, ensuring that the particles and their surfaces are free from impurities. The inert gas condensation method is also remarkably versatile. Since we have developed, at the University of Illinois, magnetron sputtering techniques for producing the small particles, virtually all metals, alloys and intermetallic compounds can be synthesized.

Finding general methods for producing ceramic powders has proved somewhat more difficult, however, we have now developed procedures to synthesize several oxides. e.g., TiO_2, ZrO_2, Al_2O_3, Y_2O_3, NiO and MgO, and many others will certainly be synthesized as the technique is further developed. We have also devised methods for producing composite nanophase materials by simultaneous magnetron sputtering of the composite constituents. These composites can be made remarkably homogeneous since the particles are mixed within the turbulent flow of the gas carrier, rather than by mixing of collected powders. To date, we have fabricated composites of TiO_2/Y_2O_3, and Zr/Al. We expect that the synthesis of all metal composites will be routine with our methods. Lastly, inert gas condensation using magnetron sputtering produces sufficient quantities of material for most research requirements. Typically 0.1-0.3 grams are produced per hour. These quantities are sufficient for mechanical property tests, and for calorimetry and neutron scattering measurements, among others.

Despite the enormous research opportunities afforded by nanophase materials, progress has been somewhat slow since the original paper by Gleiter describing these materials in 1984. Some reasons for this derive from the difficulty in producing nanophase materials, the high cost of this research, and the large number of possible avenues along which this research can lead, with each area requiring the expertise of that specific subject. Few individual investigators have the facilities and resources to construct nanophase processing systems for a single purpose. The modus operandi in the past has been that a single source (usually Gleiter) provides samples to a number of researchers for "one-time" experiments. This has led to many unconfirmed and incomplete results and poor feedback between experimenter and specimen synthesizer. The MRL, however, is ideally suited for this type of interdisciplinary research. This initiative thus combines the research interests and talents of ten principal investigators. In addition, it builds on the expertise and developments garnered from four years of nanophase research in current programs in the MRL.

The proposed research comprises a broad investigation of the synthesis and processing, structure, and properties of both monolithic and composite nanophase materials. An outline of research, showing the interrelationships between the various aspects of the work, is schematically diagrammed in Fig. 1. Averback will explore various gas phase synthesis techniques for the production of controlled nanophase metallic and ceramic systems. Since the particles can now be transported by a forced flow system, rather than by the uncontrolled convection currents in the original Gleiter design, it is possible to carry the nanoscale particles through a reactor for thermal and/or chemical treatment and then on to a compaction system. Particularly exciting is the opportunity to divert a small fraction of these particles into a UHV transmission electron microscope (TEM), which is now operating in the MRL, without exposing the particles to air. Gibson will characterize these particles in the TEM for structure, composition and size and provide critical feedback for the synthesis. This loop of synthesis, reactor and particle characterization carries synthesis and processing of nanophase

from art to science, which here-to-fore has been lacking. As shown in the diagram, the particles are then consolidated. Averback will experimentally investigate sintering and sinter-forging processes, while Gibson will investigate the initial stages of sintering directly in the UHV TEM. These experimental studies will be supported by interactive modeling of the consolidation process by Sofronis who will apply micromechanical theoretical methods to the sintering of powder compacts. The consolidated, bulk samples will then be characterized in the Center for Microcharacterization of Materials and then made available for investigations of various properties of these materials. The diagram depicts how the various relationships between synthesis, structure and properties are developed.

At the same time, a parallel effort will be made to explore the alternative methods of attrition milling (Zangvil) and colloidal (Zukoski) processing for the ceramic systems.

Overview of Nanophase Research

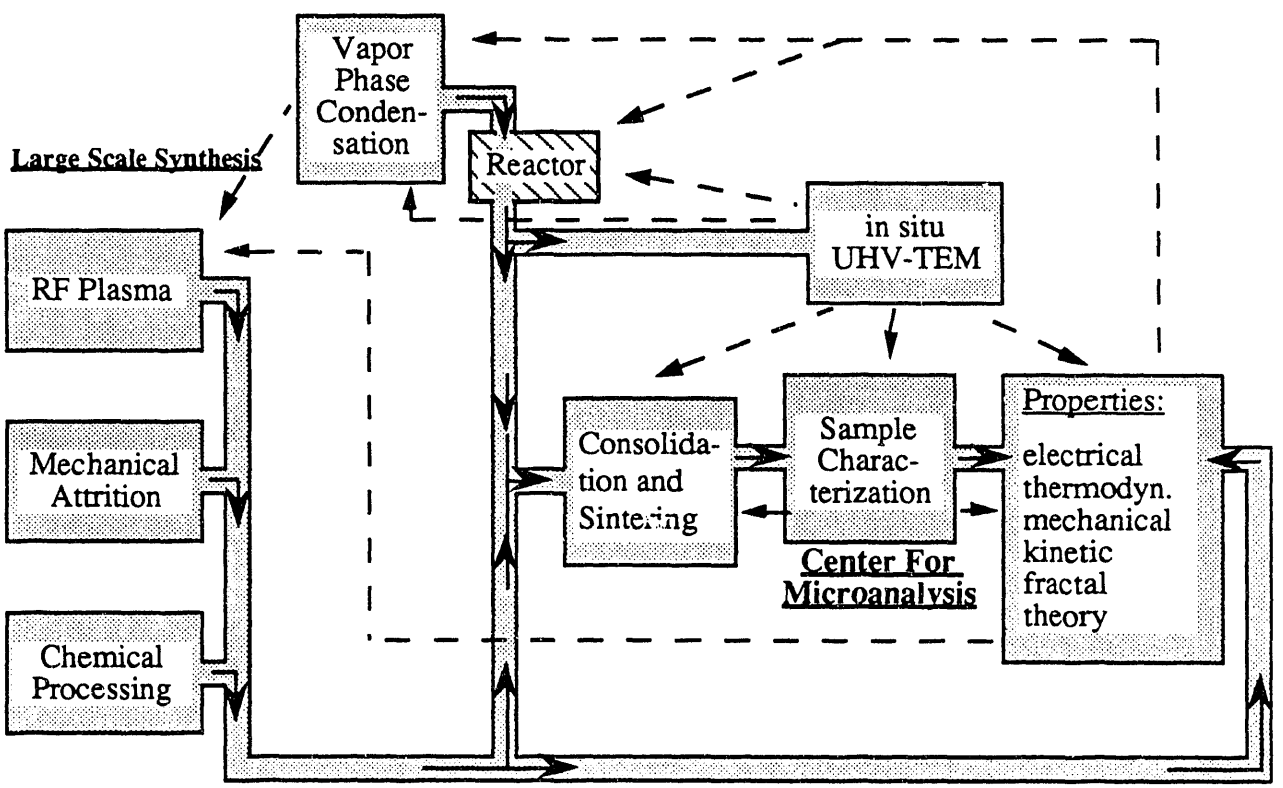

Fig. 1. Schematic diagram illustrating the organization of the nanophase research program. Solid arrows indicate flow of nanophase material; dashed arrows indicate flow of information.

The proposed research comprises a broad investigation of the structure and properties of both single phase and composite nanophase materials. A major focus of the work is the elucidation of the structure and properties of grain boundaries. Averback will investigate kinetic properties of nanophase materials of all types, focusing on superplastic deformation in ceramic oxides, intermetallic compounds and metallic glasses. Included in these studies are

fundamental tracer diffusion experiments. He will also take charge of developing the processing capabilities required by the group of investigators. Birnbaum will investigate the thermodynamics of grain boundaries in a number of systems using low temperature heat capacity measurements and neutron scattering determinations of the total phonon density of states. These measurements will provide information about local phonon modes in the grain boundaries. The effect of hydrogen on grain boundary properties is also of interest in this program. Complementary studies of the thermodynamic and kinetic properties of grain boundaries will be performed by Granato. He will be using ultrasonic measurements of the longitudinal and shear wave velocities to determine the elastic constants. These studies will provide necessary data to test various models of grain boundary structures. Adams will perform atomistic level simulations using molecular dynamics and molecular statics to relate atomistic processes to macroscopically observable quantities. He will consider the structure, mechanical properties and thermodynamics of various systems. A unique feature of this work will be determinations of the structure of amorphous nanophase materials. These materials have been produced but determination of their structures by direct experimental means is proving difficult. Shang will utilize nanophase ceramic composites to investigate basic aspects of transformation toughening. He will be concerned with the effects of particle size, volume fraction of transformable phase, and applied stress on the stability transformation toughening particles, such as ZrO_2 in Al_2O_3. Salamon will exploit the ability to synthesize binary nanophase materials to investigate manifestations of fractal behavior in various physical phenomena. These studies will include the effect of fractal dimension on magnetic and elastic properties, and the scaling behavior of tensile strength in percolation networks. The opportunity to observe fractal behavior directly is exciting as most "observations" of fractal behavior in three dimensions derive from computer simulations. Sofronis will apply the techniques of micromechanical modeling to studies of the sintering mechanisms and kinetics of the nanophase systems and to the response of nanophase composites to applied stresses under conditions where mass transport as well as deformation has to be taken into account.

Although the research interests represented above are often diverse, every aspect of the proposed work requires extensive collaboration among PI's and heavy involvement of central facilities and national centers. From fabrication, through characterization with scattering probes, to mechanical and magnetic measurement, and inelastic neutron scattering, this project cannot succeed without the combined expertise of the proposed research group. Together, however, this group will comprise a unique effort focusing on the synthesis and properties of materials that are tailored with particular nanoscale structures. In a real sense, this work complements the fabrication of nanostructures one-by-one by lithographic methods. It promises bulk materials--perhaps even structural materials--with unique properties that arise from nanostructural control.

D.3 RESEARCH SUMMARIES FOR PROPOSED NEW PROGRAMS

In the following section we would like to present several new programs which have been developed in the past few years. these have been chosen from a much larger number of efforts proposed for support to the MRL/DoE.

In the Physical Properties of Materials we can offer the following programs:

a. Molecular Tribology of Complex Liquids and Additives. - S. Granick
b. Complex Materials: A Nonlinear Science Approach - A. Hubler
c. Field-Responsive Effects in Conducting Polymers and Organic Charge Cransfer Solids - D. Campbell

In the Synthesis and Processing of Novel Materials we are offering programs in the following research areas:

d. Relationship Between Surface Chemistry and Film Properties in Chemical Vapor Deposition. - R. Masel
e. Fundamental Studies of the Electromechanical Behavior of Relaxor Ferroelectrics. - D. Viehland

D.3.a MOLECULAR TRIBOLOGY OF COMPLEX FLUIDS AND ADDITIVES

STEVE GRANICK

Objective

The objective of this research is molecular-level understanding of the flow dynamics of complex fluids and additives in intimate contact with solid surfaces, with particular emphasis on understanding tribology.

Relevance to the DOE Mission is the need for rational design in this field of great energy cost to the nation.

Approach

The approach will be experimental and will involve using a unique surface forces apparatus that has been developed at the University of Illinois [1-3]. Specifically, the research involves (1) Transport properties of aqueous fluids under extreme confinement; (2) Effects of lubricant additives on friction and lubrication; (3) In the long term, extension to questions of corrosion, earthquake prediction, and disposal of chemical and nuclear waste. No duplication is believed to exist with the research of J. Israelachvili (see section below).

Background

It is of increasing urgency to understand friction and lubrication when the thickness of the liquid film is comparable to the size of the molecules themselves -- a range of film thickness where classical continuum considerations do not apply. This situation describes an enormous range of energy-based applications in the world today. Many machine components operate with an effective lubricant film thickness of sub-micrometer dimensions; examples include gears, bearings, cams, piston rings, and traction drives. Lubrication additives comprise a large part of the engine oils and fuels sold commercially, yet the underlying mechanisms of performance are hardly known. Still other instances of practical import involve the motion of solid bodies separated by aqueous media. It is easy to take friction, wear, and tear for granted. Yet the preventable cost to the nation is arguably many billions of dollars each year.

Tribology in the US. has traditionally been an empirically-based discipline. It has been pursued largely as a branch of engineering mechanics and of fluid mechanics, and the search for molecular and atomistic interpretation has been relatively neglected. The need for sustained improvements in tribology performance requires, however, fundamental understanding. This is taking a fundamentally new, urgent cast, spurred by technological challenges and competition.

In surveying the situation, one is struck that a major impediment to progress is the paucity of direct, experimental information concerning events on a microscopic scale while solids are engaged in sliding contact. With macroscopic approaches one can measure, for example, the friction coefficient (and other global properties), but such measurements are often impossible to interpret from a molecular or mechanistic point of view. Modern surface analytical techniques and spectroscopies can obtain molecular resolution, but these methods require that the surfaces be examined before and after sliding has occurred, or that the rate of sliding be unrealistically slow. Understanding tribology calls for methods to probe the structure and dynamics of complex fluid lubricants during the process of flow itself.

This proposal is specifically concerned with understanding the nonequilibrium physical behavior of lubricants and additives. It is focused on understanding, on a molecular basis, the deformation of these complex liquids when confined to films comparable to the size of the molecules themselves. How do dynamical processes under these extreme conditions of confinement depend on the film thickness, the rate of deformation, the frequency of deformation? Can rational understanding be obtained, with predictive power, about the conditions under which wall slip may occur? How are these conditions related to the strength of adsorption to the solid surfaces? Do entanglement effects (which dominate transport properties in the bulk, for molecules of sufficient size), determine frictional dissipation between sliding surfaces? How is the transport of an ultrathin lubricant film related to the rheology of this same fluid when the film is thick? It is clear that one needs to think in new ways about dynamical effects in ultrathin interfacial films [4]. These new notions do not reflect intuitive extrapolations of bulk properties.

NEAR-TERM PROJECTS

Transport properties of confined aqueous fluids. One of the most significant aspects of aqueous media is understanding the transport properties of confined fluids. This problem is central to understanding how to apply aqueous media for lubrication. The environmental advantages of using aqueous-based lubricants are self-evident. It is also significant for corrosion and for the flow of fluids through porous media such as geological formations. While classical double layer theories describe the static surface forces in aqueous media, but it is fair to say that nothing definitive is known yet about dynamics, except in the continuum limit.

Long experience shows that in probing properties under confinement, kinetic properties are more sensitive to structural changes than equilibrium, thermodynamic measurements. Critical outstanding questions which will be studied include the following. First, studies of the frequency-dependent relaxation times and associated friction, normal forces, and elasticity will be made, as a function of strain, in the following regimes: (1) Linear response (it is noteworthy that this involves displacements <0.1 nm); (2) Onset of nonlinear response; (3) Strongly nonlinear, nonequilibrium response. The relevance of these three regimes is, respectively: (1) To understand the molecular origin of static friction phenomena; (2) To determine the longest relaxation times of the system and to characterize nonequilibrium phase transitions that may be implicated; (3) That strongly nonequilibrium flow is believed to underlie typical dynamic friction phenomena. The above issues will be investigated through measurements of the effective complex viscosity. Experimental variables of particular interest will include the rate of deformation and the chemistry of the ionic species that are present.

In addition to the effects of ionic species when they adsorb, the behavior of micellar solutions is of evident interest. Little is known even about the equilibrium organization of these important fluids in confined geometries. Less is known about their behavior under flow. The typically anisotropic structure of these fluids, and the sensitivity of the phase behavior to deformation, have interesting possible

ramifications for influencing friction and lubrication.

In all of these experiments, of particular significance is that confinement-induced elastic responses will be considered, in addition to viscous responses. It is well known that a fluid possesses viscosity; measurements of viscosity are made daily by lubrication engineers. Less well appreciated is that when the applied frequency (or shear rate) of deformation exceeds a system-specific relaxation time, the fluid microstructure can no longer support viscous deformation over the time scale of the experiment, and the fluid also possesses elasticity. The capacity to measure both elastic and viscous effects, over a wide range of shear rate, distinguishes this experimental approach from all other related approaches.

The experiments are ready for immediate implementation. The usual protocol and precautions developed in earlier studies by this laboratory (use of ultra-pure fluids, laminar flow cabinets to avoid dust particles, and so forth) will, naturally, be employed throughout.

Effects of lubricant additives. The effects of additives on flow is a vast area of major scientific and technological importance. The addition of only 0.5% of common additives has major effects on the efficacy of a lubricant's performance. Our frank discussions with industrial scientists reveal that commercial oils typically contain over 100 additives. There are strong sentiments both pro and con concerning the optimality of the diverse options. There is no unanimity regarding the molecular criteria of good performance. It is the area concerning which the lubrication industry is the most secretive.

The approach that we intend to take is well suited to clarify these obscure questions. The instrumental capability of driving these systems with a broad range of deformation amplitude (<0.1 nm to >10 μm) is particularly relevant. The resulting range of shear rate is 10^{-2} to 10^{6} sec^{-1}. Two principal problems are proposed for initial study. First, the interfacial transport properties of oils to which have been added small quantities of antiwear additives (typically, highly polar molecules) and of viscosity modifiers (typically, flexible adsorbing polymers) will be studied. Both these categories of additives are expected to adsorb strongly and thereby to modify the chemical composition of the sliding surfaces. They are expected to have very sluggish microscopic dynamics; their conformational transitions are expected to be kinetically hindered by the large energy barriers associated with adsorption. These properties are expected to depend strongly on both the chain length and the density of adsorption sites. We hypothesize, accordingly, that the performance of lubrication additives must depend, in large part, on: (1) Surface segregation; (2) The extent of structural rearrangement that can be accomplished over the experimental time scale; (3) The resulting linear and nonlinear rheological response of the adsorbed multi-component layers. We submit that a molecular-level understanding of these types of issues is required in order to develop understanding of tribology that will have predictive power.

Secondly, the interfacial transport properties of fluids that contain amphiphilic molecules will be studied. Such molecules are prone to self-assemble into ordered surface structures. As they adsorb, such additives will modify the surface chemistry, but at much shorter range than the lubricant additives discussed in the previous paragraph. Since typical lubrication formulations contain additives of both these types, these experiments should set the stage for understanding the role of each type of additive by elucidating the relative importance of various alternative effects. The consequences of competition between adsorption and micelle formation in solution will be of particular interest. It would be reasonable to expect shear-induced desorption, but prior studies directed towards this question are not believed to exist.

In summary, considering the paucity of prior work in this area, we may expect unanticipated results that will warrant being followed up. The field of tribology is a young one, and many key questions remain to be posed as well as answered, particularly at the molecular level. Opportunities for improved lubrication through development of new lubricants (liquid crystalline lubricants; lubricants of controlled extents of branching; lubricants for high temperature applications) which are based on the molecular level

understanding developed by the proposed studies, are numerous.

Comparison with DOE research at other institutions

Just as the electron microscope and the scanning tunneling microscope (STM) are used by different investigators to different purposes, and important advances of various kinds have been made using these instruments, so the surface forces apparatus is now appreciated as a fundamental instrument for studies of the solid-liquid interface. Around the world, it is finding versatile use in surface and colloid laboratories.

The research in this proposal differs in substance and in instrumental capability from that of J. Israelachvili (UCSB), who is already supported by the DOE. On the instrumental side, the present instrument, being based on AC rather than DC techniques, measures the complex viscoelastic modulus, not just the viscous portion of it. In addition, there is a significant advantage of sensitivity (10^{-9} N force resolution), and a significantly greater versatility in the chemical composition of the solid surfaces that can be studied using the Illinois instrument. On the programmatic side, we emphasize the substantially different thrust of research direction: the concern, here, with lubrication additives and with the tribology of aqueous systems.

Nor is duplication believed to exist with the tribology program at the Lawrence Berkeley Laboratory (LBL). The research proposed here is directed towards tribology of macroscopic-sized bodies, lubricated by fluid, which is substantially different from the thrust at LBL.

FUTURE DIRECTIONS

There are many other applications and extensions of the work proposed above. Of particular interest is that it should be possible to build on these studies to understand other environmental and energy problems of national concern. In particular, geological formations consist of porous media permeated by groundwater and other fluids. Therefore, to understand the motions and relaxations of fluids in ultra-thin spaces may help to understand friction and fault formation in geological zones. This, in turn, is relevant to predicting earthquakes [5]. The same argument applies to understanding the flow rates, through bedrock, of chemical and nuclear waste.

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D.3.b COMPLEX MATERIALS: A NONLINEAR SCIENCE APPROACH

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Motivation and Research Concept

"Complex" materials represent one of the most significant challenges for materials science in the twenty-first century. Although hard to define in the abstract, such materials are easily recognized in specific cases and are ubiquitous in advanced technological applications. Important examples include liquid crystals, composites, blends, gels, polymers and other macromolecules (including bio-molecules), glasses, ceramics, mesoscopic systems and other novel electronic structures, and granular materials, as well as "shape-memory" alloys and other ``smart" or "adaptive" materials. Among their common characteristics:

- Disordered, amorphous, quasi-periodic, and fractal spatial structures, widely different from the ordered periodic crystals of simple metals;

- The existence of many metastable configurations, nearly degenerate in energy, so that the dynamics becomes enormously complicated, and indeed the system may never approach conventional equilibrium;

- Inherently nonlinear responses to external perturbations, so that standard linear response theory is useless; and

- The existence of "emergent coherent structures" (e.g., dendrites in solidification) and the importance of pattern formation and competition (e.g., mesoscopic grains in metals).

These characteristics are typically impossible to explain and model within conventional linearized approaches to near equilibrium systems.

Fortunately, during the last two decades, the new interdisciplinary subject of "nonlinear science" has made tremendous inroads into

previously intractable nonlinear phenomena. For instance, within the area of dynamical systems, the theory of "deterministic chaos" has provided an entirely new paradigm for interpreting complicated, inherently nonlinear responses to external temporal perturbations. Responses previously thought to be random can now be described in quantitative, deterministic detail. Similarly, the theories of "solitons", and more generically "solitary waves", offer novel perspectives and a much deeper understanding of nonlinear coherent structures in plasmas, fluids, and solids. Further, the mathematical concept of "fractals" and the resulting developments (including the theory of wavelets) permit the quantitative treatment of objects composed of structures on (perhaps infinitely) many scales.

The goal of the "Complex Materials: A "Nonlinear Science" Approach" Program is to apply the powerful new concepts and techniques of nonlinear science to a variety of real materials science problems involving complex materials. In the specific projects discussed below -- which are meant to be illustrative rather than comprehensive -- we propose to consider materials which are produced under the influence of strong nonequilibrium forces, or which are maintained under conditions far from equilibrium by being exposed to large fluxes of heat, electric current, or other flows. We will show how the ideas of deterministic chaos lead naturally to new forms of spectroscopy, both in scattering studies to determine spatial structures of complex materials and in resonance spectroscopy to determine their temporal response. We will demonstrate that the concepts of nonlinear science can also usefully be applied to novel complex materials that appear to be adaptive and to show some features of self-repair. The ultimate aim of this research is to produce a predictive, microscopic interpretation for use in modeling complex materials relevant for technological applications.

Specific Near-Term Thrusts

- Scattering Science and Spectroscopy. Complex materials – such as amorphous solids produced far from nonequilibrium – typically exhibit short-range spatial order only. Thus conventional techniques, using nearly monochromatic sources, lead to diffuse scattering patterns. Recently, it has been shown that, in the case of a one-dimensional array of scatterers with short-range order only, it is possible to obtain a sharp diffraction peak *if the incoming wave is "chaotic."*[1] This result suggests possible novel *spatial* scattering methods using chaotic sources for amorphous materials and other short range order materials. Similarly, materials with nonlinear internal dynamics (such as spin glasses, Josephson junctions, and realistic molecular dynamics in general) react to certain aperiodic driving forces with much greater more sensitivity than to sinusoidal perturbations.[2,3] This makes it possible to design novel *temporal* spectroscopic methods which take advantage of these intrinsic nonlinearities. Although both these new techniques require considerable theoretical development before their practicability can be assured, they offer extremely exciting prospects for the future of scattering science and spectroscopy.

  As a first step we would design special aperiodic pulses which should make it possible to check models for quasi crystals experimentally. As a second step we propose to determine pulses which allow us to distinguish, with extremely high selectivity, between different types of short range order of amorphous materials. This may be used to falsify models or for quality control in industrial production. In a third step we would include a nonlinear internal dynamics of the scatterers and study optimal pulses for inelastic scattering from amorphous materials.

- Fractal, Adaptive, and Self-repairing Materials. Considerable recent evidence supports the idea that certain types of fractal structures are optimal for diffusion problems, *i.e.* a binary material with given composition has a minimum global thermal or electric resistance if the spatial structure of the density function has a specific fractal geometry.[4] In addition, those fractal structures are stable and stationary: if the material is exposed to a constant flux the system returns to its original structure after a minor external perturbation and the material repairs itself. This should make it

possible to produce and study complex materials which assume a fractal geometry and are self-repairing. Further, the branched nature of fracture dynamics in materials suggests that a hierarchical, scaling -- therefore "fractal" -- approach may be useful in developing a more complete understanding of phenomena such as crack propagation speeds and dynamic instabilities, as well as in developing a "mesoscopic" theory that links the microscopic (atomistic) theory with the macroscopic phenomenological description.

As a first step we would grow dendritic structures in an electric field from binary mixtures and study their electrical properties. In particular we would try to verify experimentally that structures emerge which are stable and stationary and minimize the global resistivity of the system. In a second step we would study thermal and mechanical properties of those structures. In a third step we would explore different production techniques.

- Modeling and Control of Granular Flow. Many significant industrial materials processing problems arise from dealing with non-Newtonian, non-ideal flows. One particularly important case is granular flow, in which the interactions of the individual grains renders the entire dynamics ``complex," in the technical sense of involving many time and length scales. Very recently, it has been shown theoretically and experimentally, that the distribution of avalanches on sandpiles -- a specific instance of granular flow -- can be explained using the concept of ``self-organized criticality." Based on this progress and earlier approaches which model the interaction of sandpiles with external perturbations,[5,6,7] we propose to develop quantitative models for the dynamics of avalanches and to study their response of sandpiles to external perturbations. We then propose to extend these models to the more general problem of aperiodic granular flow dynamics. We will study this problem both experimentally and theoretically, employing models for the prediction of large avalanches and exploring the control of the flow via acoustical vibrations and inhomogeneous forcing. A particular goal will be to apply optimal control to suppress large avalanches. As shown by the strong interest of current industrial partners, this research will have important commercial applications for seeding equipment, grain elevators, and the transportation of powders in chemical plants. On the longer term, it could also have important applications in earthquake research and prevention.

  As a first step we will set up two experiments. In one experiment we will study avalanches in a rotating cylinder; in the second we will study avalanches due to "bridging". In both experiments we will apply vibrations and study the reorganization of the ordering of the grain particles and its impact to the formation of avalanches and other catastrophes. Based on models we will try to predict major reorganizations and avalanches and to control them with external perturbations.

Specific Longer-Term Thrusts

- Chaotic Control. Much of materials processing involves controlling complicated chemical reactions. Recent studies have shown that, in some cases of industrial importance, these reactions are actually deterministically chaotic. With the modern developments in dynamical systems theory, one is able to model and, more importantly, *control* these chaotic reactions, thereby possibly increasing the yield of the end product or reducing the production of undesired by-products. As an example, in extrusion processing, undesired fluctuations arising from instabilities in the flow may be suppressed by applying chaotic control.

- Novel Transport Mechanisms in Complex Materials. Apart from studying the general properties of transport in complex materials -- which amounts to a (substantial) extension of the present work on disordered systems -- there are two specific problems in this area on which we have some preliminary ideas and results. First, we have shown that the application of aperiodic electric and magnetic fields may lead to anomalously large conductivities in complex materials. The aperiodic fields

produce infinite horizon trajectories, an effect that does not appear in the presence of static or sinusoidal fields. These techniques appear to have potential applications to advanced electronic devices. Second, in connection with the study of optimal energy exchange in biomaterials, we have shown that the resonance condition for two *nonlinear* oscillators requires not only a frequency match, but also several additional conditions. This finding will definitely affect the interpretation of transport in biopolymers and may help explain the observed catalytic effects of certain molecules.

Industrial cooperation

Elements of the manufacturing, chemical and pharmaceutical industries have become aware of the urgent need for improved understanding of disordered materials and their dynamical response. New spectroscopic methodologies which take full advantage of short range order and nonlinearities in the internal dynamics could make it possible to produce new materials and to check and improve the quality of existing materials. Scientists from Caterpillar, Dupont, Hitachi, Mitsubishi, and John Deere have visited our laboratory recently. In addition, we have received from industrial partners several unrestricted gifts in support of this research. Starting January 1993, a scientist from John Deere will spend a paid sabbatical in our laboratory.

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D.3.c. FIELD-RESPONSIVE EFFECTS IN CONDUCTING POLYMERS AND ORGANIC CHARGE TRANSFER SOLIDS

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Introduction

In the past decade experimental discoveries of several classes of novel electronic materials -- including conducting polymers, charge-density-wave inorganics, organic conductors and superconductors, "high temperature" (high T_c) superconductors, and most recently "fullerenes" -- have excited researchers and challenged technologists over a wide range of disciplines. At a fundamental level, these materials have helped rekindled theoretical interest in the complex behavior of many-body electronic systems in solid state physics. Many of these materials exhibit such highly anisotropic electronic properties that they can be considered "quasi"-one-dimensional (1-D) (i.e., chain-like) or "quasi"-two-dimensional (2-D)(i.e., layered) substances.

Among these novel electronic materials in reduced dimensions, conducting π-conjugated polymers (such as polyacetylene and the poly-diacetylenes (PDA's)) and organic charge-transfer solids (such as the Bechgaard salts) are particularly significant. Not only do they exhibit the full range of novel behavior, but they also permit extensive "tuning" of the *microscopic* composition and *mesoscopic* structure through chemical substitutions and/or variations in synthetic routes. This flexibility, which arises from the richness of organic chemistry , offers hither-to unheard of possibilities for varying *macroscopic* properties. Hence potential applications for these conducting polymeric and organic materials are incredibly broad and varying.

To understand the potential of these materials in detail, it is essential to recognize that their "reduced dimensionality" leads to several intriguing and unusual characteristics. First, because of the greater relative instability of the "normal" electron gas/Fermi liquid in reduced dimensions, novel "broken symmetry" ground states can occur. These include charge-density waves (CDW's), spin-density waves (SDW's), and bond-order waves (BOW's), superconductivity (both singlet and triplet forms), spin-Peierls states, and both conventional (anti-ferromagnetic) and exotic (parity-violating "chiral spin") magnetic phases. This variety is reflected in an equally rich range of exotic experimental phenomena, from superconductivity through the quantum Hall effect to field-induced cascades of SDW ground states (the "FISDW" phenomenon). Second, reduced dimensionality leads to important and possibly dominant roles for nonlinear "soliton"-like excitations, including "kinks" and domain walls in quasi-1-D materials, "vortices" in quasi-2-D substances, and polarons in both. These two features imply an increased importance for both the coupling of the electrons to the underlying crystal lattice -- the so-called "electron-phonon (e-p) coupling" -- and for the (nominal) band filling ρ, defined as the average number of electrons per site. In addition, in many of these materials, the role of direct electron-electron (e-e) interactions is known to be far more significant than in conventional metals. Third, and particularly relevant for the present proposal, the responses of these materials to external fields can be dramatically different from those of their inorganic analogues. For instance, in the π-conjugated polymers, the photo-induced, photo-absorption (PA) shows the signatures of the solitonic and polaronic excitations (including, in the luminescence, localized triplet excitons), and the third-order optical nonlinearities in certain PDA's are among the highest yet discovered.

One central problem in exploiting these field-responsive conducting polymers and organic solids is to develop a sound fundamental understanding of how changes in the *microscopic* structures affect the *macroscopic* properties. A vital component in achieving this understanding is the development and investigation of theoretical models that capture, as accurately as possible, the subtle many-body effects that exist in these materials.

For the past several years the principal investigator (PI) and his collaborators (chiefly at Los Alamos National Laboratory) have sought to create and study a class of theoretical models that accurately reflect the combined effects of electron-electron (e-e) and electron-phonon (e-p)

interactions in conducting polymers and organic solids. Together with other colleagues, these efforts have helped to formulate and to justify the use of "Peierls-Hubbard" Hamiltonians as unified models for this whole class of materials and to develop novel numerical many-body techniques (Lanczös exact diagonalization, quantum Monte Carlo (QMC) methods) to study these models. These investigations have led to significant contributions to several central issues of the physics of these materials, including: (1) the persistence of BOW's in conducting polymers even in the presence of strong e-e interactions[1], and the general nature of the ground states in quasi-1-D materials at arbitrary ρ and e-e interaction strength[2]; (2) the interpretation of optical absorption spectra from strongly correlated materials[3-5]; (3) the nature of the (long-lived) triplet excitations and their possible role in photo-induced photo-absorption (PA) [5]; and (4) the likely existence of a new (spin-Peierls) phase in certain quarter-filled (ρ = 1/2) charge transfer salts which exhibit the "field-induced spin density wave" (FISDW) states[6,7]. These theoretical results have been coordinated with, and in most cases confirmed by, experimental studies of several groups, including those at Los Alamos, Cambridge University (UK), UC Riverside, Princeton, BellCore, AT&T Bell Labs, and Utah.

In the present proposal, the PI suggests several coordinated theoretical studies that focus on the field-response properties of the organic charge transfer solids and conducting polymers. In each of these two classes of materials, the studies will focus on one broad class of experimental phenomena, with the aim of interpreting them in the consistent and coherent theoretical framework provided by the Peierls-Hubbard models. For the Bechgaard salts, the focus will be the FISDW phases and will address several specific questions. Can one understand these exotic phases in the context of the full phase diagram in these materials as a function of pressure, temperature, and magnetic field ? Is the recently observed very high field phase (VHFT) a correlated metal, as some theories suggest, or a spin-Peierls phase [6,7]? Can one predict the consequences for the FISDW phases of certain chemical substitutions in the organic solids ? For the conducting polymers, the focus will be on the PA and the nonlinear optical responses of π-conjugated polymers and will attempt to resolve several outstanding questions. How can one interpret the observed luminescence in a manner consistent with the known importance of nonlinear excitations in optical absorption? To what extent does the recently proposed "essential states" mechanism[9] capture the full complexities of the third-order nonlinear response of the π-conjugated polymers? The specific technical projects underlying these general questions and the methods which will be employed in them are discussed in the ensuing sections.

Near-Term Projects

A. FISDW States in Organic Solids

To introduce the specific projects on the FISDW states in organic solids, it is essential to recall very briefly the history and present status of this exotic phenomenon[10]. When magnetic fields (H) are applied at low temperatures (~ 5° K) to the superconducting $(TMTSF)_2X$ salts, superconductivity first gives way to a "metallic" state, albeit with possible unusual properties. Then for fields $H > H_f$ (~ 5 Tesla) a cascade of transitions to semimetallic SDW phases (as deduced from NMR data) is observed. The explanations of this FISDW phenomenon involve the gradual "one dimensionalization" of the anisotropic 2-D Fermi surface due to the magnetic field, and an accompanying *sequence* of nesting instabilities. Within these "standard" theories, the phase at very high magnetic fields is expected to be a commensurate, large gap SDW semiconductor. These theories thus fail to account for the recent observation in the perchlorate salt ($X = ClO_4$) of the "very high field transition" (VFHT), where for H > 17 Tesla, it is found the transition temperature T_{SDW} begins to *decrease* with field, and actually goes to zero for $H \cong 25$ -30 Tesla. Although there exists a "nonstandard" theoretical approach that claims to explain the VFHT, within this approach, the VHF phase is predicted to be metallic. Experimentally, however, the material exhibits high resistivity, activated conductivity, vanishing Hall signal and diamagnetism, all characteristics of a semiconductor or a semimetal.

Recently, an alternative theoretical framework was proposed [6,7] based an anisotropic, quasi-2-D extended Hubbard Hamiltonian, involving both parallel ($t_{\|}$) and perpendicular ($t_{\perp}$) electron hopping and onsite (U) and nearest-neighbor ($V_{\|}$, $V_{\perp}$) Coulomb interactions. In addition to incorporating the nearest-neighbor Coulomb interactions, this model goes beyond conventional models by avoiding the continuum limit and by including the quarter-filled nature of the organic stacks. Importantly, it provides a natural explanation for the VHFT -- predicting that the associated phase is a (semiconducting) spin-Peierls state -- and also unifies the theoretical understanding of the pressure and magnetic field dependence of the phases of many other families of structurally similar 2:1 cationic organic charge transfer salts, including the TMTTF, BEDT-TTF, DMET and MDT-TTF materials. Specifically, preliminary results show that the model predicts three different *non*superconducting phases, depending on the extent of the anisotropy. Further, pressure, magnetic field or any other effects that change the *effective* anisotropy can drive transitions among the phases. To attempt to confirm these preliminary results and establish the validity of this model, several specific studies will be conducted.

First, one can attempt to model the "one-dimensionalization" effects of the magnetic field *phenomenologically*, simply by altering the ratios of the transverse and parallel hopping and Coulomb interaction parameters in the Hamiltonian. Using an exact numerical diagonalization technique -- the "Lanczös" method -- the Hamiltonian can then be studied on a range of finite-sized clusters [6,7]. Although crude, this first approximation allows (1) the confirmation that as the system becomes more one dimensional, the BOW instability which underlies the spin-Peierls state *does* appear to dominate over the SDW instability; (2) the modeling of the effects of pressure, which drive the system toward a more isotropic state and to some extent "undo" the effects of the magnetic field. A first priority of the proposed research is to extend these preliminary studies substantially, not only by probing a wider range of the parameter space but also by incorporating recent improvements in Lanczös methodology (for instance, "boundary condition averaging" techniques[3]) to permit more reliable extraction of results from the small systems. Further, since the effective electronic "dimensionality" (in the sense the ratio of ($t_{\perp}/t_{\|}$) varies substantially among the different chemical compounds within this general class, a second priority of this phenomenological project is to catalog the observed behaviors of the various materials and to validate (or refute) the basis of the phenomenological model.

Second, in order to incorporate the effects of the magnetic field in a truly microscopic manner, one must develop a true many-body approach to the behavior of correlated, quasi 2-D electrons in a transverse magnetic field. Present approaches suffer from two potentially significant defects: (1) they are based exclusively on mean-field treatments of the direct electron-electron interactions, treatments which are generally questionable in reduced dimensions and highly suspect in quasi-one dimensional materials; and (2) they employ the "Peierls substitution" to incorporate the magnetic field by modifying the phase of the hopping integrals, a substitution whose validity has recently been challenged [10]. Thus it is important both to apply more reliable numerical many-body methods -- either Lanczös exact diagonalization or quantum Monte Carlo (QMC) techniques -- to the problem and to investigate the extent to which the "Peierls substitution" correctly captures the true effects of the magnetic field. The difficulty in using more exact many-body methods has been that the large difference in length scales between the atomic structure of the materials (typically a few Angstroms) and the magnetic length (~ 100 Å at 10 Tesla) implies that very large systems -- involving lattices of perhaps 25x25 -- must be studied. These systems are well beyond the capabilities of Lanczös methods and, although in principle within the capability of QMC methods, are in practice subject to the infamous "minus sign" problems that afflict most QMC calculations in two (and higher) dimensions. Similarly, the more exact alternative to the Peierls substitution is substantially more difficult to study numerically. Recently, a possible resolution of these difficulties has emerged. Since the FISDW effects arise from the orbital coupling of the electrons to the magnetic field (the Zeeman effects are comparatively small even at 30 Tesla), one may reasonably attempt to simplify the system by studying

spinless electrons. Importantly, since the mapping onto these spinless electrons takes the 1/4-filled band of real electrons to an effective half-filled band of spinless electrons and since the half-filled band in two dimensions does not exhibit the QMC "minus sign" problems, it appears possible to use QMC techniques to study systems of the appropriate size. Although there are many unresolved issues here -- e.g., the proper boundary conditions for the QMC simulations in the magnetic field - the idea represents an important new approach to a long-standing problem in this area.

B. Photo-induced and Nonlinear Optical Properties of π-conjugated polymers

In recent years much attention has been focused on field-responsive optical properties of π-conjugated ("conducting") polymers. Among the effects studied most intensively have been the photo-induced photo-absorption (PA), electroluminescence, and the nonlinear "polarizabilities", $\chi^{(2)}$ and $\chi^{(3)}$. Much of this interest stems from potential technological applications. Optical display devices based on electroluminescent conjugated polymers are already in the development stages and the potential applications for both "$\chi^{(2)}$" materials (e.g., in electro-optics) and "$\chi^{(3)}$" materials (e.g., in ultrafast all-optical switches and logic gates) are widely recognized.

Although there has been substantial progress on the experimental materials aspects of these systems, the status of the theory of the organics is in general far behind that of the more conventional inorganics. Further, there are clear reasons to believe that the theories describing the two classes of materials are quite different. For instance, in the case of luminescent response in the π-conjugated polymers, the large geometrical relaxations arising from the strong e-p couplings lead to important intermediate roles for *charged* nonlinear excitations (solitons, polarons, and bipolarons) as well as substantial changes in the behavior of *neutral* (exciton) excitations from the familiar case of the rigid-band semiconductor. Conversely, in the nonlinear optics, the combination of important e-e interactions and the quasi-1-D nature also suggest a theoretical framework quite distinct from that applied to the inorganics.

To improve on this situation in a systematic way, it is essential to develop a *microscopic* theory which provides an understanding of the underlying *mechanisms* of luminescence, optical nonlinearity, and related processes in π-conjugated polymers. From our earlier discussion of Peierls-Hubbard models, it is clear that, by incorporating both e-e and e-p interactions and correctly reflecting the quasi-1-D geometry of the materials, they are the natural framework in which to seek such a microscopic theory. Further, some exciting preliminary results have already been obtained, including a semi-quantitative understanding of the geometrical relaxation effects in excited states [6] relevant to the luminescence and the identification [9] of a limited number of "essential states" which dominate the optical nonlinearity. Our primary aim in the specific near-term project outlined below is to confirm these preliminary results by more quantitative studies.

A critical question in both luminescence and nonlinear optical studies is the nature and location of the low-lying excited states, both singlet and triplet and both one- and two-photon allowed. The experimental situation is unclear and suggests that there are perhaps substantial differences in the locations of these states in different materials[13]. Consider, for instance, the state denoted as "2^1A_g" in spectroscopic notation. This state has the same spatial symmetry as the ground state and hence is one-photon forbidden (but two-photon allowed) in optical transitions. Within quasi 1-D, single electron theories, the 2^1A_g always lies below the "optical gap" -- i.e., the peak of the one-photon allowed transition -- but e-e interactions bring it well-below the optical gap in finite polyenes and (likely) in polyacetylene. In at least some polydiacetylenes, however, it appears that this state lies near to or perhaps above the optical state. Further, the nature of the optical state itself needs to be clarified: in the presence of strong e-e interactions, excitonic effects generated by longer range Coulomb interactions causes the optical absorption to set in well below the threshold for photo-conductivity. Using the exact (numerical) diagonalization (Lanczös) methods coupled with boundary condition averaging techniques that have proven successful in linear optical

absorption[4], the locations and properties of the low-lying excited states relevant to luminescence and nonlinear optics will be studied in quantitative detail, and the appropriate matrix elements will be calculated. Importantly, these studies can and will be carried out over the full range of parameters believed to be relevant to the various different π-conjugated polymers.

Future Directions

A. FISDW States in Organic Solids

On the longer term, two specific projects are planned to clarify the nature of the FISDW states. First, the "branching" nature of the experimental diagram of the FISDW sub-phases, the theoretically noted relation to commensurate/ incommensurate phase transitions (see, e.g. Ref. 11), and the general relation to the quantum Hall effect, all suggest that there may be a topological aspect of the FISDW states. Preliminary results indicate that this idea appears sound, although the actual calculation of the topological invariant is rendered difficult by the many-body and magnetic field effects. Both further insight and additional calculations are needed to sharpen this intriguing analogy. Second, in the limit of very strong electron-electron interactions ($U > V_{\parallel} > V_{\perp} >> t_{\parallel} > t_{\perp}$), the Hubbard model reduces to a (likely frustrated) anisotropic 2-D spin Hamiltonian, with interaction constants depending on the electronic parameters. Apart from its general theoretical interest, this model can provide important (possibly analytic) benchmarks for the difficult numerical calculations of the full Hubbard model. In this regard, the nature of the ground state as a function of the effective spin couplings, the role of quantum fluctuations, and effects beyond the strong coupling limit must all be understood.

B. Photo-induced and Nonlinear Optical Properties of π-conjugated polymers

On the longer term, studies of these optical characteristics of π-conjugated polymers must confront two crucial issues. First, what is the sensitivity of the current quasi-one-dimensional approaches to effects of interchain interactions that exist in real solid samples of the polymers? A proper answer to this question may be essential to the development of a full understanding of structure-property relations that will permit the fulfillment of the promise of ``molecularly-engineered" organic optical materials. Based on the experience in the linear optical properties [5], there can be substantial differences, particularly in those cases in which the charged nonlinear excitations may play important roles. Considerable work is required in this area. Second, once the true nature of the excited states involved in the "essential states" mechanism is clarified, the *dynamics* of the nonlinear optical processes can be model by variants of the Maxwell-Bloch equations used in describing conventional semiconductors. At present, it appears that a degenerate multi-level -- perhaps three or five level -- *non*-resonant model will be necessary to incorporate correctly time-dependent phenomena in this system; complications caused by phonons and geometrical relaxations may also have to be included. Again, this is an area in which little is known and therefore much remains to be done.

Connections with other DOE interests

The proposed studies on the FISDW states of the organic solids will provide theoretical support both for the chemical synthetic efforts of Williams at Argonne, who in connection with his efforts on organic superconductivity has produced or identified many of the interesting organic solids, and for the physical characterization experiments of Schirber and Kwak at Sandia, whose pressure-dependence studies have helped initiate and sustain the field.

The theoretical work on the luminescence and optical nonlinearities of the π-conjugated polymers will complement the experimental studies by Stupp here in Urbana on organics exhibiting large values of $\chi^{(2)}$.

Industrial Cooperation

A number of recent "start-up" companies -- such as Uniax in Santa Barbara -- have recently begun development of electro-luminescent devices based on conducting polymers. Possible interactions with these and related efforts will

be investigated during the period of this proposal.

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D.3.d RELATIONSHIP BETWEEN SURFACE CHEMISTRY AND FILM PROPERTIES IN CHEMICAL VAPOR DEPOSITION AND ETCHING

RICHARD I. MASEL

Goals

Chemical Vapor Deposition (CVD) is a well established technology for production of thin films. However, process design for CVD is still done largely empirically. We, however, have been interested in a somewhat different approach, where one examines the surface chemistry of various ligands in detail, and uses that information to design suitable source gases for film growth. We and others have already used that approach to understand what kinds of precursors would yield films with the proper composition. However, when one is growing metallurgical coating or solar cells one needs to control the morphology. The relationship between surface chemistry and film properties is largely unexplored. The objective of the proposed program will be to examine the relationship between the surface chemistry of CVD source gases and the morphology and properties of the resultant film. The goal is to understand the surface chemistry in enough detail that we can design source gases and novel processes which will yield better film properties.

Background

CVD is a well established technology for film deposition. However, as device features continue to shrink, better CVD processes need to be developed to obtain more uniform films with abrupt junctions. The rate of low pressure/low temperature CVD is controlled by the surface chemistry of the source gases. As a result several groups, including our own, have been studying some of the basic surface chemical processes which occur during growth. Most of the work so far has considered the relationship between surface chemistry and the composition of the film for materials of interest to devices and for solar collectors. For example we have been examining some of the surface chemistry involved in GaAs MOCVD. We started with a typical source molecule, trimethylgallium $(CH_3)_3Ga$ and examined the mechanism of the decomposition process using a variety of surface spectrographic techniques. We discovered that there were two different reaction pathways, one involving a direct ligand loss:

$$(CH_3)_xGa_{ad} \rightarrow (CH_3)_{x-1}Ga_{ad} + CH_3\uparrow \qquad (1)$$

And one involving an intramolecular hydrogen shift:

$$(CH_3)_xGa_{ad} \rightarrow (CH_3)_{x-2}Ga(CH_2)_{ad} + CH_4\uparrow \qquad (2)$$

The later reaction leads to carbon incorporation, and therefore undesirable film properties. It happens that the rate of the later reaction varies strongly with the stoichiometry and local structure of the growing film, which makes it hard to control.

In recent work, we have been experimenting with the use of a novel intermediate monomethylgallium (CH3)Ga for film growth. Monomethylgallium reacts via a very different pathway than trimethylgallium:

$$(CH_3)Ga + (CH_3)Ga_{ad} \rightarrow (CH_3)_2Ga\uparrow + Ga_{ad} \qquad (3)$$

which leads to very low carbon films.

We have also done similar work on many other source gases for GaAlInAs growth. A related issue which has not been addressed in our laboratory or elsewhere is: How does the surface chemistry affect the morphology and properties of the resultant film? Control of the film morphology is crucial to the CVD process. The film morphology is often also very important to the electronic properties of the film since morphological defects can have an important influence on the electrical properties of the film.

Future Directions

In the next three years we propose to do a series of studies to elucidate the relationship between film morphology and growth chemistry. We plan to concentrate on deposition and etching of metals for a variety of applications including connections on solar cells, and corrosion resistant coatings on metals.

We plan to start with copper, because copper is important as an interconnect material and it forms an interesting model system for a variety of deposition processes. In the recent literature Girolami, Beech, Hampton-Smith, and others have produced a series of metal alkyls which decompose on a heated substrate to yield pure copper films. However, we still do not know how to control the morphology of the films. Experimentally, the morphology of the film has been found to vary significantly with the choice of source gas and processing conditions. Often, one observes an undesirable columnar morphology. So far it is unclear what combination of source gases and processing conditions one needs to use to get good film properties. In fact the results are often confusing. For example, Beech has found that one of his intermediates gave good film properties in a laboratory reactor but not in a commercial reactor.

At present, there is a significant ongoing effort to try to develop a CVD copper process empirically. We are interested in exploring an approach where one examines the surface chemistry of various ligands in detail, and uses that information to design suitable source gases and processes for film growth.

Surface Chemistry Of Alkyl Ligands: A Rational Basis For Source Gas Design

In the next three years, we propose to examine the surface chemistry of copper CVD and etching and use that information to design better source gases. MOCVD of copper generally utilizes source materials containing ligands such as phosphines, alkoxides, acetonates, vinyl-silanes, amines, etc. At present, there has been very little work on the chemistry of these ligands on copper surfaces. Girolami and Nuzzo have done some unpublished work on the decomposition of some of the alkyl copper compounds on Cu(111). There is also some data from Madix and Cambell on the oxidation of methanol on Cu(111). However, there has not been a systematic study of the decomposition of a wide range of ligands on copper surfaces.

Another issue which has not been addressed is the relationship between gas chemistry and film properties. At present morphological control of the copper films has been difficult. For example, Girolami has shown that when one grows copper films from t-butyl copper, one first nucleates small crystallites. The small crystallites grow more rapidly along the (111) direction than in other directions. The (111) face happens to correspond to the tops of his crystallites. As a result, the films show 3d rather than 2d growth, which results in poor film quality.

In the future, one would like to be able to design source gases which will decompose in a way that produces 2d rather than 3d growth. At present, one can only design such source gases empirically. However, in the future one would like to have a scientific basis for source gas design. Our approach will be to compare the chemistry of the ligand decomposition process on Cu(111) (i.e. the plane at the top of the crystallites) and on stepped copper surfaces (i.e. the planes at the sides), to try to see what kinds of ligands will promote 2d as opposed to 3d growth. Our experiments will involve doing some chemistry to produce interesting ligands on Cu(111), Cu(110) and Cu(210) and then examining the decomposition of these ligands with TPD and IR or EELS.

The first part of the project will be to try to find a way to produce the interesting ligands for study. Girolami found that t-butoxide ligands are useful in film precursors. However, if one wants to study the properties of t-butoxide ligands one has to find a way to synthesize t-butoxide ligands on the surface of the sample. One approach is to dose with Cu(II) t-butoxide. However, if we dosed with Cu(II) t-butoxide the copper in the Cu(II) t-butoxide will change the surface structure. As a result, we will not be able to understand how the decomposition of the t-butoxide ligand on Cu(111) is different than Cu(110) or Cu(210). Hence, we will not be able to make a connection between the growth chemistry and the film morphology.

We propose to use a synthetic approach to make interesting ligands on the surface of our samples, and then study the decomposition of these ligands with TPD and EELS. On Pt(111) one can produce a t-butoxide ligand via decomposition of t-butanol. However, Girolami found that on Cu(111), t-butanol largely desorbed before it decomposes to t-butoxide. However, many workers have found that one

can produce alkoxide ligands on transition metals via selective oxidation of alcohols. For example, my group has found that we can selectively oxidize methanol to methoxide on Pt(110). Madix and Cambell have observed the same reaction on Cu(111). Sexton observed the oxidation of t-butanol to t-butoxide on Pt(111). Therefore, it seems that selective oxidation may be a viable route to produce interesting ligands on copper surfaces.

We propose to try to use selective oxidation to produce the desired key ligands. For example, we will attempt to synthesize a t-butoxide ligand on Cu(111), Cu(110), Cu(210) by selective oxidation of t-butanol. We will attempt to synthesize a hexafluoroacetonate ligand by selective oxidation of 1,1,1,5,5,5hexafluoro-2,4-pentanedione ($CF_3COCH_2COCF_3$). In this way we believe that we can produce key ligands for study.

Once we produce interesting ligands the experiments will involve creating ligands at low temperatures, slowly heating the substrate, and using surface spectroscopy to watch the ligands decompose. Simultaneously, we will examine the production of copper alkyls. Recently, Hampton-Smith has discovered that a series of copper(I) alkyls are interesting film precursors. They react via a mechanism similar to that in reaction 3 above. i.e..

$$2\,(HFAC)Cu(I)(PF_3) \rightarrow 2\,PF_3\uparrow + Cu + (HFAC)_2Cu\uparrow \qquad (4)$$

Hence, the production of copper(II) alkyls should be very important to the growth chemistry. It will also be quite important for etching.

In addition, we will do some experiments with hydrogen and carbon monoxide in the background in order to determine how the ligands interact with various reducing agents. We will characterize the bonding of these ligands and their decomposition chemistry with TPD, IR or EELS and will systematically substitute the ligand and see how rates and mechanisms change. In our previous work, we have been able to correlate variations in rate with crystal face, the electronic structure of the surface, the electronic structure of the ligands, and the thermodynamics of the decomposition reaction. We propose to develop similar correlations for the decomposition of ligands on copper surfaces, and then use those correlations to identify ligands which decompose more slowly on Cu(111) than on Cu(210) and Cu(110). Armed with that information we will collaborate with Girolami to produce suitable precursors, and try them in the growth process to see if we can promote 2d growth.

Structural Promoters For CVD

One possible difficulty with the proposed work is that there is no guarantee that we can include the ligands which look the best in terms of their surface chemistry into a practical source material. As a result, we would like to consider another alternative, which is to add suitable reactants (i.e. structural promoters) to the CVD reactor, and try to selectively inhibit the reaction on the Cu(lll) face, thereby producing 2d rather than 3d growth.

Structural promoters are well known in the electroplating literature. No one has examined the surface chemistry of these species in detail. However, one way they can work is to selectively block sites on the (111) faces, so that the rate is slower on the (111) face than on other faces of the metal.

A similar effect of structural promoters in the CVD environment will be studied. A structural promoter, which would selectively bind to the (111) face and thereby inhibit the decomposition process on Cu(111) would be added to the gaseous environment. If we choose the structural promotor properly, we should be able to get 2d rather than 3d growth.

Since no selective poisons for Cu(111) have been reported, exploratory work will be necessary. Our idea is to start with fairly rigid compounds which bind at multiple sites and tailor the geometry of the compound so that it can only bind at one point of attachment on a stepped surface, while it can bind at two or more points of attachment on a flat surface. In that way, the compound would be expected to bind more strongly on Cu(111) than on other faces. As a result, the promotor should inhibit the reaction on Cu(111).

We propose to try out this idea by examining the binding energies of these types of compounds by adsorbing them on Cu(111) Cu(110) and Cu(210) surfaces and measuring the binding energy of the ligand to the surface with TPD. Once we find suitable ligands, we will add them to the growth reactor and see how they affect the film growth process. We may also do some work to characterize the structural promoters used in electrochemical systems using both TPD and EELS.

Chemical Enhancement Of Film Growth

As this project proceeds, we will also be interested in various chemical reactions during growth process. For example Girolami found that he can form a copper oxide from Cu t-butoxide at 200 C, but needs to go to 400 C to reduce the oxide to metal. One can imagine adding another species to the reacting mixture e.g. CO or H_2, to speed the reduction process.

There is previous work on the use of hydrogen as a co-reactant. The films are better in the presence of hydrogen, but there is no enhancement of the film morphology. The problem with hydrogen is that it does not stick well on a clean copper surface. Measured sticking probabilities are less than 10^{-3}. Note, that if one promotes copper with a small amount of platinum or palladium, the hydrogen adsorption process is significantly enhanced. Hence, there is the possibility of adding a small amount of some platinum or palladium alkyl to the growth mixture, to enhance the film growth process. We would like to explore that possibility as well.

Prospects For The Longer Term

In the longer term, we would like to expand this effort to a wide range of deposition processes. In the description in the last few pages, we concentrated on the rational design of a process for copper CVD. However, we expect that the ideas might be expanded to many other systems. In general, source gases for CVD are designed empirically. One does not know the relationship between the growth chemistry and the film morphology. The idea of adding structural promoters or catalysts is new to CVD. If this project succeeds, we would like to expand these ideas to other growth systems, and thereby develop a general design methodology for MOCVD.

D.3.e FUNDAMENTAL STUDIES OF THE ELECTROMECHANICAL BEHAVIOR OF RELAXOR FERROELECTRICS.

DWIGHT D. VIEHLAND

Introduction and Goals

Significant interest has developed in the last year in ferroelectric materials for actuator applications, due in-part to their potential uses in adaptive structures. Ferroelectric actuators can be broadly categorized into two main subgroups: (1) the polarization-controlled, and (2) the field-controlled. The polarization-controlled are characterized by the traditional lead zirconate titanate (PZT) type piezoelectric. Once poled, they are in a remnant state exhibiting memory characteristics. The field-controlled are characterized by the electrostrictive materials such as the lead magnesium niobate relaxor ferroelectric. On application of a bias a large strain develops, and on removal of this bias the strain-state reverts back to the original zero-field-cooled condition. These electrostrictive materials offer larger strains, superior field-tunability, and better thermal reversibility than the piezoelectric type. In spite of these advantages, many of the fundamental aspects of the electrostrictive materials are presently not understood. It would be the goal of this proposed investigation to answer some of the unresolved questions concerning the nature of the relaxor ferroelectric. These results could have significant impacts on the development of new sensor and actuator materials.

Highlights and Background

Lead magnesium niobate, $Pb(Mg_{1/3},Nb_{2/3})O_3$ (PMN), is a relaxor ferroelectric. It is believed to possess locally polarized regions of nanometer scale size[1]. A high polarizability ($c' \sim 10^4$) and a strong dielectric relaxation (Hz to GHz frequency range) are simultaneously observed. The relaxation is also reflected into the anelastic response through local electrostrictive couplings[2]. The physics of the relaxor has eluded researchers for many years. Various models have been proposed, most of which have some merit. Viehland[3] has recently shown that the complicated behaviors of the relaxor can be understood by analogy to the spin and orientationally disordered materials, i.e., the spin-glass-like behavior. Analogous behavior has been reported in disordered ferroelectrics such as Li-doped $KTaO_3$ [4] which is designated as an electric dipole glass, and in diluted molecular crystals such as $(KCN)_x(KBr)_{1-x}$ [5] which is designated as a quadrupolar or orientational glass. In relaxors, the local polar moments were found to freeze into random orientations below a characteristic temperature, devoid of ferroelectric long-range order[3]. This freezing was found to be coincidental with the collapse of remnance on heating from a field-cooled state. Viehland[3] subsequently has shown that the glassy behavior is reflected into the dielectric, polarization, and elastic responses.

All known glassy behaviors to date possess randomness due to an underlying disorder, usually with clustering[6]. The underlying disorder can be structural, chemical, or a phase separation. The net result is that there is a broken translational invariance, resulting in the local symmetry being lower than the global. In PMN, transmission electron micrographs reveal a contrast on the nanometer scale[7,8]. Regions (~2-5 nm in diameter) possess a doubling of the unit cell, as shown by selected area diffraction. This doubling can be interpreted to mean that the B-site cations undergo long-range ordering. The scale of the contrast (as observed near and below room temperature) does not coarsen significantly with annealing time when cooled through the ordering temperature (~750°C), and subsequently no change in the degree of relaxor character is observed. In the $Pb(Sc_{1/2},Ta_{1/2})O_3$ (PST) solid solution, quenched samples exhibit relaxor behavior, whereas annealed samples exhibit behavior more similar to that of a normal ferroelectric[9]. Transmission electron microscopy[10] reveals that the scale of the meso-structure in quenched samples is similar to that for PMN (ordered regions~2-5 nm), whereas in annealed samples the scale coarsened significantly (ordered regions~100 nm). Many other Pb-based perovskites with mixed B-site cations, $Pb(B_1,B_2)O_3$, exhibit similar relaxor behavior and meso-structures. Relaxor behavior

is also found in the tungsten bronze structure family, such as $Sr_xBa_{1-x}Nb_2O_6$ (SBN).

The remaining sections of this proposal will focus on answering some of the unresolved questions concerning the nature of the relaxor ferroelectric. Efforts will be focused on understanding the glassy electromechanical and elasto-dielectric behaviors in various relaxor families, and their relationship to an underlying inhomogeneity. Efforts will also be focused on understanding the nature of the meso-structure of the $Pb(B_1,B_2)O_3$ family, and the role of its scale on the electrostrictive behavior and glassy responses.

Future Directions

Investigations of the Glassy Behavior.

The focus of this research would be to extend the dipole-glass-like model applied to the dielectric and anelastic behaviors of PMN to other cross-coupled properties and relaxor families. Attention would be paid to determining how the glassy behavior is reflected into the piezoelectric and electrostrictive properties, and to examining some of the differences between the perovskite and tungsten bronze families of relaxors. Several of the unresolved questions which would be investigated are discussed in more detail below.

In the zero-field-cooled (ZFC) state no piezoelectric response is observed for PMN, under weak fields a strong response (d_{33}~1500 pC/N) develops which is highly dispersive[11]. At field levels near saturation, the response decreases approaching the value for poled PZT (d_{33}~400pC/N). Correspondingly, in the ZFC state no domain structure is observed, whereas in the field-cooled (FC) state normal micron-sized domains are found. The question remains to be answered as to the nature of the exceptional piezoelectric response under weak fields. It is proposed to study the kinetics of the electromechanical relaxations for various DC bias levels, and to further correlate these results with an optical microscopy study (also under bias). The complex piezoelectric response would then be measured as a function of temperature at various frequencies and applied DC biases. The corresponding temperature dependent relaxation time distributions would be calculated, and compared to the respective dielectric and anelastic ones (which are known to differ).

The electrostriction coefficient has also been shown to be frequency dependent[12]. (The degree of dispersion is significantly less than for the induced piezoelectric response.) The origins of this relaxation are presently unknown. One of the goals of this proposed investigation would be to measure the temperature and frequency dependence of the complex electrostriction coefficient using an interferrometric technique[12]. Information concerning the glassy electromechanical behavior(s) could then be obtained by calculating the relaxation time distribution, and comparing with that for the induced piezoelectric response. Alternative compositional systems which might be investigated include: (1) the La-modified $Pb(Zr_xTi_{1-x})O_3$ (PLZT) where the oxygen tilt structure gives an additional ferroelastic response[3], and (2) $Pb(Sc_{1/2},Ta_{1/2})O_3$ where the scale of the ordered regions can be changed as a function of annealing time[10]. Questions of fundamental interests which could potentially be addressed include:

(i) What is the mechanism underlying the large induced piezoelectric response and how is it related to the glassy polarization behavior? Can ways be found to enhance this induced response? Can the induced response be correlated to any changes in the optical microscope?

(ii) What is the nature of the relaxation of the electrostriction coefficient? Is there an imaginary contribution? How is the relaxation related to the piezoelectric, dielectric, and anelastic properties? How is the glassy polarization behavior reflected into the electrostriction?

(iii) What is the effect of scale on both induced piezoelectric response and the electrostrictive behavior?

In the tungsten bronze structure ferroelectrics, a strong dielectric relaxation has been reported at temperatures more than 100°C below the maximum in the dielectric permittivity[13]. This relaxation is found perpendicular to the polar axis, for both the field-cooled (poled ferroelectric) and zero-field-cooled states. The nature of this relaxation is

presently unknown, analogous behavior has previously not been reported for either dipolar or orientational glasses. It is proposed to measure the complex dielectric and anelastic responses as a function of frequency and temperature, under various DC bias levels for both (100) and (001) orientations. The relaxation time distributions and nonlinear susceptibilities for both responses would then be calculated and compared. This would also allow for the identification of the freezing temperatures and spin-glass exponents. The "spin-glass" order parameter would also be calculated from both responses, following the Sherrington-Kirkpatrick relationship. Transmission electron microscopy and x-ray line broadening measurements could also be done. Questions of interest which could potentially be addressed include:

(i) Are there two freezing temperatures for parallel and perpendicular fields?

(ii) Is the relaxation at low temperature driven by a polar instability or an orientational instability? How is the low temperature glassy state affected by poling the high temperature ferroelectric state?

(iii) What is the nature of the underlying chemical inhomogeneity (meso-structure) of this material?

Investigations of the Meso-structure in the $A(B_1,B_2)O_3$ Family

The focus of this research would be to investigate the nature of the meso-structure in the $A(B_1,B_2)O_3$ materials. Attention would be paid to the determination of the occupancy on the B-site cations in the ordered regions, the possible role of lattice strain, compositional effects in solid solutions, and the development of a thermodynamic theory.

The ordering in PMN has been suggested to arise due to a compositional segregation, resulting in some regions being Mg-enriched[7,8]. The ordered regions were hypothesized to have Mg/Nb ratios of 1:1, relative to the global ratio of 1:2. This would require the lifting of the constraint of local charge neutrality, and the development of charge density waves. Although nonstoichiometry may be important, the Mg-Nb occupancy on the B-sublattices in the ordered structure has yet to be determined. It is proposed to study $Pb(Mg_{1/3},Nb_{2/3})O_3$ with high resolution transmission electron microscopy. Computer simulations of the images could then be done, for various Mg/Nb ratios and long range order parameters (S), to estimate the occupancy. Microchemical analyses might also be performed to determine if the composition of the ordered regions is significantly different from the global average. Empirically it is known that relaxor behavior occurs primarily when the B_1 and B_2 cations are of similar size. This suggests that lattice strain may play a significant role in determining the B-site occupancy and the development of the ordered structure. It is thus proposed to also systematically investigate various $Pb(B_1,B_2)O_3$ compositions as a function of Δr, where $\Delta r = r_{B1} - r_{B2}$. Some of the possible combinations of B-site cations include Mg (0.66 Å) and Nb (0.69Å), Zn (0.74 Å) and Nb, In (0.81Å) and Nb, and Cd (0.97 Å) and Nb. Similar studies could also be performed on $Pb(Sc_{1/2},Ta_{1/2})O_3$ for various thermal histories.

Other compositional modifications are possible within the $A(B_1,B_2)O_3$ family, which may give avenues for altering the meso-structure and polar properties. $Ba(Mg_{1/3},Nb_{2/3})O_3$ (BMN) and $Ba(Mg_{1/3},Ta_{2/3})O_3$ (BMT) have ordered structures which exhibit a tripling of the unit cell. This ordering process goes to near completion on annealing, unlike that for $Pb(Mg_{1/3},Nb_{2/3})O_3$. It is proposed to perform microscopy studies on solid solutions of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Ba(Mg_{1/3},Nb_{2/3})O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Ba(Mg_{1/3},Ta_{2/3})O_3$, and $Pb(Sc_{1/2},Ta_{1/2})O_3$-$Ba(Mg_{1/3},Nb_{2/3})O_3$ to determine how the meso-structure changes with composition. Changes in size of the ordered regions, B-site occupancy, and ordered structure can certainly be anticipated. This raises interesting possibilities for manipulating the dielectric and electromechanical behaviors in a controlled manner, as BMN and BMT are nonpolar. Investigations of these possibilities would be done in concert with the microscopy study.

At the present time, little is known about the thermodynamic stability of the observed meso-structure, although several important experimental observations can be made. Most

relaxor compositions in the $Pb(B_1,B_2)O_3$ family seem to be close to the stability limits between the perovskite and pyrochlore structures[14]. In fact single phase perovskite ceramics cannot be formed by a simple calcination of the individual oxides. This suggests that intimately involved in the formation of the meso-structure, is an underlying drive for structural decomposition. The main difference between the two structures is that the pyrochlore is an oxygen deficient distorted perovskite, which has tetrahedral coordination rather than octahedral. Secondly, the morphology of the meso-structure in $Pb(Mg_{1/3},Nb_{2/3})O_3$ is reminiscent to that observed during the early stages of recrystallization in vycor glass[15], suggesting a continuous separation mechanism which is arrested during the initial stages of evolution. In addition, the morphology observed in the $Pb(Sc_{1/2},Ta_{1/2})O_3$ after annealing exhibits a high degree of interconnectivity, similar to a continuous mechanism at the latter stages of evolution. Finally, the introduction of a donor into the $Pb(Mg_{1/3},Nb_{2/3})O_3$ solid solution increases the scale of the meso-structure, whereas the addition of an acceptor decreases it[8]. This suggests that the inability to coarsen is a result of a charge stabilization, similar to a colloidal state. In ionic systems, wavelengths of periodic compositional variations resulting from spinodal decomposition have been reported to be of the order of 50-1000Å [16,17] and the Debye lengths[18] of the order of 20-10,000Å. Consequently, one can see why a proper treatment of instabilities in ionic systems must include the possibility of charge density waves (periodic compositional variations that include locally non-neutral compositions).

It would seem then that in the $Pb(B_1,B_2)O_3$ relaxor family that a thermodynamic theory may need to be developed to describe a continuous diffusion-controlled separation process which includes contributions from the relative phase stabilities (compositional gradient), structural relaxation of the oxygen framework (strain gradient), and off-stoichiometric ordering (charge gradient). Gupta and Cahn[19] developed a phenomenological theory to describe continuous transformations in ionic systems. Calculations using reasonable values of system parameters showed that equilibrium structural non-uniformities could be expected on the order of 100 Å. Similar fine scale non-uniformities should also result from extending Khachaturyan's model of congruent ordering to ionic systems[20], allowing for decomposition accompanied by off-stoichiometric ordering. It is proposed to extend these phenomenological theories to the study of relaxor ferroelectrics, simulating the concurrent processes of ordering and decomposition. Questions of interest which could potentially be addressed include:

(i) Is decomposition arrested in the early stages of evolution between perovskite polymorphs? Is the meso-structure an equilibrium state? Why does the scale not coarsen for systems with a B-site cation ratio of 1:2? Why does it coarsen for systems with a B-site cation ratio of 1:1? Is the local composition nonstoichiometric?

(ii) How strongly would a charge gradient effect the scale of the structural nonuniformity? How strongly would a strain gradient? How closely do these predictions match the experimental results observed with TEM?

(iii) Might the scale of decomposition be controlled? Might macroscopic phase separation be triggered? Might it be further suppressed? Might the glassy behavior be manipulated by controlling phase separation? Might an optimum scale be identified for enhanced electrostrictive strain? Might an optimum scale be identified for enhanced piezoelectric sensitivity?

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D.4 RESEARCH SUMMARIES FOR NEW PROGRAMS STARTED IN FY93

In this section, the program description for a new program which is being started in FY 1993 is presented in greater detail than is possible in Sections D.

D.4.a NEW PROGRAMS IN FY93; KC-02-01-02

MAGNETIC BEHAVIOR OF NANOPHASE MATERIALS

M. B. SALAMON

Many technologically important properties of materials arise from the interplay between intrinsic behavior and microstructure. In magnetic materials, key parameters--coercivity, remanent magnetization, and energy product--are crucially dependent on such factors as grain size and interfacial effects. In magnetic recording, for example, the effectiveness of individual magnetic particles depends sensitively on surface treatment, and thin-film media are strongly affected by interface features. In this program, we propose to prepare materials by nanocrystalline methods in order to study interfacial effects that arise when magnetic nanocrystals are embedded in a non-magnetic matrix. We will vary the nanocrystalline volume fraction, following the development of magnetic order as the density of nanocrystals approaches and then exceeds the percolation threshold. We expect this work to establish the basis for future work on elastic properties and fracture in percolating nanocomposites. In addition to overall magnetic properties of nanophase materials, a number of issues of fundamental importance can be addressed. Among them are the nature of spin waves on percolating magnetic structures, the possibility of quantum tunneling of the macroscopic magnetization of a particle over anisotropy barriers, and the detection of macroscopic quantum coherence effects accompanying tunneling between two equivalent states.

The work proposed here will be done in part in collaboration with R. Averback, and in part using MRL Central Facilities. Composite structures will be prepared by dual source sputtering in a dense atmosphere. Magnetic particles will be mixed in varying volume fractions with nanocrystals of both metallic and insulating materials and compacted *in situ*. We will also use conventional techniques to produce metastable films of immiscible elements, followed by heat treatment to form nanocrystal precipitates. In preliminary work in the gas-phase system, we have prepared Fe/Cu and Fe/Ge nanocomposites. X-ray studies of the Fe-Cu system indicate that the Fe particle size is predominantly 2 nm. This suggests that we can achieve the goal of embedding monodisperse magnetic nanocrystals of single domain size (approximately 5 nm) uniformly in the matrix material. The magnetic behavior of the as-grown Fe-Cu samples is shown in Fig. 1. The different approaches to saturation are expected; as the concentration increases, Fe nanocrystals in contact act magnetically as single entities, changing the magnetization curves. We propose to examine these samples by Mössbauer spectroscopy, and to study the effects of heat treatment.

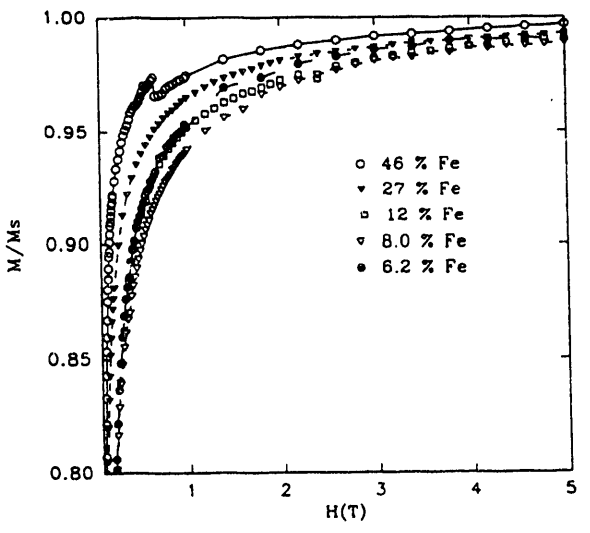


Fig. 1: Approach of the magnetization toward saturation for Fe-Cu nanocomposites of varying composition.

A great deal of interest has been generated by the discovery of giant magnetoresistive effects in multilayer magnetic structures. Quite recently, analogous effects have been reported in Cu and Ag films with precipitated magnetic particles. We have entered a Joint Study Agreement with IBM's Almaden Research

Laboratory focused on magnetothermal transport in multilayer structures. Large thermoelectric changes accompany the magnetoresistance, and provide a key to understanding the source of the effect. In Fig. 2, we show the inverse relationship between thermoelectric power and magnetoresistance. We propose to study these effects in nanophase solids. While Fe precipitates in Cu show such effects, our as-grown Fe-Cu nanocomposites do not. We will prepare Fe-Cu films in the same composition range, to compare the microstructure and magnetoresistance. The absence of a giant magnetoresistance in the nanocomposite may reflect a short mean-free path in the matrix, due to its nanocrystalline structure. Other transport properties, such as Hall angle and thermal conductivity, will be measured. The thermal conductivity is particularly important in understanding the physical basis for this effect, and particularly difficult to measure on thin films.

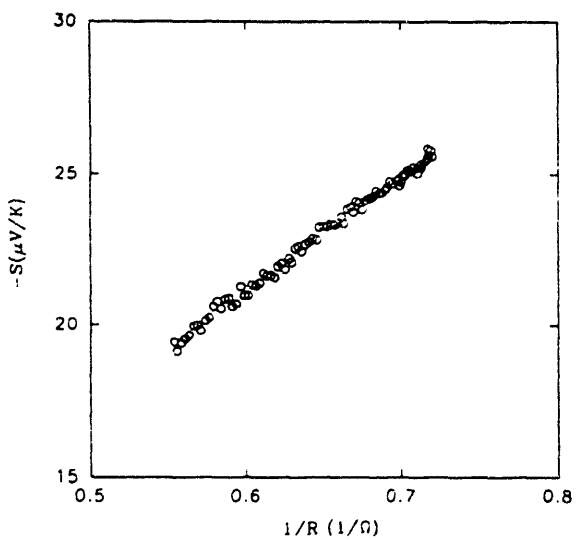


Fig. 2.: Inverse relationship between magnetoresistance and thermoelectric power in a Co-Cu multilayer that exhibits giant magnetoresistance.

In the more concentrated magnetic metal/insulator nanocomposites, our focus is on the development of long-range magnetic order as the magnetic component becomes connected. We will monitor connectivity through the electrical conductivity, which will indicate when the percolation point has been reached. There have been, over the years, many numerical simulations of the behavior of percolation clusters in three dimensions, but very few measurements. It is important that the entities that contact to form a percolating structure be as small as possible, but still magnetic at low temperatures. Below the percolation threshold p_c, the nanocrystals aggregate into clusters that are distributed in size, ranging from single nanocrystals to near-macroscopic agglomerates. Above p_c, long range order appears on an extended cluster that has distinctive fractal properties on length scales shorter than the so-called percolation length. We will be able to explore length scales ranging from the nanocrystal dimension ($\approx$ 2 nm) to the range accessible to small-angle neutron or x-ray scattering ($\geq$100 nm). The Fe-Ge system is useful because the elements differ significantly in both x-ray and neutron atomic scattering factors, so that structural studies are possible. There have been some structural studies, for example x-ray scattering in glasses and on aerogels, but relatively little on percolating magnets. An advantage in these structures is that structural and magnetic data can be compared in order to deconvolute the purely magnetic effects.

Just at the composition where electrical conductivity appears and long-range magnetic order becomes possible, the connected cluster has fractal geometry at all length scales. Excitations such as phonons and spin waves, which are propagating modes on regular structures, become localized on a fractal. The density of states of these excitations differs sharply from that of typical spin-wave or phonon spectra. Once we have established the existence of a percolating structure through static measurements, we propose to explore fractal spin waves on these magnetic systems. There has been extensive theoretical work on this problem, but little experimentation. Neutron Brillouin scattering will be used, a technique recently developed by Robinson at LANSCE. One concern in interpretation is the effect of long-range dipole interactions in providing a bridge between parts of the cluster that are physically nearby, but magnetically separated. We will address this problem by constructing comparable structures using a low-spin ferromagnet such as Ni. Although percolating antiferromagnetic structures would be highly desirable for such measurements, the random orientation of nanocrystals in a composite would almost certainly destroy coherence.

While ordered antiferromagnetic nanophase samples are probably not possible, synthesis of antiferromagnetic/ferromagnetic nanocrystal composites might open a path to new classes of magnetic materials. It has been established that antiferromagnetic layers on a ferromagnet significantly enhance the coercive field, resulting in a magnetically hard material. For example, CoO on Co and MnFe alloys on Fe are very effective at increasing coercivity. Similarly, significant enhancements of the anisotropy energy have been reported to arise from interface effects with various overlayers on Co. We propose to form nanocomposites of ferromagnets and antiferromagnets as a possible path to new hard magnets. Obvious candidates are FeMn nanocrystals in an Fe matrix and CoO in Co. Partial oxidation of Co nanocrystals before compaction could also result in a CoO interface phase, significantly modifying the magnetic properties of the material.

This program has strong ties to Averback's nanocrystalline work, and can foresee interactions with the calculational program of James Adams and interface microscopy research of J. Murray Gibson. In future work, we anticipate the synthesis of composites of hard and soft materials in order to study the elastic and fracture properties of percolating structures and the propagation of phonons on a fractal backbone.

E. RESEARCH SUMMARIES FOR METALLURGY AND CERAMICS

E.1.a RESEARCH SUMMARIES FOR STRUCTURE OF METALS KC-02-01-01

JAMES B. ADAMS

Theory of Defects and Interfaces in Transition Metals

GOALS

a) Comprehensive study of all diffusion processes related to nucleation and growth of metallic thin films.
b) Investigation of grain boundaries in metals.
c) Improvement of an Embedded Atom Method with angular forces.

HIGHLIGHT

The EAM was used to study the diffusion of adatoms at steps. In agreement with FIM experiments by Wang and Ehrlich, we found a "depleted" region near steps, and provided the first explanation of its existence. We also investigated how atoms jump over steps, provided the first theoretical evidence of an exchange mechanism, and explained why it occurred on only some surfaces. Finally, we studied the diffusion of adatoms along steps, and found that they could enhance or hinder the rate of diffusion along the surface

We also completed a study of the mechanical properties of twist grain boundaries, including low, medium, and high-angle boundaries. Their Young's moduli, shear moduli, and critical shear stress were calculated, and found to be closely related to the twist angle of the boundaries.

In collaboration with A. Carlsson (Washington U.) and S. Foiles (SNLL), we developed an improved version of the EAM which includes angular forces. The results for W, Mo and V are extremely encouraging; the complex W(100) and Mo(100) reconstructions are predicted correctly, in good quantitative agreement with experiment. Moreover, preliminary applications of this model to surface diffusion yield results in good agreement with experiment.

We are also developing a new method of generating semi-empirical potentials from first principles calculations. First, we use our *ab initio* LDA codes to generate thousands of atomic configurations. Then, using this massive data base (instead of the typical 6-10 experimental data points), we are able to generate EAM potentials that closely mimic the *ab initio* results over a wide range of structures. This is a revolutionary concept in how to develop highly-robust semi-empirical models.

Finally, as mentioned on the next page, we began carrying out a detailed study of polymer-material interfaces.

FUTURE DIRECTIONS

1) Study surface diffusion on BCC metals.
2) Study interstitial diffusion at grain boundaries.
3) Continue development of empirical models for transition metals.
4) Continue *ab initio* studies of polymer-material interfaces.

SIGNIFICANT ACCOMPLISHMENT

Adhesion at Polymer-Material Interfaces

Scientific Achievement:

During the last year we have carried out the first quantum mechanical studies of the structure and adhesive strength of polymer coatings deposited on metal, metal oxide, and semiconductor surfaces. We have successfully carried out our "proof of principles" studies by simulating systems which could be compared with experimental data. We found that simple hydrocarbon structures (such as polyethylene) bind only very weakly to the various substrates, in good agreement with experiment. On the other hand, polymers with carbonyl groups (C=O double bonds) react violently with a pure Al substrate, resulting in the dissociation of the molecule, in agreement with recent experiments at ALCAN. On aluminum oxide surfaces the reactions are slightly less strong, and the

polymers bind strongly to the substrate, in agreement with experiments at ALCAN and ALCOA. Also, several studies of polymers on Si substrates were carried out. As expected, simple polymers with carbonyl groups bonded strongly to the substrate, but a more complex polymer (polyimide) bonded via its benzene ring instead of via its carbonyl groups. This studies clearly demonstrated that a wide variety of polymer-material systems can be reliably simulated with our *ab initio* models.

Significance:

Polymer adhesion is a major industrial problem and is not well-understood at a fundamental level. Experimental adhesion tests are difficult to carry out, but they only provide rough information on the strength of the bond; our calculations explain in detail why the adhesion is strong or weak. This understanding will aid in designing new polymer material systems for adhesives, protective coatings, insulators for microelectronics, and many other areas. We are working closely with several major US companies in choosing polymer-material systems for future study. Together, we hope to be able to develop new polymer-material systems with enhanced adhesion properties.

This work is funded by the Federation of Materials Industries (Ford, Alcoa, Inland Steel, Boeing, Corning, Motorola, and Amoco), with computational support provided by the DOE-BES Materials Research Laboratory at UIUC.

Performer: James B. Adams, University of Illinois at Urbana-Champaign.

RICHARD C. ALKIRE

Transport Processes during Localized Corrosion

GOALS

The purpose of this program is to relate localized corrosion to molecular behavior at the solid-liquid interface. Of interest is the effect of defects and inclusions on breakdown and repair of protective surface films including inhibitor films. Experiments provide microscopic resolution of the chemical environment during early stages of crevice, pitting and cavitation corrosion. Mathematical models based on transport and reaction phenomena are used to guide verification of mechanism.

HIGHLIGHTS

Initiation, growth and repassivation of corrosion pits on aluminum was found to depend critically upon transport phenomena which control local concentrations. On pure Al in 1 M NaCl, single pits grow at a rate controlled by a sparingly soluble oxychloride surface film, and repassivate upon dissolution of the film. On alloys 6061-T6 and 5454-H34, pitting in 0.5 M NaCl initiates at the edges of Al_3Fe inclusions which support oxygen reduction and thereby create locally alkaline conditions that cause depassivation of the adjacent Al host matrix.

With Gewirth, an atomic force microscope (AFM) was used to observe *in situ* effects of benzotriazole on Cu electrodissolution, to follow the outbreak of single pits at inclusions on Al and 304 stainless steel. Ion selective microsensors with a tip size of 10 microns were fabricated to measure local pH and $[Cl^-]$ distributions by a scanning technique.

A numerical code was written in collaboration with Sani (U. Colorado) to simulate two-dimensional transport in a space charge region. The code represents a general platform suitable for analysis of two-dimensional diffuse double layer effects during zeta corrosion in low dielectric fluids.

FUTURE DIRECTIONS

The effect of competitive thiosulfate and chloride ion adsorption on the passive film of 304 and 316 steels in NaCl will continue in collaboration with **Wieckowski** by using radiotracer methods. In collaboration with **MacDonald** (Penn State), results will combined with the point defect model to investigate why a critical concentration ratio of these ions causes breakdown of the passive film. With **Gewirth**, AFM studies will continue on the related phenomenon of initiation of corrosion pits at MnS inclusions. Scanning photoelectrochemical impedance spectroscopy will be used to monitor the local electrical properties of the passive film adjacent to MnS inclusions during pit initiation. The effect of convection on initiation of pits at MnS inclusions will be mathematically modeled and compared with experimental data.

The role of trace organic additives on corrosion inhibition will be investigated at the molecular level with use of AFM, spectroscopy, and impedance techniques and with the collaboration of **Gewirth**, **Bohn**, **Wieckowski**, and **Nuzzo**. For thin adsorption films, stochastic molecular simulations will be incorporated into boundary conditions in macroscopic models. For thick membrane-like films, models of surface processes will be based on the concept that transport occurs by hopping along defect sites.

SIGNIFICANT ACCOMPLISHMENT

Initiation of Pitting Corrosion at Surface Defects

Scientific Achievement:

Early stages of pitting corrosion on stainless steel and aluminum were found to depend critically upon transport processes, such as diffusion, which control the buildup of locally high concentrations of aggressive agents. In 304 stainless steel in 0.1M NaCl, it was found that pits formed primarily at MnS inclusions which dissolved and created a locally aggressive solution containing sulfur and chloride species that caused depassivation of the adjacent steel. On 99.999% Al in 1 M NaCl, single pits were created by a focused laser initiation technique and were found to grow at a rate controlled by diffusion owing to the presence of a sparingly soluble oxychloride surface film. A necessary condition for repassivation was dissolution of the film. On Al-6061-T6, pitting in 0.5 M NaCl was found to initiate at the edges of Al_3Fe inclusions, which served as sites for oxygen reduction and thereby created locally alkaline conditions in the solution that caused loss of passivity of the adjacent Al host matrix.

Significance:

The annual cost of corrosion to the US economy represents approximately 4% of the Gross National Product. Pitting corrosion, which occurs in hidden crevices and cracks in airplanes, pipelines, and chemical and nuclear reactors, can cause sudden failure and loss of life. There is high economic leverage for understanding the cause of pitting corrosion, for predicting situations when failure is likely, and for developing lower cost materials. The significance of these studies resides not only in the recognition of local transport processes but also in the establishment of new experimental techniques which may be used in a variety of investigations in the future.

Performer: Richard Alkire, David Buzza, Chi Paik and Ruoru Ke, University of Illinois at Urbana-Champaign.

SIGNIFICANT ACCOMPLISHMENT

New Techniques for Monitoring Corrosion at the Microscale

Scientific Achievement:

Three new experimental techniques were developed for studying the outbreak of pitting corrosion at a single site and for measurement of local concentration distributions at the micron scale.

(1) with **Gewirth**, an atomic force microscope (AFM) was used to observe metal surface immersed in electrolyte and under potential control. The device was employed to follow, for the first time, the outbreak of single pits at Al_3Fe inclusions in

Al and also at MnS inclusions in 304 stainless steel, as well as to observe the evolution of morphology during Cu electrodissolution and deposition in H_2SO_4 solutions containing benzotriazole.

(2) Ion selective sensors housed in multi-barrel glass microcapillaries with a tip size of 5 microns were fabricated and used to measure local pH and [Cl^-] distributions at single corrosion sites.

(3) Techniques were demonstrated for creating a single corrosion site so that its electrochemical behavior could be studied in the absence of adjacent pits. For both 304 stainless steel and Al-6061-T6 specimens, a microlithography procedure was used to mask the surface except for a single region which contained a single inclusion where corrosion began. For pure Al, a focused laser was used to initiated pitting corrosion.

Significance:

Superior technology in corrosion prevention arises from superior science, and both rest in large part on experimental tools for observing corrosion processes directly at the interfaces where they occur. The direct in situ observation of natural corrosion processes while they are occurring is extremely difficult to accomplish. The three methods reported here make possible, for the first time, direct and simultaneous characterization of visual, chemical, and electrical behavior with resolutions that are orders of magnitude superior to previous work.

Performer: Richard Alkire, Andrew Gewirth, Rebecca Mohr Rynders, Chi Paik, Thomas Jarvi and Ruoru Ke, University of Illinois at Urbana-Champaign.

R. S. AVERBACK

Non-Equilibrium Processing of Materials

GOALS

This program investigates non-equilibrium processing of materials using ion beam irradiations or inert gas condensation of nano-sized particles. The ion beam studies include both experimental and computer simulations to examine the fundamental interactions of energetic particles and clusters with metals, semiconductors and insulators. Radiation damage problems are included; they focus on the primary state of damage and radiation-enhanced diffusion. The research on nano-grained materials investigates the relationships between the structure and chemistry of these materials and their high temperature mechanical properties.

HIGHLIGHTS

Molecular dynamics (MD) computer simulations of the bombardment of Au surfaces with 10 keV Au atoms revealed a surface mechanism of defect production unrealized before. The energetic Au atom locally melts a volume of substrate near the surface, ≈ 1000 nm^3, and because the melt is less dense than the solid, it expands through the surface. Upon subsequent resolidification, many atoms freeze in place above the surface, leaving a shortage of atoms below. Thus, similar to void formation during chill casting, the melt zone freezes with too few atoms in the center and defects are created. In this case, the defects are dislocations rather than voids. In other MD work, the "soft" landings of clusters on surfaces were examined. We find for small clusters the surface energy is sufficient to shear the cluster atoms into epitaxial alignment with surface, but for larger clusters, ≈ 1000 atoms, the surface to volume ratio is too small and a grain boundary is generated in the cluster (Fig. 1).

Radiation-enhanced diffusion (RED) experiments were performed on Cu_3Au and MgO; they constitute the first direct measurements of RED in any oxide ceramic or

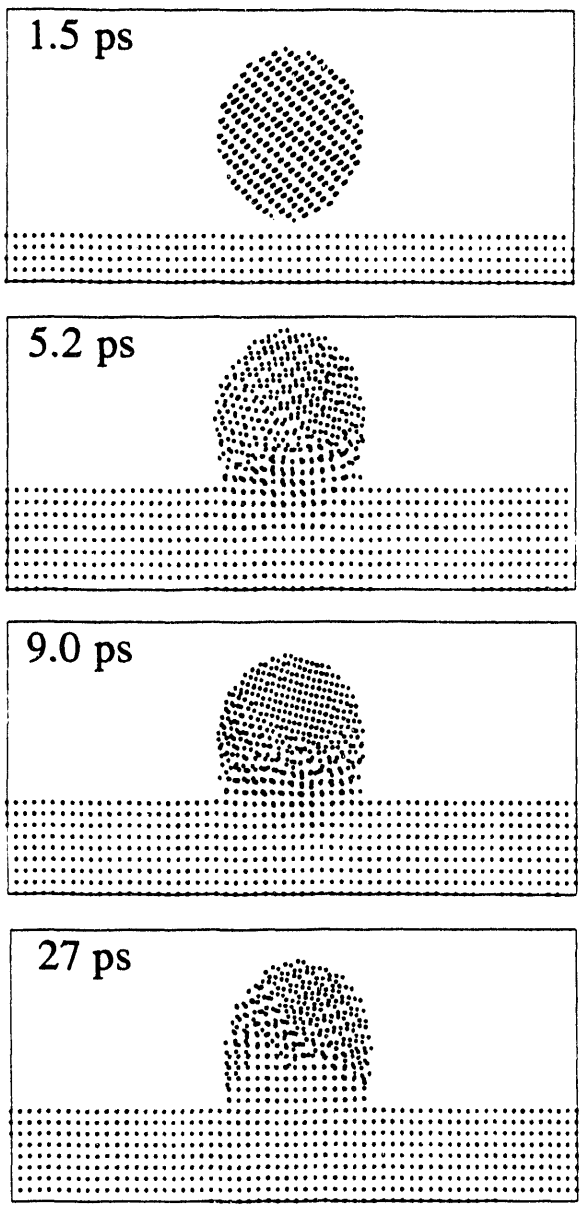


Fig. 1. Interaction of a cluster of 957 Cu atoms with a Cu surface. The cluster has been misoriented with respect to substrate, its initial kinetic energy is 0.2 eV. Notice the formation of a grain boundary in the interior of the cluster.

intermetallic phase. The results on Cu_3Au are particularly interesting because the measurements could be carried out both above and below the ordering temperature, and on both sublattices. We find that RED is reduced by a factor of ≈ 7 for the ordered phase. Differences in RED on the two sublattices are also observed.

Research on nano-grained materials focused on sintering, sinter-forging and grain growth in ceramics and diffusion in metals. An empirical constitutive law for sinter-forging in nano-grained TiO_2 was obtained. The experiments yield a stress exponent , n =2, and activation enthalpy ≈ 210 kJ/mole, and an extremely strong dependence on density, exp[-30r] where r is the density. Other features of sinter forging in these materials indicate a threshold stress for deformation, which is not observed in larger grained materials, and virtually no strain transverse to the direction of the applied stress. These results are significant for near-net shaping as well as providing a fundamental understanding of the relative motion of interfaces during deformation at elevated temperatures. Constitutive law modeling is currently in progress in collaboration with Sofronis. Diffusion measurements on nano-grained Cu revealed that the average grain boundary energy in these materials is ≈ 10% larger than in large grained Cu polycrystals. We tentatively associate the higher energy with the large fraction of triple junctions in these materials.

FUTURE DIRECTIONS

The research on nano-scale materials will focus on the relationships between nano-particle chemistry and structure with diffusion, grain growth, sintering and high temperature deformation. A significant part of this work will be devoted to *in situ* observation of nano-particles that are transported from a synthesis chamber directly into a UHV, high resolution electron microscope (with Gibson). Efforts to stabilize grain size during sintering and deformation will focus on doping of nano-grained ceramics and synthesizing composite ceramics (for example Si_3N_4/SiC with Zangvil). Diffusion measurements will be performed on nano-grained alloys to probe segregation effects and the effects of segregation on grain boundary energies.

Computer simulations of radiation effects will further explore the effects of surfaces on defect production and surface phenomena in general (sputtering, desorption, cluster deposition, laser ablation). In conjunction with the simulations, experiments will be performed to reveal the thermal history of spikes in metals and insulators, and the damage created at surfaces. Experimental investigations of defect

production, radiation enhanced diffusion and impurity segregation to interfaces will be performed on insulating materials and amorphous alloys.

SIGNIFICANT ACCOMPLISHMENT

Molecular Dynamics Simulations of 10- keV Au Bombardment of Au

Scientific Achievement

A new mechanism of defect production near metal surfaces during ion irradiation was elucidated by molecular dynamics computer simulations. Simulation of the impact of a 10 keV Au atom with a Au surface revealed that a complex tangle of dislocation loops are generated in the near surface region. What is surprising is that these dislocations, which had previously been experimentally observed by electron microscopy, are not created by ordinary defect production processes in metals but rather by a surface effect. We found that local melting of the cascade volume, a phenomenon previously demonstrated for the first time in our group, results in the flow of liquid metal onto the surface, where it freezes- see Fig. 1. Upon resolidification of the cascade volume below the surface, too few atoms are available to fill the lattice sites. Hence, similar to void formation in cast metals, the central region is devoid of atoms and regrowth defects are formed; in this case, dislocation loops are produced rather than voids. The number of missing atoms is somewhat larger than that predicted by the Kinchin-Pease model of defect production, although that mechanism is not relevant here.

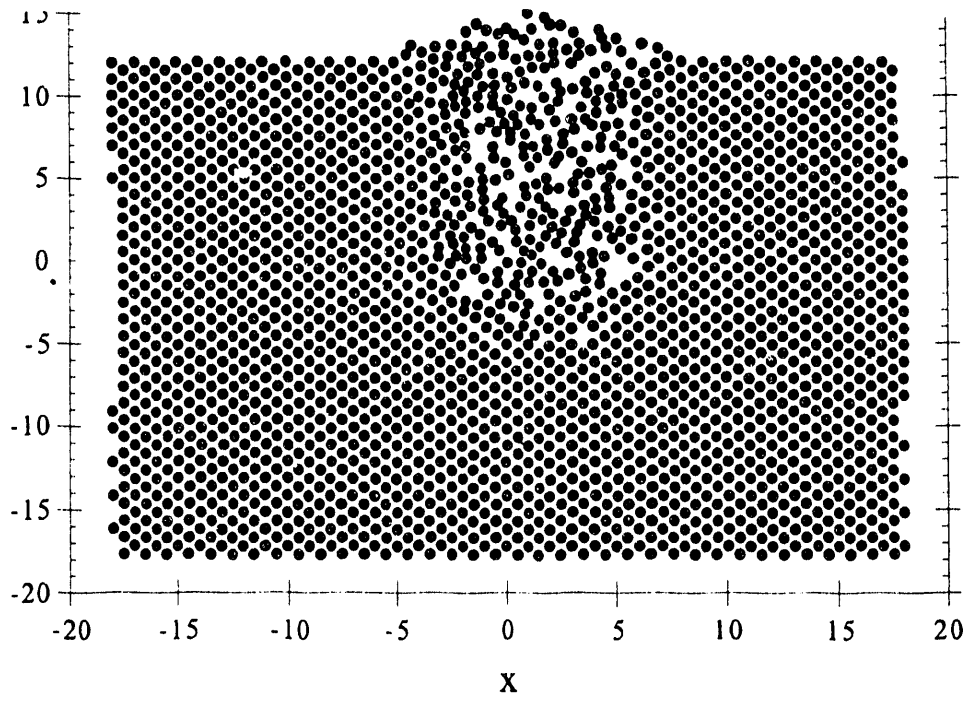


Fig. 1. Surface melting of Au due to the impact of a 10 keV Au atom. Notice the flow of atoms onto the surface. Approximately 1,000 atoms freeze above the surface, which leads to the formation of a complex dislocation tangle in the near surface region.

Significance

The demonstration that defect production at surfaces of ion irradiated materials can be fundamentally different than defect production in the bulk, in regards to mechanisms, defect structures and amount of damage, calls into question the interpretation of years of past research on radiation damage and ion beam modifications of materials. The observations of large vacancy dislocation loops in ion-irradiated metals have often been cited as "clear" evidence for efficient separation of interstitial atoms and vacancies; our simulations reveal that only three interstitial atoms are produced away from the cascade while several hundred vacancies derive directly from the surface melting. These results may also provide the answer why interstitial dislocation loops are not observed in the primary state of damage in electron microscopy studies. Since all ion beam simulations studies of neutron damage and all applications of ion beams for materials modification involve surfaces, these new findings will impact many areas of research and technology.

Performer: R.S. Averback, University of Illinois at Urbana-Champaign.

PAUL W. BOHN

Molecular Properties of the Solid-Liquid Interface and Their Relation to Corrosion

GOALS

We are using *in situ* molecular spectroscopic probes to investigate the structural chemistry of N,S-containing aromatic heterocyclic molecules of interest as corrosion inhibitors on various metal oxide surfaces. We are studying (1) the molecular structure of corrosion inhibition reagents, especially as the structure is affected by external perturbations, such as extremes in ionic strength, temperature, and pH, and (2) the permeability of monolayers of such reagents under such perturbations. By comparing the two pieces of information for a particular inhibitor and metal oxide surface, we are developing a molecular level understanding of the relative importance of physical blocking of active corrosion nucleation sites vs. generic blocking of all surface sites. We are using the results of these experiments to compare with the uhv results on similar systems obtained by Wieckowski, and we are collaborating with Alkire and Gewirth to develop atomic-resolution images of the structures which we characterize spectroscopically. Naturally a long-term goal of developing this type of molecular-level understanding is the design of new and more effective corrosion-inhibition systems from the molecular perspective.

HIGHLIGHTS

We are pursuing two parallel sets of experiments, both of which are focused on the system benzotriazole (BTA) with Cu_2O and CuO. In one set of experiments we have developed a capability for performing ultraviolet absorption measurements at ultrathin ($t \leq 150$ Å) Cu oxide films. This ability removes the difficulties associated with studying adsorption of organic molecules at the solid-liquid interface by traditional solution difference techniques, and it makes possible the use of polarized spectroscopies to address structural questions. A correlated set of ultraviolet absorption, Auger electron spectroscopy, and x-ray photoelectron spectroscopy measurements have been performed at various points along the

adsorption isotherm. Auger measurements were used to calibrate the surface coverages, and correlation with integrated uv absorption band intensities showed that the much simpler uv absorption measurement could be used directly to calibrate surface coverage. A critical control experiment involved demonstrating that the orientation of adsorbed BTA does not change as a function of surface coverage, as had been postulated from uhv results. At saturation coverage the surface density is ca. 12% smaller than would be predicted for a close-packed layer. This difference can be explained either by a tilting of the adsorbates relative to the surface normal, or the presence of a large number of two-dimensional grain boundaries, or a combination of the two. The nonlinear optical experiments and atomic force imaging experiments (*vide infra*) to be performed in the coming year will resolve the issue. These experiments have been augmented by a set of semi-empirical structural calculations on the BTA system. Of particular interest for these calculations are the development of an understanding of the charge distribution in the BTA^- anion (the adsorbed species) and its second and third order hyperpolarizability properties. The computations show clearly the uniqueness of the central nitrogen atom and support the perpendicular geometry inferred from the polarized absorption and coverage measurements. In the other set of experiments we have developed an ultrahigh vacuum second harmonic generation capability and have tested it on a set of model systems. We are now ready to use the SHG capability to extract absolute orientations from BTA/Cu oxide systems.

FUTURE DIRECTIONS

In the coming year we will pursue a number of goals. Foremost among these is the measurement of molecular orientations and orientational order parameters utilizing the nonlinear optical experiments. A key component of these measurements will involve computations of the dispersion curves for the molecular hyperpolarizability, $b_{ijk}(w)$, tensor components. In addition we will pursue the use of the uv absorption technique for measurement of thermodynamic and kinetic parameters associated with the development of the BTA monolayer from aqueous solution. We are also working closely with **Gewirth** to construct a cell which will allow us to examine the vibrational (Raman) spectroscopy of adsorbed anions in the underpotential deposition (upd) region. Anion coadsorption has been posited as an explanation for the observation of enlarged adlattices in upd layers, but there is no structural information at present on these anions. Finally we will work with **Alkire** to develop atomic force microscopic data to address the question of the size of ordered two-dimensional regions in adsorbed BTA layers.

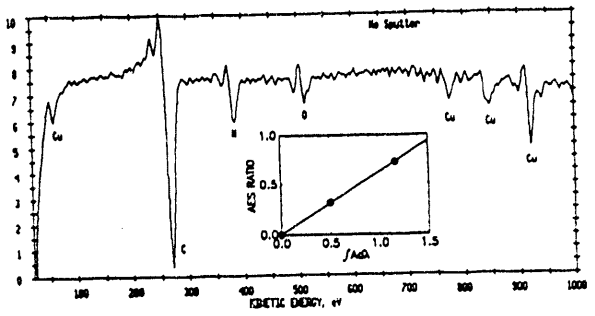
SIGNIFICANT ACCOMPLISHMENT

Benzotriazole Adsorbs as Saturated Layer on Cu_2O

Scientific Achievement:

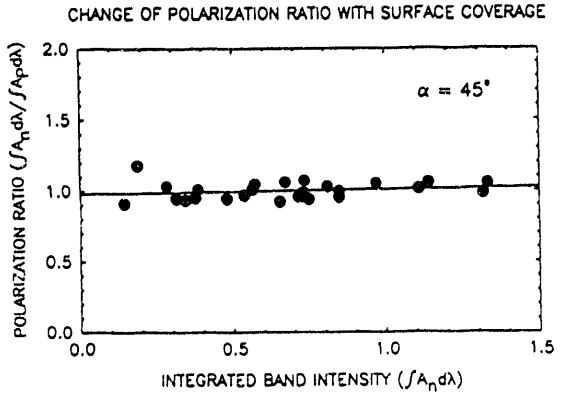
There has been a great deal of controversy in the literature over the structural nature of the first adsorbed layer in the BTA/Cu oxide system with results from a wide variety of experiments indicating everything from monolayer coverage with the triazole and phenyl rings parallel to the surface to multilayer formation of a polymer-like structure with stoichiometry $(Cu^+BTA^-)_x$. We have now conclusively demonstrated that adsorption at open-circuit potential from aqueous solution at neutral pH yields: (1) monolayer coverage at saturation, (2) an orientation with the triazole ring predominantly perpendicular to the surface plane, independent of surface coverage, and (3) adsorption as the anion, BTA^-. The latter point is not controversial, however there had been much debate in the literature over the saturation coverage and orientation issues.

The fact that the coverage is monolayer is established from the correlated uv absorption and quantitative Auger measurements of N/Cu ratios. Figure 1 shows the Auger spectrum, which is used to establish the N/Cu ratio for saturation coverage, and the relationship of coverage to integrated band intensity. The saturation coverage of 7.0×10^{14} cm^{-2} is slightly



smaller than the closest-packed coverage of 8.3 x 10^{14} cm^{-2} based on an orientation in which the rings are completely perpendicular to the surface at full monolayer coverage. The small discrepancy may be explained either by assuming a small tilt of the aromatic ring systems ($\theta \leq 30°$) or the existence of two-dimensional grain boundaries. In any case, the coverage is clearly not multilayer.

The coverage-independence of the orientation is established from polarized monolayer absorption measurements. Again these are made possible by the unique ultrathin film Cu_2O and CuO substrates developed in this project. In particular the data in Figure 2 are obtained by forming the ratio of absorbance at



normal incidence to that at 45° for p-polarized radiation. The ratio depends on the a complex function of the field amplitudes and the orientation of the transition dipole. Since the field amplitudes do not change among the different coverage values, the constancy of the A_n/A_p ratio demonstrates conclusively that the orientation is not coverage-dependent. Together these detailed structural measurements are beginning to allow us to build a complete picture of the initial adsorption steps in the BTA-Cu oxide system.

Performer: Paul W. Bohn, University of Illinois at Urbana-Champaign.

J.A. EADES

Microanalysis of Defects and Interfaces

GOALS

This program seeks to develop new microcharacterization techniques and equipment through research projects on important microstructural problems in materials science. While the effort is principally directed towards the development of techniques, it is the philosophy of this program that such development is best carried out when coupled to important materials problems.

HIGHLIGHTS

1) The main focus of the group's work is now the study of surfaces by reflection electron diffraction and reflection electron microscopy. This technique is of growing importance because of its unique ability to image and characterize surface steps and other surface features. The particular focus of this work is to provide a more complete understanding of the diffraction from perfect and defected surfaces, in order to complement reflection imaging. Computer simulations have been used to simulate perfect surfaces (next section) and are now being applied to defects.

2) RHEED (reflection high-energy electron diffraction) has long been used for the characterization of surfaces. However, the interpretation of the patterns has been very limited. Positions of reflections are used to determine the unit cell, and intensities have been used qualitatively: for example in RHEED oscillations. By using computer techniques originally developed for transmission electron microscopy, we have been able to use the intensities in RHEED patterns to make an accurate determination of the atomic positions in a reconstructed surface.

The multislice method of calculating electron diffraction patterns has been used to write computer programs that can give accurate simulations of RHEED patterns. These programs were used to simulate the pattern from a (001) surface of GaAs with a 2x4 reconstruction. Various models for the reconstruction were tried. Comparison with experimental data was made by means of a reliability factor, R, analogous to that used in x-ray diffraction. Only one structure fit the experimental data and this was further refined to determine exact atomic positions.

The missing dimer model was shown to be correct and the surface relaxation as shown to be +8%. The dimer twist was shown to be zero within the accuracy of the method.

3) Preparatory work has been undertaken on the design of a new kind of scanning electron microscope for surface characterization. This will be developed into a completed design and a proposal for construction will be submitted. The instrument will be a field emission SEM with non-conventional detection systems. It will make it possible to image both surface steps and sub-surface dislocations. It will be installed on the EpiCenter MBE system and used to study crystal growth and epitaxial structures.

4) Convergent-beam diffraction is a powerful and established method for the characterization of crystalline samples in the transmission electron microscope. Nonetheless, several problems remain in this field. During the last year, contributions have been made to the understanding and accuracy of the use of HOLZ lines for crystal strain determination and to the understanding of dynamical extinctions; an important aspect of space group and structure determination.

FUTURE DIRECTIONS

This program will continue its focus on the coupling of instrumentation and physical property determination. In particular the work on reflection diffraction and imaging will continue. The next phase will be to experimentally study surfaces in a UHV microscope with energy filtering of the patterns. Computationally we will to study surfaces with defects.

INTERACTIONS

This program is an integral part of the Center for the Microanalysis of Materials and provides the scientific base for many of the developments being pursued in the Center. The program interacts with many of the other efforts in the MRL through its instrumentation development and its application of advanced microanalytic methods to materials characterization. This research group acts as a resource for the MRL in developing new microanalytic methods and assisting in the application of these for many other programs.

SIGNIFICANT ACCOMPLISHMENT

Quantitative Surface Structure Determination from RHEED

Scientific Achievement:

RHEED (Reflection High Energy Electron Diffraction) is a powerful technique for the characterization of surfaces. However, the interaction of electrons with matter is very strong and the kinematic approximation that can be used to describe x-ray and neutron diffraction cannot be used in the electron case to account for diffracted intensities. As a result RHEED patterns have rarely been interpreted quantitatively.

By using the dynamical diffraction theory, developed for use in transmission electron microscopy, we have been able to make a quantitative analysis of the reconstructed GaAs(001)-2x4 surface. It was possible to distinguish between different competing models of the reconstruction and to determine the key parameters that describe the system.

An experimental pattern from the GaAs(001)-2x4 surface (obtained by P. K. Larsen of Philips Research Labs) was compared with computed patterns, made with a program using the multislice algorithm. This computational method is well established for high-resolution transmission electron microscopy but was used here in a form especially suited to calculating diffraction patterns in grazing incidence reflection.

The experimental pattern had been acquired photographically so that the intensities of the reflection were estimated visually rather than measured. Therefore, the comparison with the simulated patterns was made using methods from early x-ray work in which intensities are classified as strong, medium or weak.

For each simulation an R-factor was calculated, again following x-ray methods.

$$R = \hat{A} \frac{| I_{obs} - I_{calc} |^2}{\hat{A}\ I^2_{obs}}$$

Because of the novelty of this approach many tests and checks were made in order to establish the validity and usefulness of the method.

We can draw the following conclusions:

1. Dynamical theory is necessary and (as expected) a kinematical approach would give quite the wrong answer.

2. The GaAs (001)-2x4 surface has a dimerized surface structure with one dimer in four missing (at the stoichiometry of the surface prepared for the experiment). Other proposed models can be eliminated.

3. The surface relaxation of the dimers is d = 8%.

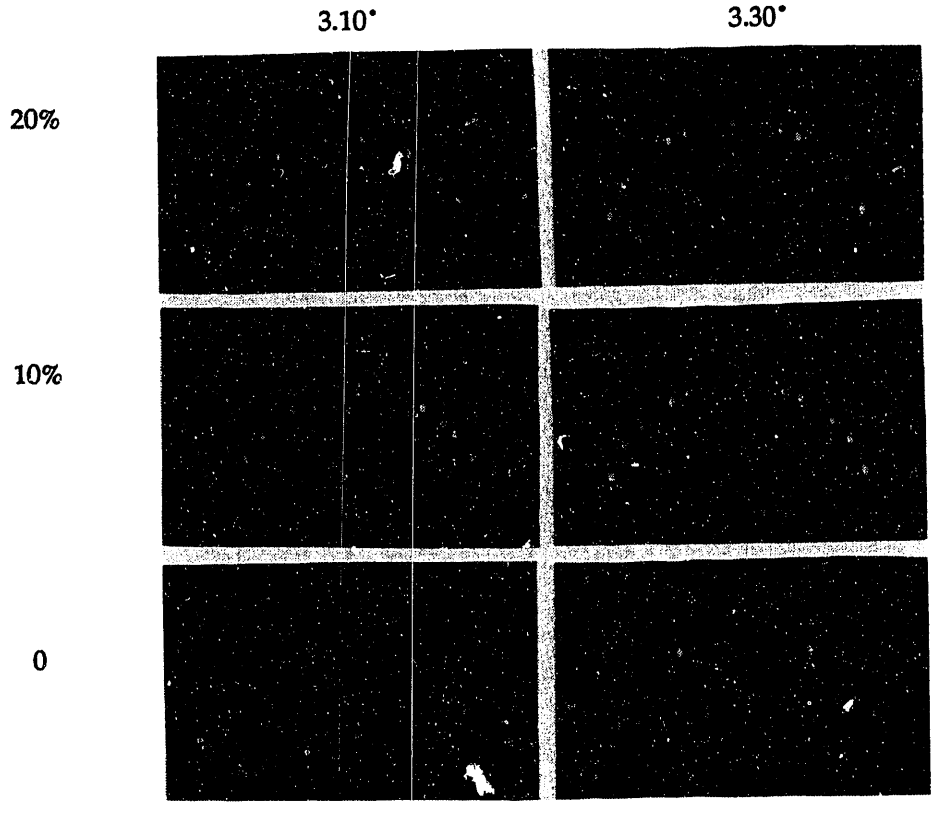
4. The dimer length is $l_d = 2{\cdot}2 \pm 0.3$A°.

5. There is no dimer twist (to the accuracy of this method).

6. The simulations are optimized for values of absorption and Debye-Waller factor that are consistent with expected values.

7. The method has been shown to work well and may be expected to be of rather general applicability.

Because RHEED is such a non-intrusive method of *in situ* characterization, the ability to provide a quantitative determination of surface structure is a very important advance.



Simulated RHEED patterns as a function of angle of incidence and relaxation parameter for the missing-dimer model.

Performer: J. A. Eades, University of Illinois at Urbana-Champaign.

G. EHRLICH

Atomistics of Growth and Transport at Metal and Semiconductor Surfaces

GOALS

The individual atomic events contributing to the growth of films and overlayers on crystals are being explored on the atomic level through the use of the field ion microscope.

HIGHLIGHTS

Efforts to characterize the atomic processes participating in growth on metals are continuing, with special emphasis on the transport of atoms toward growth sites on densely packed planes. Taking advantage of the unique ability of the field ion microscope to reveal individual adatoms, we have carried out detailed measurements of displacement distribution functions for both Ir and W adatoms on W(110). These have demonstrated that diffusion is quite a complicated process, even though it occurs by jumps of individual atoms over the surface. At low temperatures, at which motion is just barely perceptible, transport has been found to occur by jumps between nearest-neighbor sites along the closepacked $[1\bar{1}1]$ directions. At higher temperatures, however, other transitions become more important, and double jumps along the close-packed directions, as well as jumps along [001] and $[1\bar{1}0]$ begin to contribute significantly. This appears to be a general phenomenon, not just limited to self-adsorbed atoms – we have observed this trend for both tungsten and iridium adatoms on W(110). Under the usual growth conditions, atoms carrying out long jumps may therefore contribute significantly to the rate at which material can reach growth sites.

We have also been able to demonstrate, for the first time, how adatoms reach ascending lattice steps at which they can incorporate. In the standard view of crystal growth, it is assumed that adatoms carry out ordinary diffusive jumps until they strike a step and become attached there. We have completed extensive observations of the movement of iridium adatoms on Ir(111) surfaces on which a central cluster had previously been formed. These studies reveal that the actual behavior at steps is quite different from the standard picture. Detailed mapping experiments, in which the positions of individual adatoms are determined, have established that clusters are surrounded by an "empty region". As shown in Fig. 1, there is a strip of sites around a cluster, ~ 3 nearest-neighbor distances deep, in which adatoms are never seen. Our experiments lead to the conclusion that in the region immediately around a cluster, diffusion toward the steps occurs much more rapidly than on a smooth crystal terrace, so that atoms entering the zone are swept toward the step. This new phenomenon appears to arise from the distortion of normal atomic spacings in the vicinity of a lattice step, an effect which has not been considered in past theories of crystal growth, but appears to strongly affect the atomic events there.

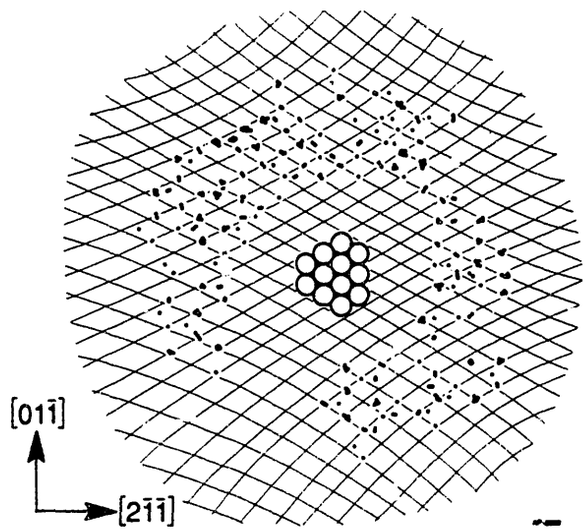


Fig. 1 Location of iridium adatoms after diffusing over Ir(111) with Ir_{12} cluster at the center. Adatoms are *never* found in region immediately around the central cluster.

FUTURE DIRECTIONS

Our studies of atomic behavior at steps on Ir(111) suggest that incorporation is a much more complicated and interesting event than envisioned in the past. One objective of our work will therefore be to explore more fully the

possible atomic processes that may contribute to incorporation of Ir atoms into a cluster on Ir(111). Our second objective will be to examine how general these events are, by investigating incorporation phenomena with other adatoms, and also on other closely packed substrate surfaces.

ANDREW A. GEWIRTH

Atomic Resolution Electrochemistry of Corrosion and Deposition Processes

GOALS

Our research is directed toward developing an atomic-level understanding of processes occurring at the solid-liquid interface. We utilize high resolution microscopic techniques which provide in situ atomic resolution images of electrode surfaces. We focus on the dissolution of bulk metal and semiconductor materials, especially those from single crystal surfaces, and on the role of organic molecules in inhibiting the corrosion process. In the first area we examine the shape evolution of pure materials and alloys during anodic dissolution. We are particularly interested in identifying with high resolution the spatial origin of corrosion processes on the surface and their course of development. In the second area, we examine small molecule binding to electrode surfaces in order to correlate the structure of the bound small molecule with electrode reactivity.

HIGHLIGHTS

A) In collaboration with **Alkire** we have studied the anodic dissolution of polycrystalline Cu electrodes. We have shown that the initial stage in corrosion is the removal of the amorphous damage layer which originated in electrode pretreatment and that only after removal of this damage layer does preferential faceting occur. Protection from corrosion can be effected by exposure of the surface to an organic inhibitor. This inhibitor forms a smooth coating atop the surface which breaks down only under significant overpotentials.

B) We have shown that the Cu(100) surface in acidic solutions exhibits a (+2 x +2) R45° overlayer of oxide or hydroxide (Figure 1a) at all but the most cathodic potentials. This overlayer can be removed at very negative potentials leaving the bare Cu(100) surface (Figure 1b). While bulk Cu_2O is unstable at the potentials and pHs used in these experiments, our results suggest that the chemistry of Cu surfaces -- even in acidic solutions -- must consider the partial oxide monolayer. This insight has been

extended to monolayers of urea -- a widely used corrosion inhibitor -- which form a c(2x2) adlattice on Cu(100).

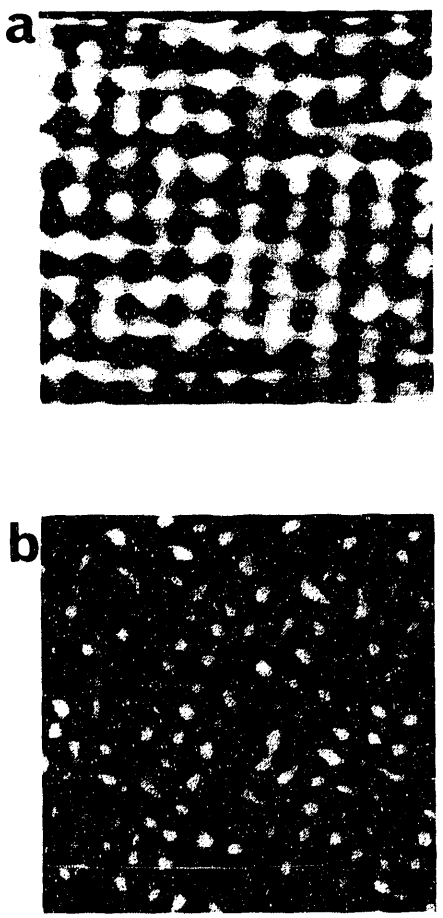


Figure Caption: 3 x 3 nm AFM images Cu(100) surfaces. A) Image obtained in 0.1 M $HClO_4$ at -0.45 V vs Hg_2SO_4 exhibiting a (+2 x +2) R45° overlayer of oxide or hydroxide. B) Image obtained at -1.0 V vs Hg_2SO_4 exhibiting the bare Cu(100) surface.

FUTURE DIRECTIONS

Our ability to routinely obtain atomic resolution images of electrochemical processes on electrode surfaces has enabled us to begin to correlate electrode surface morphology with electrochemical response. We will continue to examine the structures of small organic molecules on Cu and other materials. These molecules are important not only to a variety of catalytic phenomena, but also as corrosion inhibition and deposition agents. We will also evaluate anodic dissolution from low Miller index Cu single crystals where well-defined step and terrace features are available.

SIGNIFICANT ACCOMPLISHMENT

Correlation of STM, AFM and Surface X-ray Scattering Structures of Monolayers on Electrode Surfaces

Scientific Achievement:

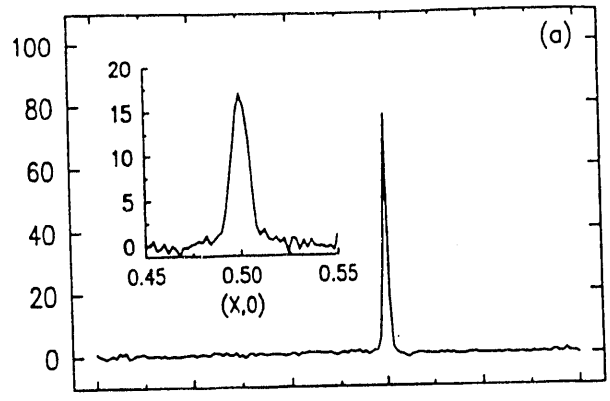
We have used the three available *in situ* structural techniques -- Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and Surface X-ray Scattering (SXS) -- to characterize monolayers of Bi on Au(111) electrode surfaces. We have demonstrated that all three give the same structures in the same potential regions. The figure shows the (2 x 2) - Bi overlayer on Au(111) as determined by a) SXS, b) AFM, and c) STM. This is the first proof that the probe techniques -- STM and AFM -- provide true images in metal-on-metal systems. This is also the first time an open metal-on-metal system has been observed with SXS.

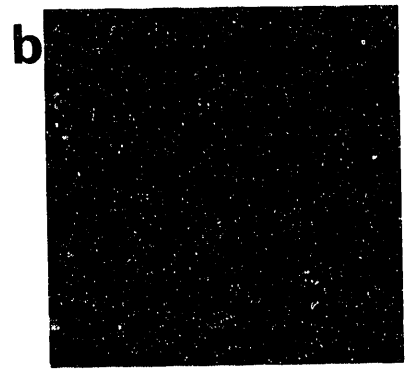
Significance:

A major question in Scanning Probe Microscopies such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) concerns the representativeness of images. This is especially true in the electrochemical environment where we have observed open (not close packed) structures of metals on other metals. These metal-on-metal structures, which are without precedent in the Ultra High Vacuum (UHV) environment, act as catalysts for a variety of electrochemical processes. Bi monolayers especially act as catalysts for efficient reduction of H_2O_2 to H_2O. Until this work there was significant uncertainty about whether the structures observed with the AFM and STM were, in fact, truly representative of the real atomic arrangement on the electrode surface. Our demonstration, for the first time, that all three *in situ* structural techniques -- STM, AFM, and SXS -- give exactly the same structures of Bi

on Au(111) allows us to proceed with characterization of this and other catalytically important surfaces.

Performer: Andrew A. Gewirth, University of Illinois at Urbana-Champaign and Benjamin M. Ocko, Brookhaven National Laboratory.





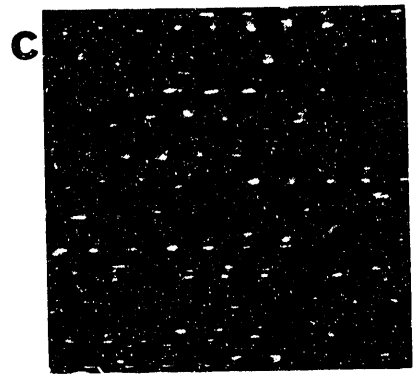


Figure caption: Electrodeposited (2x2)-Bi adlattice on Au(111) as determined by three different *in situ* structural techniques. a) Surface X-ray Scattering diffraction shows a peak at (1/2, 1/2) in reciprocal space consistent with a (2x2) adlattice. b) AFM and c) STM images of the (2x2) structure.

J.M. GIBSON

Transmission Electron Microscopy of Surfaces and Interfaces

GOALS

We are interested in studying atomic structure at surfaces and interfaces, and in developing new quantitative techniques of transmission electron microscopy for this purpose. Corrosion, wear and electrical properties of solar cells are aspects of materials important to DOE in which knowledge of properties at surfaces and interfaces is fundamentally important. A specific theme is the use of in-situ techniques for the monitoring of structural development during film growth and processing. In this way we can better understand surface processing and growth. The phenomena which we have studied have ranged from the oxidation process to nucleation and growth of thin films. A new ultra-high vacuum electron microscope, just coming on-line, is key to future progress.

HIGHLIGHTS

The Si(111) 7x7 surface reconstruction is a classic example of a surface structure that has been well-studied and thus is a good benchmark for the development of new quantitative scattering techniques with transmission electron microscopy. With careful quantitative analysis we have found that the atomic structure of this surface can be determined to approximately 0.1 Å accuracy by quantitative analysis of transmission electron diffraction patterns making the kinematical approximation. The structure obtained is almost identical to that measured by synchrotron X-ray diffraction (which takes hours compared with seconds for TEM) and from massively parallel ab-initio calculations. The electron diffraction technique therefore provides a rapid method for studies of surface and interface structure which rivals synchrotron diffraction, and permits high-resolution imaging. During the initial stage of Si oxidation, we can use these techniques to identify which bonds in the surface are broken by oxygen or water vapor.

The epitaxial growth of Pd_2Si on Si (111) is an interesting system in which to study fundamentals of nucleation and growth on surfaces. We deposit Pd at room temperature and control the solid-phase reaction with in-situ annealing. The as-deposited films are metallic Pd and they react just above room temperature to form the silicide. The films grow in an incommensurate, strain-relaxed fashion. The films can be quite uniform when grown at low temperature, but clearly are not in equilibrium, since thermal annealing at > 400 °C leads to pinhole formation, which is the precursor to balling-up of the film. We find that pinhole nucleation is greatest on regions of the surface which have a high density of surface steps. This has important implications for the growth of uniform continuous films, e.g. as contacts to solar cells or for corrosion resistance.

Much of the last year has been spent assembling the new SHEBA (Surface High-energy Electron Beam Apparatus) machine, which is a TEM in which well-controlled surface science can be achieved, arguably for the first time. We have in-situ access to LEED, Auger spectroscopy, MBE deposition, gas reaction and deposition in a large and well-controlled ambient with base pressure in the low 10^{-10} torr. As of writing, we are beginning experiments with this instrument.

FUTURE DIRECTIONS

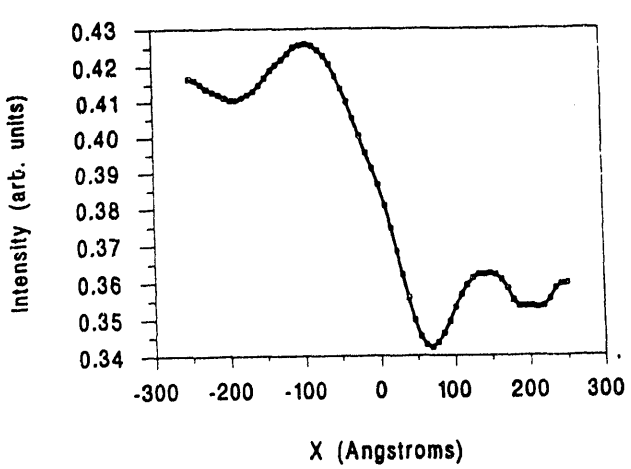
With the new SHEBA machine we will not only be able to study a wider variety of surface and in-situ growth phenomena on novel materials for the first time, but we will also have much better control over conditions with access to simultaneous chemical characterization of the surface. This unique facility is likely to provide important new insights into near-surface phenomena, and it offers the attraction that "real-world" buried surfaces are also amenable to study due to the penetrating power of high-energy electrons. This is best exhibited by our past work on the oxidation of silicon. We are also endeavoring to develop quantitative techniques of analysis using complementary "conventional" high-resolution electron microscopy to study interface structure.

SIGNIFICANT ACCOMPLISHMENTS

Strain Fields at Atomic Surface Steps

Scientific Achievement:

Theorists studying the equilibrium shape of surfaces have recently considered the interaction of surface steps, through long-range sub-surface strain fields, as an important factor both in thermodynamics and kinetics. The latter is particularly significant during crystal growth. Although these effects have been indirectly observed from step behavior, until this year, they have never been directly observed, to our knowledge. On the Si (111) surface we have used diffraction contrast Transmission Electron Microscopy (TEM) to reveal the strain fields of individual atomic steps. This is possible in our UHV TEM, in which we can clean and anneal surfaces so that well-ordered atomic terraces form. However, the strain contrast can also be seen after exposure of such a surface to atmosphere, but the magnitude is different because it is now characteristic of steps at the buried Si/SiO_2 interface. We have used a model of the strain field at steps to match our experimental images and can deduce the magnitude of the line force which is effectively applied at the step. This force is sensitive to the surface energy and step reconstruction, and thus can be used to locally monitor these important but difficult to measure phenomena.



Caption: This is a line trace across the image of a monatomic step on the Si(111) surface obtained in a weak beam image at 100 kV in a UHV transmission electron microscope. The step corresponds to the change in average intensity near x = 0. The oscillations in contrast are due to the strain field round the step, and these are similar, for example, to features in weak-beam dislocation images.

Performer: J. M. Gibson, University of Illinois at Urbana-Champaign.

G. S. GIROLAMI

The Chemistry of New Transition Metal Ceramic Compounds Synthesized by MOCVD

GOALS

The goals of our program are (1) to prepare ceramic thin films by low-temperature CVD from suitably designed transition metal organometallic precursors, (2) to study the deposition mechanisms of the films so produced, (3) to develop methods to grow films of metastable phases by controlling the kinetics of the growth processes, and (4) to investigate the physical and mechanical properties that are characteristic of thin films prepared at low temperature.

HIGHLIGHTS

Mechanistic Studies of the Deposition of Titanium Nitride. We have extended our studies of the gas phase and surface reactions that are responsible for the low-temperature deposition of titanium nitride films from the metal-organic precursor tetrakis(dimethylamido)titanium. Unlike many CVD process, the most important chemical reaction takes place in the gas phase: ammonia reacts with $Ti(NMe_2)_4$ to give products that contain amido (NH_2) or imido (NH) groups. These gas phase products then are transported to the surface where they transform into TiN. In the absence of ammonia, we have determined that $Ti(NMe_2)_4$ undergoes a β-elimination process that results in the formation of one equivalent of dimethylamine and a titanium-containing product that contains a Ti-N-C three-membered metallacycle. This observation accounts for the fact that films grown from $Ti(NMe_2)_4$ in the absence of ammonia are heavily contaminated with carbon, since Ti-C bonds that are formed in the gas phase are not broken in subsequent steps.

Surface Selective Chemical Vapor Deposition Processes. There has been much recent interest in the development of chemical vapor deposition processes that occur selectively; i.e. deposition occurs on some surfaces but not on others. We have discovered that passage of palladium(II) bis(hexafluoroacetylacetonato), $Pd(hfac)_2$, over silicon, aluminum, tungsten, or glass substrates at 10^{-4} torr and 250 °C to 425 °C does not result in film deposition; in contrast, deposition occurs readily on copper to give pure Pd/Cu alloy films whose composition is dependent on the deposition temperature and total flux. Similar results are observed on iron substrates. In both cases, the deposition is actually the result of a redox transmetallation reaction:

$$Pd(hfac)_2 + M \longrightarrow Pd + M(hfac)_2$$

where M is Cu or Fe. Passage of the silver containing CVD precursors $Ag(hfac)(PMe_3)$ or $Ag(hfac)(PMe_3)_2$ over copper substrates yields silver deposits by a similar redox transmetallation reaction. These observations suggest new methods by which films can be deposited selectively from metal-organic precursors.

FUTURE DIRECTIONS

We will increasingly pursue the application of in situ and ex situ surface analytical probes to study surfaces dosed with MOCVD precursors and to determine what chemical intermediates are present and what reactions are responsible for the growth of ceramic thin films. The development of novel 'designed' MOCVD precursors that allow ceramic thin films to be grown at lower temperatures will be expanded; for example, we intend to explore possible new methods to deposit lanthanide and actinide borides. In addition, we are particularly interested in the possibility of growing previously unknown metastable phases by taking advantage of the kinetic control of deposition mechanisms achievable at lower temperatures.

SIGNIFICANT ACCOMPLISHMENT

The Chemistry of New Transition Metal Ceramic Compounds Synthesized by MOCVD

Scientific Accomplishment:

There has been much recent interest in the development of chemical vapor deposition processes that occur selectively; i.e. deposition occurs on some surfaces but not on others. We have discovered that passage of palladium(II) bis(hexafluoroacetylacetonato), $Pd(hfac)_2$, over silicon, aluminum, tungsten, or glass substrates at 10^{-4} torr and 250 °C to 425 °C does not result in film deposition; in contrast, deposition occurs readily on copper to give pure Pd/Cu alloy films whose composition is dependent on the deposition temperature and total flux. Similar results are observed on iron substrates. In both cases, the deposition is actually the result of a redox transmetallation reaction:

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Significance:

The selective deposition of thin film materials is of great interest for a wide variety of applications. Most chemical vapor deposition processes are non-selective; that is, film growth occurs on all surfaces at more or less equal rates. The development of CVD processes that allow films to be deposited selectively on one surface (e.g., copper) but not on other surfaces may solve some long-standing issues in CVD technology. One of the principal advantages of surface-selective depositions is that it is a more efficient process; less starting material is necessary and smaller amounts of byproducts are generated. Equally importantly, surface-selective depositions create new possibilities for the construction of surface structures, since growth of the film can be made to occur in one place but not in another. Scientifically, our studies have elucidated the exact chemical steps by which these depositions occur; furthermore, this accomplishment represents a wholly new way in which to conduct such surface-selective depositions. We have already discovered several examples of this process, and we are currently investigating the extension of this method to the deposition of other phases, including ceramic materials.

Performer: G. S. Girolami, University of Illinois at Urbana-Champaign.

J.E. GREENE

Crystal Growth and Physical Properties of Metastable Semiconducting, Ceramic, and Metallic Alloys

GOALS

The objectives of this research program are twofold: (1) to understand the role of low-energy ion/surface interactions during crystal growth from the vapor phase in order to controllably manipulate microchemistry and microstructure and (2) to investigate the physical properties of unique new thermodynamically-metastable materials produced by such techniques. A detailed understanding of nucleation and growth kinetics from energetic condensing species, surface chemistry, and elemental incorporation probabilities is necessary to achieve these goals.

HIGHLIGHTS

We have developed film growth techniques utilizing low-energy ion/surface interactions *during* deposition to grow unique single-crystal metastable semiconductor, ceramic, and metallic compounds and alloys. The structural, thermodynamic, optical, electronic, and vibrational properties of a homologous series of new ternary and quaternary $(III\text{-}V)_{1-x}(IV_2)_x$ semiconducting alloys and strained-layer superlattices have been investigated. $(GaAs)_{1-x}(Si_2)_x$, in particular, has been shown to have potential applications in optoelectronics. We have recently used high-resolution x-ray photoelectron spectroscopy (XPS) measurements of valence-band densities-of-states (VBDOS) to show that: (1) published band-structure calculations based upon the virtual crystal approximation are incorrect, (2) there are no significant concentrations of III-III and V-V "wrong" bonds (in agreement with our previously reported Raman results), and (3) group-IV atoms are not incorporated randomly. We have also continued to make rapid progress in the growth of high-quality epitaxial wurtzite (a) and metastable zincblende (b) structure wide bandgap GaN. Some of the highest reported electron mobilities, as well as room-temperature photoluminescence, have been achieved in GaN(0001) on Al_2O_3. The optical bandgap of b-GaN was found to be 3.21 eV, 0.2 eV lower than a-GaN, consistent with pseudopotential bandstructure calculations. The first metastable epitaxial zincblende-structure b-AlN layers have also been grown.

TiN, used as a diffusion barrier between the metallization layer (typically Al) and Si (or a silicide overlayer) in microelectronic devices, fails at temperatures between 500-600 °C. We have grown the first single-crystal Al/TiN(001) bilayer structures and used a combination of XRD, TEM, XTEM, STEM, and RBS to determine the interfacial reaction path upon annealing. Contrary to previous proposals, the primary mobile species is Ti. Based upon these results, we have developed new diffusion barrier materials. Metastable NaCl-structure $Ti_{1-x}Al_xN$ alloys with $x \leq 0.3$ have similar resistivities to TiN, but exhibit much improved high-temperature stability. Interfacial reaction kinetics, while following a similar reaction path, were found to be orders of magnitude slower.

We have grown epitaxial transition-metal nitride ceramic superlattices, TiN/VN(001) and $TiN/Ti_{1-x}Al_xN(001)$, and observed quantum size effects in electronic transport properties. These results have been modeled using modified Boltzmann transport theory.

Crystal growth and microstructure of epitaxial 45°-rotated bcc W and metastable bcc $W_{1-x}Ti_x$ ($0 \leq x \leq 0.85$) layers on fcc NaCl-structure MgO(001) substrates and TiN(001) buffer layers have been investigated. This work is of fundamental interest for understanding mechanisms of heteroepitaxial growth in film/substrate systems with different crystal structures. Moreover, W and WTi are also presently used as diffusion barriers between Al and Si and we have initiated studies of Al/W and $Al/W_{1-x}Ti_x$ interfacial reaction paths and kinetics.

Together with Professor Angus Rockett (MRL), we have developed *room-temperature* techniques, employing O_3, for the oxidation of Ge and, very recently, $Si_{1-x}Ge_x$ alloys. This is the first report of a stable, clean, stoichiometric oxidation process for Ge-based alloys.

FUTURE DIRECTIONS

Our emphasis in the area of semiconductor growth will focus primarily on microchemistry using materials such as GaN (in which N_2 does not chemisorb on Ga and for which there is still no well-behaved shallow dopant) as test systems. Low-temperature microstructural modification will continue to be the primary emphasis in the area of ceramic and metal films. We are interested, in particular, in understanding the role of very low energy (below the sputtering and lattice-atom-displacement thresholds), very high flux (ion/neutral flux ratios $G \geq 10$) ion irradiation during deposition for controllably altering nucleation and growth kinetics, preferred orientation, and film morphology. Initial results show, for example, that the preferred orientation of polycrystalline nitride alloys can be varied from completely (111) to completely (002), with no detectable residual ion-induced defects, using N irradiation with E_i = 20 eV N_2^+(i.e., 10 eV per N) and $G > 5$ at T_s = 250 °C ($\simeq$ 0.15 T_{mp}). This has very important implications for the growth of wear and abrasion resistant coatings.

SIGNIFICANT ACCOMPLISHMENT

Electronic Transport in Epitaxial TiN/VN Ceramic Superlattices with Extremely High Hardness and Wear Resistance

Scientific Achievement:

Extending our pioneering efforts in the development of hybrid growth techniques for metastable semiconductors, we have previously reported the growth of the first epitaxial ceramic superlattices, TiN/VN, on MgO(001)1x1 substrates by ultra-high vacuum magnetron sputter deposition in pure N_2. The films were typically 2.5 μm in thickness with compositional modulation periods L ranging from 1 to 16 nm, on MgO(001)1x1 substrates. The superlattice (SL) structures exhibited abrupt smooth coherent interfaces in XTEM and a comparison of XRD results with those calculated using a kinematic scattering model showed that all strong superlattice reflections were observed. Hardness values H for these SL structures were found to be extremely high and strongly dependent upon both L and the ratio of the layer thicknesses l_{TiN}/l_{VN}. For SL structures with equi-thick layers ($l_{TiN} = l_{VN}$), H increased from 2035 kg mm^{-2} for L = 0 (i.e. metastable $Ti_{0.5}Al_{0.5}N$ alloys) to reach a maximum of 5560 kg mm^{-2} at L = 5.2 nm and then decreased rapidly to 3950 at L = 7.5 nm. Further increases in L resulted in a slower decrease in H to 3640 kg mm^{-2} at L = 32 nm. In comparison, we have measured H for single crystal TiN and VN films to be 2200 and 1620 kg mm^{-2}.

Electronic transport measurements carried out as a function of L showed that the room-temperature electron carrier concentration n remained constant at 4.5×10^{22} cm^{-3} while the resistivity r (see figure below) increased, and the electron mobility m decreased, rapidly with L< 6 nm. For superlattices with longer periods, r $\simeq$ 30 mΩ-cm, the expected value for bulk TiN and VN connected in parallel, and $\mu \simeq 5$ cm^2 V^{-1}s^{-1}. The temperature coefficient of resistivity (TCR) between 80 and 300 K decreased with decreasing L but remained positive (i.e. metallic). The electronic properties as a function of L were explained using a modified quantum size effect model based upon the Boltzmann transport equation, known values for the Fermi energies and effective masses of TiN and VN, and accounting for both diffuse (70%) and specular (30%) scattering of electrons at interfaces. No anomalous electrical effects were observed at SL wavelengths near those corresponding to the maximum in hardness, L $\simeq$ 5.2 nm. This argues that the maximum is not due to a singularity in the band structure (e.g., resulting from a reduced Brillouin zone becoming tangential to the alloy Fermi surface), but is more likely related to changes in dislocation generation and propagation mechanisms in these small-period modulated structures.

Significance:

Since the publication of our work on the enhanced hardness of *epitaxial* TiN/VN SL, many industrial laboratories worldwide have developed processes for depositing *polycrystalline* multilayer nitride coatings, which also exhibit significant enhancements in H, for increasing the wear and abrasion lifetime of mechanical devices such as tools and dies. The

present results expand the utility of these materials showing that they also have tailorable electronic properties suitable, for example, for use as high-temperature resistors and sensors. We are also interested in exploiting their diffusion-barrier properties. Equally important, however, is the contribution of the present work to the understanding of the enhancement in H as a function of L and to providing guidance for the development of new artificially-structured hard coating materials.

Combining the electronic transport results with previous XTEM and TEM analyses indicates that the maximum in H as a function of L occurs at SL wavelengths at which interfacial coherency strains are at a maximum. Interdiffusion minimizes the coherency strain at sufficiently small values of L while the interfaces become incoherent at high values of L. The slowly varying hardness enhancement at longer wavelengths is due to a Koehler-type strengthening mechanism.

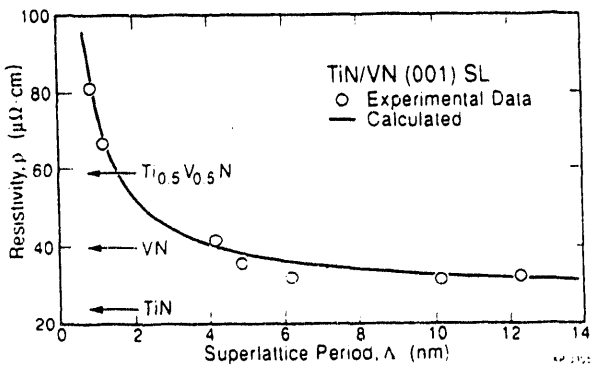


Figure Caption:
Quantum size effects in measured and calculated (using Boltzmann transport theory) room-temperature resisitivity r[100] of epitaxial ceramic TiN/VN(001) SL structures as a function of the superlattice period L. For comparison, resistivity values are also plotted for epitaxial TiN, VN, and $Ti_{0.5}V_{0.5}N$ alloy films.

Performer: J.E. Greene, University of Illinois at Urbana-Champaign.

I. K. ROBINSON

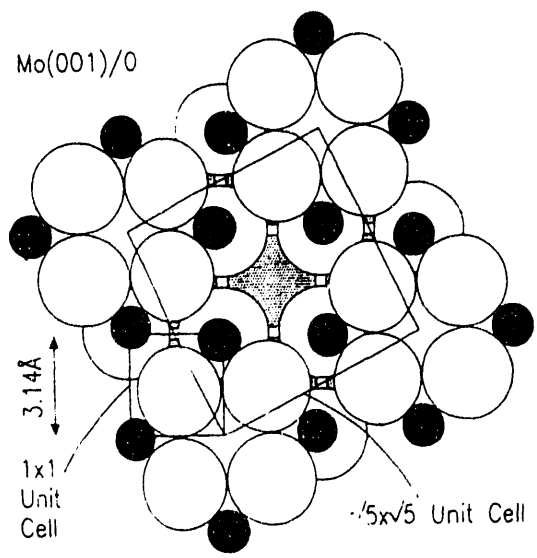
Surface and Interface X-ray Diffraction

GOALS

We aim to understand the structure, morphology and dynamics of all kinds of 2-dimensional interfaces, including surfaces (ie crystal-vacuum), as well as crystal-solid and crystal-liquid interfaces. The means to investigate these are a combination of facilities both in the MRL and at NSLS, Brookhaven. In the MRL we are starting to explore metastable structures that can be stabilized by MBE to understand the relationship of structure to growth conditions. At NSLS we are investigating various surface/adsorbate systems, both from the point of view of structure and kinetics of formation. Instrumentation is under development that will allow us to investigate solid-liquid interfaces routinely.

HIGHLIGHTS

This year we have made significant progress on Mo(001). With the help of Detlef Smilgies, we learned how to prepare the clean surface, which is described below. We also investigated the critical pathway to high temperature oxidation (1000K) of this surface, and were able to stabilize a well-ordered Mo(001)/O $\sqrt{5}x\sqrt{5}$ state. The coverage had been estimated at 0.66-0.8 monolayers in a previous LEED study. Our x-ray structure, shown in the figure, is made up of 4-atom clusters of Mo surrounded by



four O atoms. This gives a coverage of 0.8 in good agreement. These are packed together to leave a vacancy in the center of the unit cell. The ideal terminated surface would have 5 atoms in this cell, so one is lost in the oxidation, presumably by migration to a nearby step. The cluster has a Mo-Mo bondlength 4.6% longer than the bulk; this is similar to the clean reconstructed Mo(001) surface in which it is 4.5% longer. The Mo-O bondlengths are both 2.12Å, which is in the middle of the range seen in bulk oxides. The packing together of the clusters is asymmetric because the $\sqrt{5}x\sqrt{5}$ unit cell does not have mirror symmetry. This leads to a rotation of 5.5° of all the clusters and provides a slightly greater clearance of the O of one cluster and the Mo of its neighbor. This packing of clusters can be elaborated to generate other unit cells, and may explain some of the other structures seen in O/Mo(001) at different coverages.

In other experiments involving Peter Eng, we looked at the surface phases encountered during the formation of Pt(110)1x3 by impurity segregation from the bulk. Thermodynamically, the impurities change the chemical potential, so we are exploring the m-axis of the phase diagram at fixed T (600K). The fractional-order lineshape along *(h, 0, 0.05)* was found to move continuously from close to *h=1.5* at early times, indicating a 1x2 reconstruction, to *h=1.667* indicating 1x3. The Hendricks-Teller lineshape gave an excellent fit to the data over most of the time range, but not with the simple mixture-of-two- states version; in was necessary to randomly mix 1x2, 1x3 and 1x5 regions. The results indicate the presence of a new, partially-ordered intermediate 1x5 surface state in the phase diagram. This may correspond to a structure with an alternation of 1x2 and 1x3 unit cells.

Experiments on true solid-liquid interfaces have not yet started (see below), but several *ex-situ* investigations of electrode morphology have been carried out in collaboration with the Naval Research Laboratory. We examined Au(100) surfaces before and after flame-annealing and looked at the effects of electrochemical cycling on the microscopic roughness (atomic length scale). We found that electropolishing reproducibly yielded relatively flat surfaces, but either flame annealing or cycling into the hydrogen region gave rise to increased roughness. Surprisingly, cycling into the oxide region did not change the roughness.

FUTURE DIRECTIONS

We are at present in the middle of a very active construction phase. We are building a UHV x-ray diffractometer for use in the MRL 'EpiCenter' for the investigation of MBE materials. Two new graduate students are involved and we expect to be operational during 1993. We plan to investigate surfaces that are hard or impossible to prepare by conventional means, such as Cu_3Au or other binary alloys, where segregation may play a dominant role in the surface modification of the bulk order-disorder phase transition.

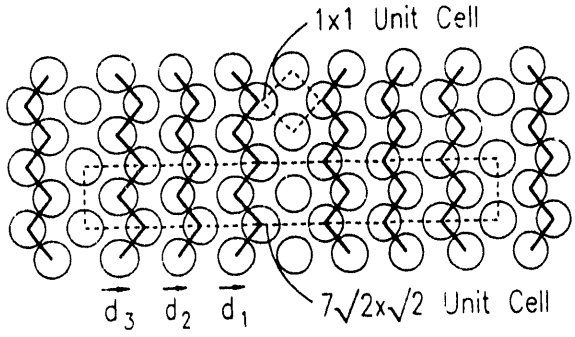
In parallel, we are close to completion of a revolutionary new x-ray diffractometer that uses the single-sided 'kappa' geometry. Based on high-torque servomotor technology, this unit is expected to significantly outperform traditional geared machines. Two instruments are being built, one destined for NSLS and one for the European Synchrotron Radiation Facility in Grenoble. The NSLS diffractometer will be used for studying solid-liquid interfaces, such as exist between an electrode and an electrolyte. We thereby expect to make significant progress in the understanding of corrosion on the atomic scale.

SIGNIFICANT ACCOMPLISHMENT

Mo(001) Reconstruction

Scientific Achievement:

Measuring the low-temperature reconstruction of the clean Mo(001) surface with x-ray diffraction was a major *tour de force* because of its extreme sensitivity to H contamination. Even then, we could only study it for 8 minutes following each preparation. Using much repetition, we were able to determine the clean surface structure, which has $7\sqrt{2}x\sqrt{2}$ symmetry. As illustrated in the figure, the structure consists of alternating striped regions that locally resemble the W(001) reconstruction, with its familiar zig-zag chain pattern of displacements, originally dis-



covered by Debe and King. The three independent sideways displacements shown are 0.23Å, 0.23Å and 0.21Å respectively, indicating a uniform structure. The value for W(001) was 0.24Å. There are also analogous second-layer displacements, but the magnitude is smaller. The displacements cause the top layer atoms to each have two additional neighbors with a 'bondlength' 4% longer than the bulk. The reconstruction therefore increases the surface coordination number. The similarity of Mo and W is attributed to the similarity of the *4d* and *5d* orbitals that are primarily responsible for cohesion in the solid.

The antiphase relationship of the stripes and the domain walls of undisplaced surface Mo atoms between them, highlighted by the dashed mirror lines in the figure, is the feature that is novel to Mo(001). It is probably associated with a surface phonon, seen by He atom scattering, that appears to soften upon cooling and freeze at the same temperature (120K) and same q-vector (3/7 of the <11> zone boundary) as the ordered 7√2x√2 phase. Whether this arises through electron-phonon interactions with a charge density wave is not yet known.

Performer: I.K. Robinson, University of Illinois at Urbana-Champaign.

A. WIECKOWSKI

Organization of Solid-Liquid Interfaces: Energy, Structure and Electronic Distribution

GOALS

The past record and new reports indicate that electrochemistry contributes to emergence of new technologies that may satisfy requirements in waste processing, materials protection and in clean and efficient energy production. On the research level, better knowledge of surface chemistry at the solid/liquid interface is required. We study metal/solution interfaces and our main aims are: (i) to learn how geometry and electronic distribution of ultra-thin metallic films control structure and reactivity at metal/solution interfaces (structure/function), (ii) to advance understanding of *in situ* and *ex situ* surface chemistry of corrosion-active compounds, and (iii) to develop new methods to study metal/solution interfaces.

HIGHLIGHTS

The first ever, and until now the only reports of solid-state nuclear magnetic resonance spectra of ^{13}C adsorbates at the solid/liquid-electrochemical interface have come from our laboratory. The development of this technique was possible due to DOE support. We are now demonstrating (in collaboration with Oldfield) that we have NMR sensitivity to measure ^{13}C cyanides on powdered platinum electrode, and we have observed a strong pH effect on the spectra. Therefore, our goal of making solid-state NMR an analytical probe for *in situ* surface electrochemistry is very close to completion. In a parallel development, we have provided evidence that ultra-thin metal films of copper, cadmium and silver on Pt(111) and polycrystalline electrodes are partially oxidized. Evidently the oxidation process is an integral part of the film formation mechanism. Since such an oxidation process, and its significance, has previously been overlooked, the current understanding of the thin metal film formation on platinum electrodes will have to be reinterpreted. Also, we have progressed with the understanding of surface chemistry of

thiosulfate in relation to pitting corrosion and sulfur inclusion processes (in collaboration with Alkire). We have demonstrated, for the first time, a successful application of an *in situ* radiochemistry to perform adsorption measurements of corrosion-active species with smooth surfaces and in relatively high bulk concentration regimes.

FUTURE DIRECTIONS

The goal of the PI's laboratory in the next contract year is to improve the signal-to-noise ratio, and the resolution, in surface NMR-electrochemistry measurements with high area electrode surfaces. The work will be done with ^{13}C-cyanides on powdered platinum and rhodium catalysts, and is expected to lead to the development of surface-electrochemistry of cyanides on these electrode materials. The ultra-thin metallic film formation on platinum and gold substrates, as well as the adsorption of solution anions on such films, are proposed for more advanced investigations by a multi-instrument approach utilizing Radiochemistry, Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), Temperature Programmed Desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS). The research by XPS will require construction of a UHV-electrochemistry transfer system at the Surface Analysis Facility of the Materials Research Laboratory. We also propose to continue the corrosion related work on adsorption of thiosulfate and bisulfate on stainless-steal electrodes, which would be followed by adsorption measurements of urea and thiourea. Our already completed work on adsorption of phosphorus-containing corrosion inhibitors on iron will be reported from our laboratory.

SIGNIFICANT ACCOMPLISHMENTS

Progress in *In Situ* Analysis of the Solid/Liquid Interface

Scientific Achievement:

Using surface-NMR electrochemistry technique, we have obtained spectra of ^{13}C labeled cyanide on high area platinum surface as a function of solution pH. In acidic solutions, expected featureless spectra were found, Figure 1-A. In the alkaline electrolytes, two solution-like NMR peaks were obtained, which were superimposed on the broad, solid-like spectral profile. Notably, the T_2 analysis shows that only one of the peaks can be assigned to solution cyanide, Figure 1-B. The second NMR feature has been attributed to a reversible adsorption component which is in equilibrium with solution cyanide. These findings represent a new contribution to the study area. For a full identification of all the species observed, a joint ^{13}C NMR and infrared spectro-electrochemistry analysis of the data is currently under way. Other accomplishments in the PI laboratory consist of providing evidence as to the occurrence of the oxidation processes during the ultra-thin metal film formation on platinum electrodes, and the development of surface chemistry of thiosulfate at stainless steel/solution interfaces. The data have either been reported or are prepared for publication.

Significance:

The three research avenues which are supported by DOE in the PI laboratory are: surface-NMR electrochemistry method development, ultra-thin metallic film formation on foreign metal electrodes and studies of solid/liquid interfaces in relation to corrosion. With the progress achieved, we continue to contribute to the development of a fundamental understanding of physical chemistry of metal/solution interfaces and report on new data that can be used in the applied areas, such as energy production and materials protection. Specifically: (i) surface-NMR electrochemistry may emerge as a new research and diagnostic procedure in fuel cell and electrosynthetic technology, (ii) we characterize metal/solution interfaces containing monolayers and submonolayers of foreign ad-metals. The data may explain interesting results from electrocatalysts, and perhaps even to create a new types of catalysis, and (iii) the corrosion oriented work provides an insight into mechanisms of corrosion protection. In brief, our work promises progress in surface electrochemistry methodology, and corrosion protection, and attempt to explain how heterogeneous electrocatalysis functions.

Performer: Prof. A. Wieckowski, Dr. K. Franaszczuk, Dr. M. Gamboa, E. Herrero, Y. Sung and J. Wu, University of Illinois at Urbana-Champaign.

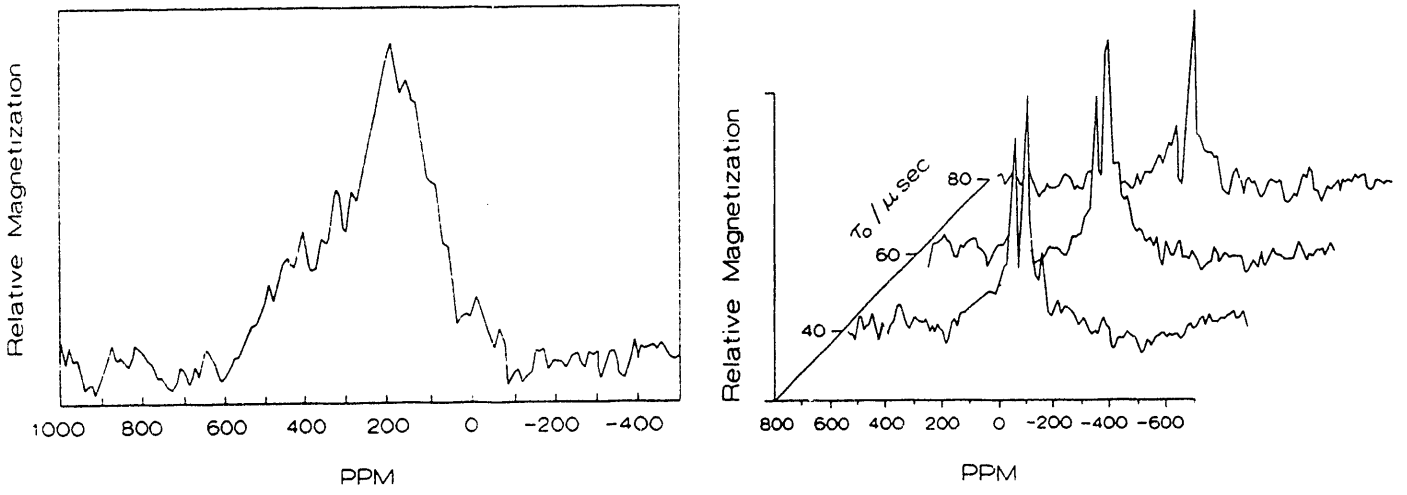


Figure 1 A & B. ^{13}C-NMR spectra of sodium cyanide adsorbed on the rough, polycrystalline platinum electrode at 0.100 V (vs. Ag/AgCl). A: pH = 1; B: pH = 9.

A. ZANGVIL

Microstructure Evolution, Interfaces and Properties in Structural Ceramics and Ceramic Matrix Composites

GOALS

The central goal of this program is to attain a basic understanding of the dependence of ceramic microstructure and microchemistry on processing conditions. The interrelations of these aspects of complex ceramic materials (alloys and composites) with the mechanical properties of interest for high temperature and/or structural applications are of direct interest. Generally, these studies are aimed at (1) devising ways to improve processing conditions and control the microstructure and properties; and (2) developing novel ceramic systems with potentially superior properties. To achieve these goals, we focus on (1) evolution of microstructure and interfaces, as affected and controlled by the processing conditions of the material; (2) mechanisms by which the microstructure, and particularly the interfaces, affect the mechanical properties of the material; and (3) stability of the interfaces and the mechanisms of their degradation under critical conditions.

HIGHLIGHTS

Microstructure evolution during sintering of amorphous alkoxy-derived mullite/(ZrO_2,PSZ) is being investigated. The formation of zirconia through nucleation and growth, precipitation from mullite and/or decomposition of zircon (formed at 1300°C) can be controlled by varying processing conditions. g-alumina, followed by Al-Si spinel, is the precursor of mullite. We have modified the sol-gel process to obtain more homogeneous materials.

Fractographic studies of hot-pressed mullite/ZrO_2/SiC-whisker composites tested in bending at 1250°C showed matrix transgranular fracture and whisker debonding/pullout. The addition of Y_2O_3 or MgO stabilizer, however, caused a drastic decrease in strength. The fracture mode changed to intergranular with almost no whisker contribution to strength, due the presence of a low viscosity glassy phase.

The effects of several structural parameters on the fracture toughness of a SiC-TiC particulate composite have been determined in order to maximize toughness. Increasing TiC particle size was found to improve toughness by increasing microcrack toughening. Particle shape was found to have an effect on crack deflection, and the type of matrix used (a or b SiC) was found to affect the interfacial strength. Toughness of SiC was almost doubled by the addition of 35 vol% TiC.

Crystal structures and grain morphologies were determined and interfaces investigated in nanocrystalline TiO_2, TiO_{2-x} and Y_2O_3-doped TiO_2. In the latter system, $Ti_2Y_2O_7$ grain boundary precipitates limited TiO_2 grain growth during sintering of powder prepared through gas-condensation.

Nano-particle reinforced ceramics were prepared by *in situ* and by conventional milling techniques (Lonza, Germany). In these materials it was observed that pinning by intergranular SiC suppressed elongation of Si_3N_4 grains. Nanocrystalline SiC dispersions were observed to inhibit subgrain boundary migration in an Al_2O_3 matrix.

FUTURE DIRECTIONS

Work on phase separation and diffusivity in the SiC-AlN system will be concluded in 1993. In the alkoxy-derived mullite-based systems, work on microstructural evolution and control will continue until early 1995. It will be further developed if the results justify additional efforts. Work on the high temperature mechanical properties and their mechanisms will also continue. Work on nanocrystalline ceramics and ceramic matrix composites, as well as on particulate composites, will continue and expand. This will include phase evolution and stability, as well as strengthening and toughening mechanisms. The study of oxidation of SiC-AlN will include composites as well as solid solutions, and is expected to be completed in 1994. Experimental work on oxidation modes in ceramic matrix composites will be renewed in early 1993 (with a new Research Assistant). Currently there is limited work on theoretical predictions.

SIGNIFICANT ACCOMPLISHMENTS

Towards Microstructure Optimization of SiC-Based Particulate Composites

Scientific Achievement:

The increase in fracture toughness (which results in decrease in brittleness) of ceramic matrix composites can be attributed to several simplified "toughening mechanisms." These are various mechanisms by which energy is absorbed during fracture and cracks are arrested or slowed down. The operation of each of these toughening mechanisms is strongly dependent upon microstructural and microchemical features, such as the reinforcing particle size and shape, the grain size and morphology of the matrix, as well as the interface chemistry and bonding. Toughness increments have been reported for SiC-TiC and SiC-TiB_2 particulate composites, but there has been no attempt to optimize the microstructural parameters for maximum fracture toughness.

In the present study we determined that crack deflection, crack multiplication at debonded interfaces, as well as crack bridging are the operating toughening mechanisms in TiB_2- and TiC-reinforced SiC. An increase in reinforcement (TiC) volume fraction resulted in the higher toughness, due to operation of more crack deflection (Fig. 1). We also further

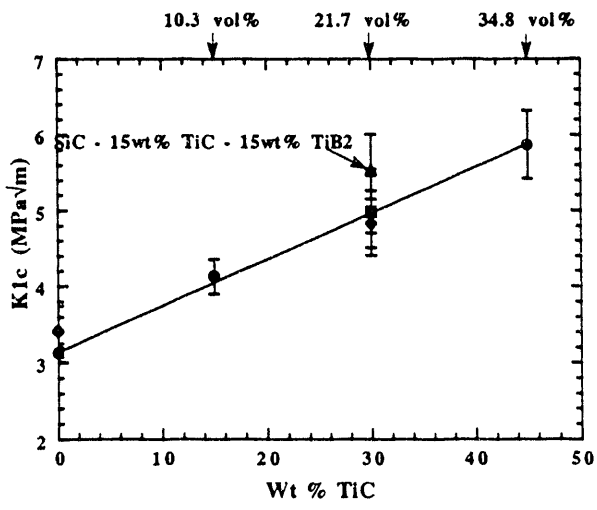


Fig. 1. Fracture toughness of SiC-TiC as function of reinforcement volume fraction.

determined that increase in reinforcement particle size from below 1 μm to about 5 μm results in a considerable increase in toughness (Fig. 2), mainly due to increased debonding at

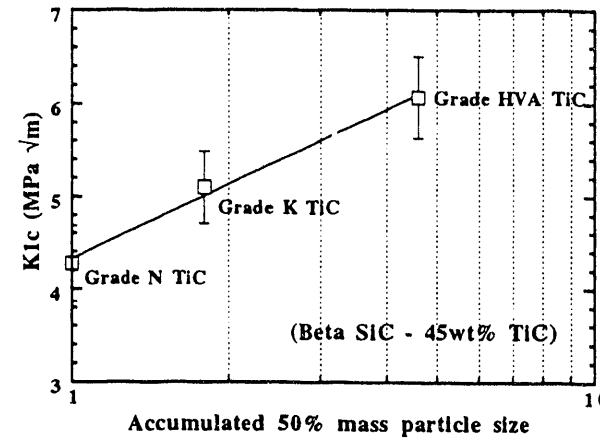


Fig. 2. Fracture toughness of SiC-TiC as function of reinforcement particle size.

particle/matrix interfaces (observed in TEM, Fig. 3). This is caused by the higher thermal expansion coefficient of TiC (or TiB_2) than that of the SiC matrix, which results in residual debonding stresses at interfaces following fabrication. The tendency towards crack-

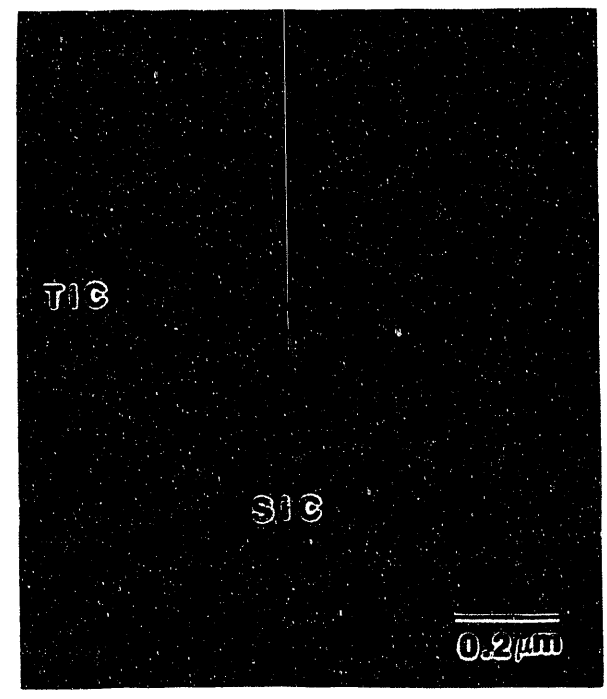


Fig. 3. Debonding at SiC-TiC interface.

induced debonding increases with particle size, resulting in more extensive debonding, or microcracking, at interfaces. The type of matrix raw material used, α- or β-SiC, was also found to have an effect on the extent of debonding, by affecting interfacial strength. The β material provided lower toughness, because upon transforming to α it formed stronger bonding with the reinforcement, thereby limiting interface debonding. Bonding was generally weak in all samples because of the negligible reaction between the composite constituents (Fig. 4).

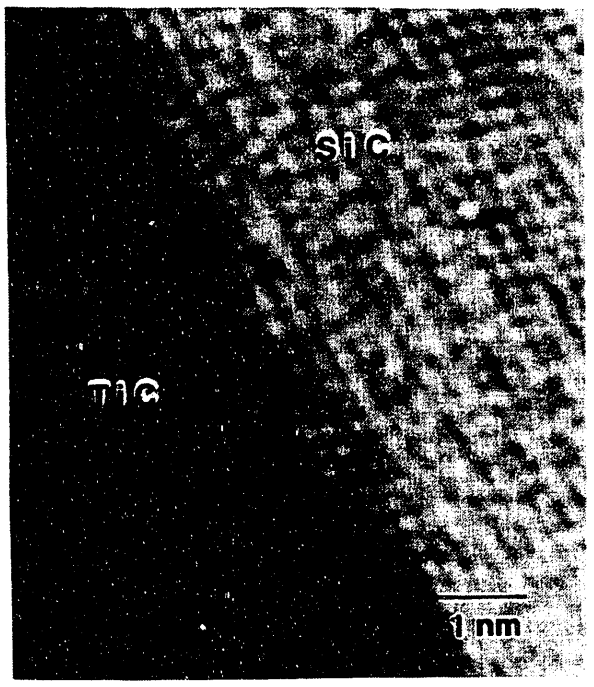


Fig. 4. High resolution TEM image, showing an SiC-TiC interface with no evidence of reaction.

Particle shape and particle size distribution were seen to affect crack deflection and crack bridging mechanisms (Fig. 5). Based on these findings, further microstructural optimization is expected to increase toughness to at least 8 $MPa.m^{1/2}$, compared to about 3.2 $MPa.m^{1/2}$ of pure SiC.

Significance:

Silicon carbide is a leading candidate material for high temperature structural applications in engines and heat conversion systems. Its fracture toughness (low in the monolithic form) can be increased by fiber or particulate reinforcement. Particulate-reinforced

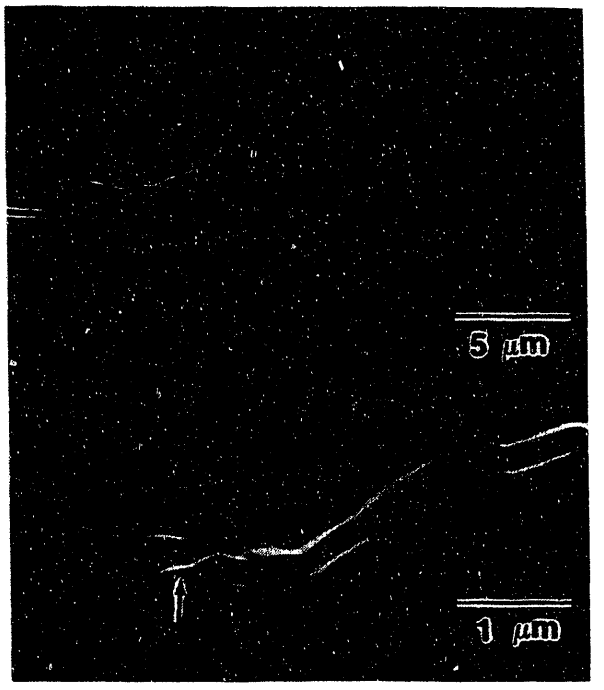


Fig. 5. Crack bridging in SiC-TiC, hot-pressed at 2050°C for 1.5 hours (arrowed).

SiC composites have the advantage of being (potentially) isotropic in their fracture toughness and other mechanical properties. They are also far easier to process, compared to fiber-reinforced composites. The present study has shown that considerable improvements in the fracture toughness of SiC-TiC, SiC-TiB_2,, and similar systems can be achieved by the optimization of material and processing parameters. Furthermore, it points to several promising directions of study, based on the optimization of individual toughening mechanisms and their combination. Actual economical application of SiC-based materials depends strongly on the achievement of higher fracture toughness values in easily fabricable composite systems. Our study is an important step towards achieving this goal.

Performer: A. Zangvil, University of Illinois at Urbana-Champaign.

E.2.a RESEARCH SUMMARIES FOR MECHANICAL PROPERTIES KC-02-01-02

H. K. BIRNBAUM and I. M. ROBERTSON

Environmental Effects on Mechanical Properties - The Role of Grain Boundaries and Interfaces

GOALS

The primary thrust of this program is to understand the effects of aggressive environments on the mechanical behavior of materials. Since many properties are determined by the behavior of interfaces and grain boundaries, these provide a major focus of our efforts. These studies make extensive use of *in situ* TEM environmental cell techniques, and microchemical methods. The systems presently being studied include the intermetallics, and high strength Ti based alloys.

HIGHLIGHTS

Calculations of "hydrogen shielding" of the elastic interactions between defects have proceeded (in cooperation with P. Sofronis) and are in the final stages of preparation for publication. The solutions have been extended to include interactions between dislocations and between dislocations and point defects. In addition to the first order effect due to the volume change associated with the hydrogen, the second order modulus effect has been studied and shown to be significant. This latter effect arises due to the change in the local elastic moduli caused by the local hydrogen concentration. As a consequence of the second order modulus change interaction, we predict the formation of significant hydrogen atmospheres at screw dislocations. The presence of this atmosphere decreases the interaction of screw dislocations with solutes such as carbon; as observed experimentally. Such a decrease in the interaction energy is consistent with the previously reported enhancement of dislocation velocity due to hydrogen in Fe-C alloys.

The bonding of polymers to metals is being studied using polyimide bonded to Ti, Ni. and Cr. The techniques applied are cross sectional TEM, SIMS, SAES, and XPS. TEM studies have shown that the bonding of the polyimide to Ti and Cr is quite strong but was severely degraded by thermal cycling; particularly in the presence of a hydrogen atmosphere in the case of polyimide/Ti. In the Cr/polyimide case the Cr film fractured in tension due to the differences in thermal expansion coefficients and the tensile stresses which developed. In the Ti/polyimide system the failure was dominated by the very large stresses produced by transformation of the Ti to TiH_2 and complete delamination occurred. XPS studies of the interface showed that the primary bonding was between the carbonyl groups of the polyimide and the active metal, Cr or Ti.

A small amount of interdiffusion of the Ti into the polyimide was observed. This interdiffusion of a metal and a polymer is a very interesting phenomenon which has not been previously studied with any care. We will be studying this in the next contract period. When the debonding on thermal cycling in hydrogen occurs, it was shown that the fracture occurs in the polyimide just adjacent to the interdiffusion zone.

In situ environmental cell fracture studies were carried out on A533B pressure vessel steels to study the effects of hydrogen on deformation and fracture. The basic fracture mechanism in both vacuum and hydrogen was ductile with the principal effects of hydrogen being a reduction in the stress to cause fracture. In hydrogen the deformation at the crack tip was highly localized and the fracture occurred by microvoid initiation and growth. Hydrogen embrittlement of this high strength multicomponent alloy, of great importance for the performance of nuclear systems, is totally consistent with the Hydrogen Enhanced Localized Plasticity mechanism developed on much simpler metallic systems.

FUTURE DIRECTIONS

The in situ environmental cell studies of the interactions of hydrogen with dislocations will continue. We will focus on establishing the H - screw dislocation interactions and the effects of H on the stacking fault energy. We will continue

to explore the effects of H on the mechanical behavior of high strength b phase Ti alloys.

SIGNIFICANT ACCOMPLISHMENT

Hydrogen Induced Crystalline - Amorphous Phase Change

Scientific Achievement

While the crystalline ↔ amorphous phase changes have been observed in a number of pure and alloy systems the mechanism for this transition has not been established. In general, amorphization occurs when systems are driven far from equilibrium by deformation, radiation damage or ion implantation. Our studies of phase changes in the Ti_3Al DO_{19} intermetallic which are driven by the introduction of hydrogen show the first case where solid state amorphization occurs under equilibrium conditions. As hydrogen is introduced into the crystalline hydride structure in equilibrium with a gas phase grain boundaries are formed and the grain size becomes increasingly small. As this process continues the structure becomes truly amorphous as judged by the pair correlation function measured by electron scattering. The mechanism by which this phase transition is thought to occur is shown in Fig. 1. The crystalline hydride phase and the amorphous structure are in equilibrium at high hydrogen concentrations. As the hydrogen concentration increases, the amount of the grain boundary phase, which is considered to be the precursor of the amorphous phase, increases. The increased stability of the grain boundary phase is believed to result from the lower free energy of hydrogen in the grain boundary relative to hydrogen in the lattice. Thus the system reaches equilibrium by creating additional grain boundary sites to accommodate the increased hydrogen concentration.

Significance

Crystalline ↔ amorphous phase changes degrade the mechanical properties of many alloy systems during materials processing. Since many processing procedures are carried out in high hydrogen activity atmospheres, it is necessary to understand the role of hydrogen in causing this amorphization. Furthermore, the use of complex materials in hydrogen containing atmospheres can cause amorphization and this must be understood to avoid degradation of properties during use. The present results contribute to the understanding necessary for materials processing and applications in aggressive environments.

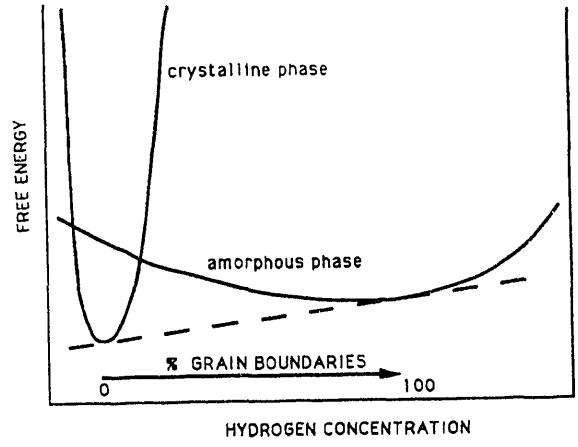


Fig. 1 Schematic of the Free Energy of the Crystalline Phase and the Amorphous Phase as a Function of H/M

Performers: H. K. Birnbaum, I. M. Robertson, and H. Z. Xiao, University of Illinois at Urbana-Champaign

HELEN FARRELL

Materials Surface Physics

GOALS

It is the goal of this project to improve our understanding of the surfaces of materials of potential technological importance. Steps along this path include the construction of a multipurpose surface analysis system, better quantification of both the bulk and surface composition of multicomponent materials and studies of the initial stages of heteroepitaxial growth.

HIGHLIGHTS

Currently, construction of the surface analysis system is nearing completion. The early completion of this versatile system bodes well for our future investigations.

Improvement in the quantification of multicomponent materials is proceeding as a collaborative effort with staff members in the Center for the Microanalysis of Materials. Materials currently under consideration include AlAs, SiC and the Ni_3Al alloy. Quantification of multicomponent materials has been a somewhat neglected area and our efforts should contribute not only to a better understanding of the specific materials under investigation, but also to a physically sound basis for improving this process in general.

FUTURE DIRECTIONS

Our future goals emphasize the quantification studies of multicomponent systems. Thereafter, we will investigate the AlAs (100) surface and study the chemisorption of group VI atoms as a precursor to II-VI heteroepitaxy on this substrate. A parallel program on the Si_xC_y (100) surface, with eventual application to wide band gap III-V heteroepitaxy will also be initiated. These latter two goals provide an exciting opportunity for combining pure surface science with the development of technologically desirable materials. Finally, we also hope to begin a series of studies on intermetallic interfaces later in the year.

D.F. SOCIE

High Temperature Mechanical Behavior of Ceramics

GOALS

Advanced heat engines require higher operation temperatures for greater efficiency. Ceramic materials offer great potential for use in these heat engines. The aim of this project is to develop a mechanistic damage accumulation model. These models will result in a predictive tool that can be used for new component designs and materials systems and will extrapolate beyond the database used to establish the model. This work is focused on determining the mechanisms that control the long term durability of ceramic materials at high temperatures and stresses. Damage due to mechanical fatigue and time dependent processes as well as the interaction between them are quantified to develop durability assessment methodologies for these materials systems.

HIGHLIGHTS

The mechanical behavior of polycrystalline alumina and silicon nitride has been studied under static and cyclic tensile loading at high temperatures using smooth cylindrical tensile specimens. Cyclic loading at high temperatures has been shown to have a beneficial effect to extend the life when compared on the basis of the duration of the maximum stress. Mechanical tests have shown that creep rates are substantially reduced during cyclic loading. Extensive SEM and TEM observations of failed specimens reveal that the crack tip driving force is reduced by several intrinsic toughening mechanisms including: crack deflection, interlocking grains, contact of fracture surface asperities, unbroken ligaments, trapped grains, and crack tip bridging by a viscous boundary phase. These observations have led to a life prediction model that includes microstructure, temperature, and loading rate effects.

FUTURE DIRECTIONS

Modeling the mechanical behavior of ceramics at high temperatures and stresses remains the focus of this work. This includes the overall deformation which is controlled by the bulk material properties and fracture which is controlled by the growth of microcracks. The relative importance of crack tip bridging and crack closure effects behind the crack tip and void formation and microcracking must be established through critical experiments and observations. High temperature torsion tests of thin walled tubular specimens are used to discriminate between shear mechanisms such as grain boundary sliding and tensile mechanisms such as microcrack growth. Studies on materials with crystalline boundary phases will provide a comparison to establish the role of the viscous phase in the alumina studied in this work.

SIGNIFICANT ACCOMPLISHMENTS

Durability Modeling for Ceramic Materials

Scientific Achievement:

The mechanical behavior of polycrystalline alumina has been studied under static and cyclic tensile loading at high temperatures using smooth cylindrical tensile specimens. Alumina was selected as a model high temperature material because it is readily available in several forms and has been shown to behave in a manner similar to other ceramics and ceramic composites. A common observation in these materials is that cyclic loading at high temperatures has a beneficial effect in extending the lifetime when compared on the basis of the duration of the maximum stress. Extensive SEM and TEM studies of the damage mechanisms have been conducted. At high temperatures, crack tip bridging by a viscous boundary phase

Figure Caption: High magnification SEM view of the crack profile in an axially cut section of a static loading specimen (s_{max} = 37.9 MPa): (a) Viscous glassy ,phases bridging the crack surface which is nearly perpendicular to the loading axis, and (b) Shows the same phenomenon when the crack surface makes an angle of nearly 45° with the loading axis.

(a) (b)

and grain boundary sliding is observed. Crack bridging by the viscous glassy phase behind the crack tip was modeled as a series of viscous ligaments and incorporated into a simple model for computing the effective stress intensity factor which is used to obtain a quantitative estimate of the lifetime. The model shows that only viscous ligaments near the crack tip are effective in reducing the crack tip driving force. This is in contrast to ceramic composites where unbroken fibers farthest behind the crack tip are more effective. Microstructural parameters such as grain size, viscosity of the grain boundary phase and modulus of the ceramic are included in the model. As a result, temperature, loading frequency, and stress level effects are an intrinsic part of the model and good quantitative agreement with the experimental data is obtained.

Significance:

Advanced heat engines require higher operating temperatures to achieve greater operating efficiency to meet more stringent economic and regulatory requirements. Ceramic materials offer great potential for these applications. Analytical methods for determining the long term performance and expected durability of ceramic components from short term laboratory test data are essential for American manufacturers to remain competitive in the world marketplace. Results obtained in this study provide the quantitative understanding of the failure process which is needed for developing mechanistically based damage evolution models.

Performer: Prof. D. F. Socie, University of Illinois at Urbana-Champaign.

P. SOFRONIS

Microstructure-Based Continuum Modeling of the Mechanical Behavior of Materials.

GOALS

A major goal of this program is the micromechanical modeling of hydrogen embrittlement and powder consolidation for nanocrystalline materials. Continuum mechanics is used to study deformation mechanisms which are dominant on the microscale and then to draw conclusions about their effects on the macroscopic mechanical behavior. In the case of hydrogen embrittlement mechanisms such as hydride precipitation at crack tips, stress driven hydrogen diffusion, constitutive property changes, hydrogen interactions with dislocations and interstitial atoms are investigated. In the case of powder consolidation the aim is at devising macroscopic constitutive laws for the powder aggregate based on the action of the local densification mechanisms which depend upon the consolidation conditions such as temperature, applied stress and stage of densification. An important aspect of the program is the development and use of robust numerical techniques to simulate the nonlinearity and coupling of the phenomena. The latter results from the numerous interdependencies between the variables and mechanisms involved. Lastly, effort is made so that modeling proceeds concurrently with experiments so that both can be changed or re-directed accordingly.

HIGHLIGHTS

Hydrogen is known to expand the lattice, create atmospheres around stress inducing defects and change the local material constitutive behavior. Those phenomena are modeled by estimating the disturbance to the singular dislocation stress field when the hydrogen is in equilibrium with stresses due to dislocation and other elastic singularities. The Eshelby interaction effects are modeled via the transformation strain that accompanies the solution of hydrogen and other defects into the lattice. Rigorous boundary value problems are set and solved by the finite element method.

The hydrogen effect on the interaction between an edge dislocation and a carbon atom in the case of the niobium system is demonstrated in the reduced interaction between the defects when the elasticity moduli changes are taken into account. These interaction energy changes are in excellent agreement with the shielding theory measurements of thermally activated deformation in nickel.

Unit cell finite element calculations are currently carried out in order to model the densification of a nanocrystalline powder under hot isostatic press and shear. The analysis is based on interface viscous slip between grains and diffusional mass transport due to stress gradients coupled with elastic deformation of the grains.

FUTURE DIRECTIONS

The interaction of hydrogen with a screw dislocation will be investigated in view of the fact that the interaction of a tetragonal defect with a screw dislocation is roughly of the same order of magnitude as the hydrostatic interaction with an edge dislocation. The transient hydrogen diffusion around a dislocation will be studied and its effect on the interaction energy will be quantified in comparison to the steady state calculation results. Experiments will be carried out to measure the constitutive moduli of the hydrogen metal system under constant chemical potential, that is, equilibrium conditions. The effect of the iso-chemical potential moduli on the interaction energies will be investigated through the existing elasticity solutions for given iso-concentration moduli.

In the study of nanophase materials emphasis will be placed on the mechanism based approach in order to clarify the power law dependence of the densification rate upon the applied stress with an exponent roughly equal to 2 or 3. It should be mentioned that current theories are deficient because they predict a linear dependence.

SIGNIFICANT ACCOMPLISHMENTS

Hydrogen Effects on Dislocation-Carbon Interactions

Scientific Achievement:

A finite element code which simulates the interdependence of stress and hydrogen concentration under steady state conditions has been developed and tested in the case of the singular elasticity dislocation field. The code was used to carry out large scale calculations of the interaction energy between microstructural defects in the presence of hydrogen. The results of these calculations provide a theoretical explanation and understanding of the hydrogen shielding theory in the context of the hydrogen enhanced localized plasticity model of hydrogen

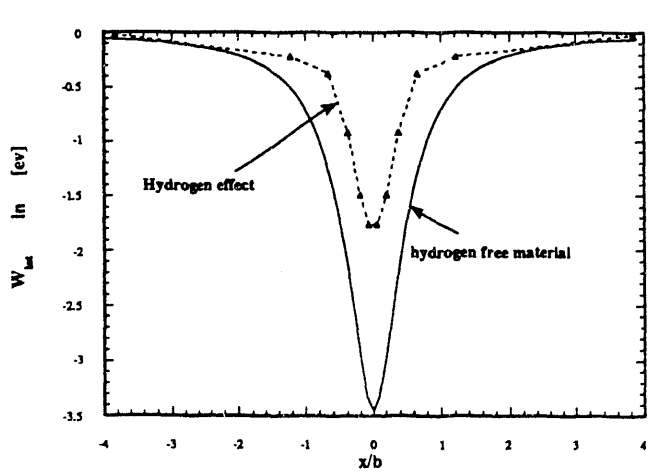


Fig. Caption: Interaction energy of an edge dislocation fixed at x/b=0, y/b=0 with the hydrostatic component of an interstitial carbon atom in the bcc niobium plotted against carbon atom position x/b with y/b=-0.505. The hydrogen concentration at distances far remote from the dislocation is 0.1 hydrogen atoms per niobium atom. The parameter b is the dislocation burger's vector.

embrittlement. The figure shows that hydrogen reduces the hydrostatic interaction of an edge dislocation with an interstitial carbon atom.

An important aspect of the hydrogen effect is that it is minimal when the hydrogen induced constitutive moduli changes, measured by Birnbaum and his co-workers, are neglected. The numerical calculations reveal no significant interaction energy changes for distances between the dislocation and the carbon atom which are greater than 4 burger's vectors. As a result, the hydrogen effect can be characterized to be local because it is observed only at very close dislocation-defect proximities. This is explained by the fact that the stress field of an interstitial hydrogen atom decays within a brief spatial outreach ($1/r^3$ dependence), and that drastic changes of the constitutive moduli take place mainly in the very vicinity of the core due to the enhanced hydrogen concentration. Therefore, it is only when the carbon atom is very close to the dislocation that the second order effect of the moduli change can become comparable to the first order effect associated with the $1/r$ dependent dislocation stress field.

Performer: Professor Petros Sofronis, University of Illinois at Urbana-Champaign.

J.F. STUBBINS

Subcritical Crack Growth in Structural Ceramics

GOAL

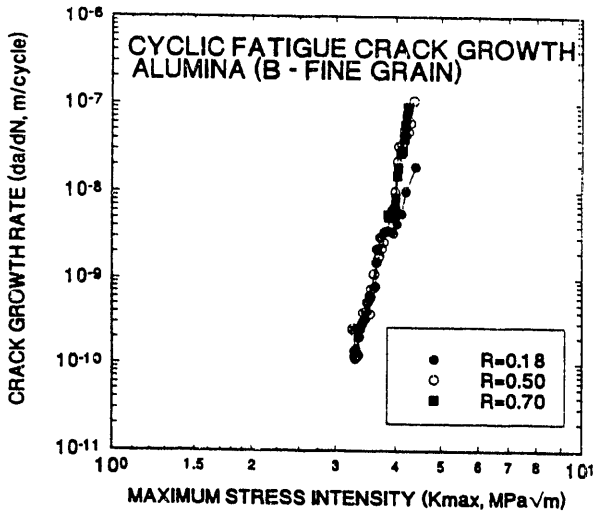
The goal of this program is to understand the underlying mechanisms involved in crack initiation and early growth in structural ceramics and to use that understanding in the development of improved materials performance. Attention has been focused on crack advance mechanisms in high temperature structural ceramics. The program is primarily experimental in nature, relying on mechanical testing and microstructural analysis to study crack properties at room and elevated temperatures. The role of environment on crack initiation and propagation characteristics is also examined.

HIGHLIGHTS

The highlights of the program in the past year include fatigue crack studies of various aluminas and a 2-D SiC_f/SiC composite. In alumina, the influence of grain size and load ratio (R-ratio) on crack growth was studied at room and high temperatures. In addition to commercial materials, some aluminas were processed in-house to produce various grain sizes.

It was observed that coarse grained alumina exhibits more crack growth than fine grained alumina, and the variation can be attributed to some extent to the different toughness characteristics of the two materials. In fine grained alumina, fatigue crack growth rate is well correlated by the maximum stress intensity factor (Figure 1). Efforts were made to identify fatigue damage mechanisms using electron microscopy. It appears that crack growth is due to extrinsic mechanisms such as loss of contact shielding of crack tip due to crack wake damage processes.

Figure 1



Elevated temperature static and cyclic tests on aluminas and SiC_f/SiC are being carried out at a variety of loading conditions, with the intention of understanding cyclic fatigue and creep in these materials.

FUTURE DIRECTIONS

The future efforts will be focused on the SiC_f/SiC material, and additional static and cyclic testing at elevated temperatures on alumina and SiC_f/SiC. The experimental conditions have been chosen to cover all the expected temperature and stress regimes in these materials and will include fatigue crack growth, fatigue-creep and creep processes.

Theoretical modeling of crack growth would be performed for the various materials, and would incorporate the unique microstructural features found in the materials.

Portions of the work described above and to be performed in the future is in collaboration with the High Temperature Materials Research Laboratory at Oak Ridge National Laboratory.

SIGNIFICANT ACCOMPLISHMENT

Measurements of Subcritical Crack Growth in Structural Ceramics

Technical Achievement:

Controlled crack growth tests under static and cyclic loading conditions have been performed on ceramic materials under tension-tension loading. The results obtained for alumina using center notched panels, are unique to this study. The results show that significant differences are found in crack growth rate as a function of grain size, but that the limiting fracture toughness is not affected by grain size. These differences are also noted in the fracture surface morphology. Further testing also indicates that subcritical crack growth correlates well with the maximum stress intensity parameter in tests with varying load ratios (R-ratios). High temperature fatigue crack growth data for any ceramic material is very scarce in literature, thus the data obtained in this study is valuable. Also, cyclic testing of SiC_f/SiC is being performed for the first time.

Significance:

Conventional ceramic materials have low toughness and fail catastrophically with little crack growth. Advanced ceramic materials have toughened microstructures that enable them to resist crack propagation. The toughening mechanisms in most advanced materials derive from crack wake processes. It is generally perceived that ceramic materials are not susceptible to cyclic fatigue due to limited crack-tip plasticity. However, cyclic fatigue can occur through processes other than crack-tip processes. One outstanding issue is whether or not the toughening mechanisms loose their effectiveness under cyclic loading conditions. Ironically, the crack wake processes that provide toughness in advanced ceramics can become responsible for cyclic fatigue itself. Since these materials would be used in rotating components undergoing cyclic loading, cyclic fatigue and subcritical crack growth is a major concern. The materials selected for this research (alumina, SiC_f/SiC) exhibit the most important non-transformation toughening processes. Alumina is also a model ceramic with reproducible characteristics and hence ideally suited for assessing cyclic fatigue effects. SiC_f/SiC is an

important structural material envisioned for several future applications.

Performer: J. F. Stubbins, University of Illinois at Urbana-Champaign.

E.3.a RESEARCH SUMMARIES FOR PHYSICAL PROPERTIES KC-02-01-03

HAYDN CHEN

Structure and Dynamics of Diffusional and Displacive Phase Transformations in Solids and Thin Films

GOALS

The overall objective of this research is to gain a fundamental understanding of the governing mechanisms and the associated kinetics of solid-to-solid phase transformations in bulk solids and thin films. Both thermally induced diffusional transformations, e.g. order-disorder, phase separation, etc., and diffusionless (displacive) transformations, e.g. ferroelectrics, martensites, etc., are of concern. Of particular interest are the effect of coherency stress on the phase separation in Ni-Al-Si ternary alloys, the transformation kinetics of metal-silicides from deposited metal thin films and multilayers, and precursory phenomena of displacive transformations in several ferroelectric perovskites.

HIGHLIGHTS

(1) Ni-Al-Si System

The current advancement in the field of coarsening theories has lent itself to various interesting discoveries, among which is the effect of lattice mismatch coherency strain on coarsening kinetics. There is an acute need for experimental evidence to support or dispute the theoretical notions. The lattice mismatch between the g matrix phase and g' precipitate phase can be altered by varying the Si to Al ratio. *In-situ* time-resolved SANS measurements were carried out at IPNS of Argonne National Laboratory. Results show that Ostwald ripening is generally observed at long aging times, yielding an activation energy of 39.7 kcal/mole for solute diffusion. This value is much lower than those observed in the binary Ni-Si (66.5 kcal/mole) and Ni-Al (62.3 kcal/mole) systems in previous studies carried out in our laboratory. It is believed that this discrepancy is due to enhanced diffusion from non-equilibrium concentration of vacancies. An overall slowing down coarsening rate is observed with increasing degree of coherency strain, consistent with the theoretical prediction. However, the effect of solute concentration on the lattice diffusion coefficient must be removed before the effect of misfit strain on the coarsening rate can be indisputably discerned.

(2) Silicide Thin Films

The reaction rate kinetics of the solid-state reaction between Pd thin films and the underlying hydrogenated amorphous silicon were studied *in situ* using time-resolved x-ray diffraction and four-point probe resistivity measurements during isothermal annealing. These two techniques yielded activation energies and prefactors of E_a=1.36±0.11 eV with k_o=4.29 cm^2/sec for the x-ray experiments; and E_a=0.97±0.22 eV with k_o=3.42x10^{-4} cm^2/sec for the resistivity measurements. Comparisons of the kinetics from the current work with the previous studies of silicide formations from crystalline Si(111) substrates showed that the silicide formed from the a-Si:H reacted approximately 3 times faster. The difference in the reaction rates is attributed to the difference in microstructure of the reacted silicide interface layer. The silicide formed from a-Si:H is not epitaxial but polycrystalline with a mosaic spread of ~13°. This looser structure apparently promotes diffusion, thereby giving a faster rate of silicide reaction.

In a separate study, the kinetics of the formation of a deleterious, metastable $TiSi_2$-C49 phase from amorphous Ti-Si multilayers grown on Si(100) substrate has been studied using a time-resolved x-ray diffraction technique at elevated temperatures ranging from 270°C to 310°C. A linear position-sensitive proportional counter was used to simultaneously collect the (131) and (150) Bragg peaks of the C49 phase. The kinetics data were analyzed using the Johnson-Mehl-Avrami equation. The Avrami exponent was found to be 2.0; the reaction rate constants follow a familiar Arrhenius-type behavior resulting in an activation energy of 2.5 eV. Our current results agree with the previous indirect measurements based upon the film stress analysis. A strong correlation of the C49 phase formation and the film stress can now be made.

FUTURE DIRECTIONS

Continuing research on the effect of lattice mismatch strain on the coarsening behavior and morphology change in Ni-Al-Si will take place. It is necessary to perform diffusivity measurements in this ternary system to remove the solute concentration effect on interdiffusion coefficient that is an integral part of the coarsening rate constant. Collaboration with Prof. Dayanada of Purdue University is already underway. Our work on buried interface structure and displacement fields of Si substrates covered with C_{60} bulky ball or noble metals will be continued using surface-sensitive synchrotron radiation diffraction techniques.

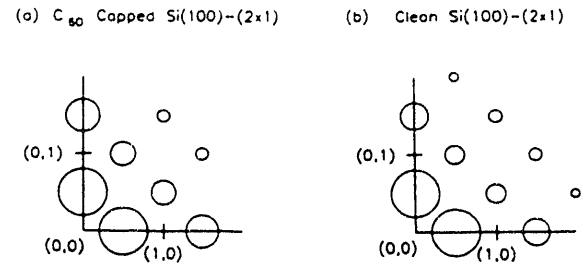
Our past research on thermally induced, diffusional phase transformations has laid a solid foundation for our future research into diffusionless/displacive transformations in ceramics. The current level of understanding with regard to the transformation mechanism, nucleation, kinetics and crystallography of ceramic systems undergoing displacive transformations is lacking in depth and completeness, and has not paralleled that of similar investigations with metals. Work has already begun to study the pre-transitional phenomena and the governing principles of displacive transformations in $PbTiO_3$ and $KNbO_3$. Approaches used accomplish this goal include both theoretical analysis (e.g. electronic structure, total electron energy calculations, rigid-shell model for phonon dispersion relationships) and experimental investigations (e.g. inelastic and quasi-elastic neutron scattering and diffuse x-ray scattering). This combined effort can allow us to investigate the roles of the electronic energy contribution and the phonon properties (e.g. soft modes, anharmonicity) in the displacive transformations, as well as to investigate the pre-transitional phenomena heralding the transformations.

SIGNIFICANT ACCOMPLISHMENT

Interaction of Reconstructed Si Surfaces with C_{60} Overlayers

Scientific Achievement:

The structures of the reconstructed Si(111)-(7x7) and the Si(100)-(1x2) surfaces, after room-temperature deposition of a thin film of C_{60}, has been examined with grazing-incidence synchrotron x-ray diffraction. Our earlier work showed that while other materials such as Ag and amorphous Si also seem to retain certain structural features of the (7x7) reconstruction, C60 is the only known case where all essential structure details of the (7x7) are preserved, including the outmost Si "adatoms" on the surface. All of the other aforementioned materials, upon deposition on Si(111)-(7x7), appear to destroy the ordered adatoms feature. The (1x2) surface reconstruction is also well preserved under C60 overlayer. The measured fractional-order diffraction intensities, similar to those reported for the clean Si(100)-(1x2) surface, have been analyzed in terms of a buckled-dimer model. Thus, the deposition of C60 on Si(100)-(1x2) has minimal effects on the surface structure.



Integrated and averaged intensities of (1x2) reflections from (a) C60-covered Si(100)-(1x2) and (b) clean Si(100)-(1x2) in vacuum. The area of each circle is proportional to the integrated intensity.

Significance:

From the successful encapsulation of Si(100)-(1x2) and Si(111)-(7x7) surfaces, it is demonstrated that a C_{60} film can be used to cap at least some clean surface structures. These surfaces are characterized by surface dangling bonds and different degrees of atomic rearrangement. Based on these studies, it is reasonable to suggest that the relative chemical

inertness of C_{60} makes it a fairly good capping material, thereby facilitating studies of reconstructed surfaces without the need of an ultra high vacuum environment.

Performer: H. Chen and T.C. Chiang, University of Illinois at Urbana-Champaign.

WALTER G. KLEMPERER

Materials Chemistry of Oxide Ceramics; Field Responsive Organic Inclusion Complexes

GOALS

This program is concerned with understanding and controlling ceramic processing on a molecular level and examining the relationships between bulk properties of ceramics and their structural features on a molecular size scale. This approach may be regarded as an attempt to extend traditional polymer processing techniques to ceramic processing by utilizing molecular building block precursors whose structures are retained in the ultimate product. Two specific areas have been targeted for investigation: sol-gel processing of oxide ceramics and hydrothermal processing of new organic/inorganic composites comprised of organic guest molecules in a crystalline silica host framework, i.e., zeolites.

HIGHLIGHTS

A protocol has been developed for evaluating the stability of molecular titanites $[Ti_xO_y](OR)_z$ under sol-gel processing conditions. First, the titanate is dissolved in the parent alcohol ROH and ^{17}O NMR spectroscopy is used to determine whether it is stable toward alcohol. Species displaying stability toward alcoholysis are then reacted with a different alcohol R'OH to observe tranesterification, i.e., alkoxide exchange with retention of the titanium oxide core structure. Such observations can be made using ^{13}C NMR spectroscopy. Finally, the titanate is hydrolyzed in solution, and selective ^{17}O labeling experiments are performed, using ^{17}O CPMAS NMR techniques, to determine whether the titanium oxide core structure of the precursor is retained in the oxide xerogel ultimately obtained (see below). Using these techniques, we have demonstrated that the Ti_7O_4 core in $[Ti_7O_4](OC_2H_5)_{20}$ and the Ti_3O core in $[Ti_3O](OCH_3)(OCH(CH_3)_2)_9$ are <u>not</u> stable toward sol-gel processing conditions, but the $Ti_{16}O_{16}$ core of $[Ti_{16}O_{16}](OC_2H_5)_{32}$ <u>is</u> stable. This discovery opens up the possibility of engineering titania gels, films, and fibers at the molecular level using sol-gel processing.

The recently developed technique for seeded-growth of large, single zeolite crystals has been expanded and refined. First, reaction conditions have been optimized such that crystals as large as 7.2 x 6.0 x 4.4 mm can be grown. Second, these same reaction conditions now allow seeded growth at 150°C, a temperature sufficiently close to ambient temperature to insure in many cases that the phase stable under hydrothermal growth conditions is the same phase stable at ambient temperature. For the case of ZSM-39 zeolites, which have an orthorhombic to cubic phase transition at about 160°C, extensive twinning is observed when crystals grown at T>160°C are cooled to ambient temperature. The new conditions should eliminate this problem. Finally, epitaxial growth of one structure upon a closely related structure has been achieved, specifically, piperidine dodecasil 3C has been grown epitaxially on pyridine dodecasil 3C.

FUTURE DIRECTIONS

Attempts will be made to control the microstructure of titanium xerogels through judicious choice of polytitanate precursors. Attention will focus on two stable precursors, $[Ti_{12}O_{16}](OPr^i)_{16}$ and $[T_{16}O_{16}](OEt)_{32}$, and the microstructure of materials derived from them will be compared with the microstructure of $Ti(OR)_4$ -- derived materials using gas adsorption and microscopic techniques.

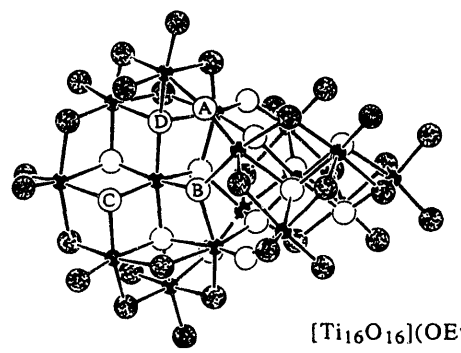
Research in the field responsive materials area will proceed in two directions. First, efforts will be made to prepare single domain seed crystals so that untwinned crystals can be grown hydrothermally. Second, an effort will be made to extend crystal growth methods successfully employed for clathrate type zeolites such as ZSM-39 to channel type zeolites such as ZSM-5.

SIGNIFICANT ACCOMPLISHMENT

An ^{17}O-Label Crossover Probe of Molecular Structural Evolution During Sol-Gel Processing

Scientific Achievement:

Hydrolysis/condensation of ^{17}O-labeled $[Ti_{16}{}^{*}O_{16}](OEt)_{32}$ using labeled $H_2{}^{*}O$ yields a gel which, after drying, displays five resonances in its ^{17}O CPMAS NMR spectrum. Three of these resonances are assigned to the $[Ti_{16}O_{16}](OEt)^{32}$ oxygens O_A, $O_{B/C}$, and O_D shown below on the basis of their chemical shift values. The remaining oxygens



$[Ti_{16}O_{16}](OEt)_{32}$

are assigned to "linker" oxygens that link the $[Ti_{16}O_{16}]$ cores into a gel network. The kinetic stability of the $Ti_{16}O_{16}$ core toward hydrolysis/condensation can then be probed by crossover experiments performed by reacting $[Ti_{16}{}^{*}O_{16}](OEt)_{32}$ with unenriched H_2O and reacting unenriched $[Ti_{16}O_{16}](OEt)_{32}$ with $H_2{}^{*}O$. The former gel showed >90% ^{17}O present as "core" oxygen and the latter gel showed >90% ^{17}O present as "linker" oxygen according to ^{17}O NMR spectroscopy. Failure to observe significant label crossover demonstrates that $[Ti_{16}O_{16}](OEt)_{32}$ undergoes sol-gel polymerization with >90% retention of its oxide core structure.

Significance:

A major goal of modern materials chemistry is to control the structure of ceramics on the molecular level using low temperature processing techniques such as sol-gel polymerization. Many researchers have developed molecular precursors to ceramics

designed to control the structure of the ultimate product on a molecular level. The success of these efforts has been difficult to evaluate, however, due to the difficulty of monitoring molecular structural evolution during processing. The ^{17}O-label crossover probe just described can be easily generalized to many condensation ploymerization processes and should be very useful in establishing ceramic processing procedures capable of controlling structure on a molecular level.

Performer: Walter G. Klemperer, University of Illinois at Urbana-Champaign.

DAVID A. PAYNE

Synthesis and Properties of Electrical Ceramics

GOALS

The electrical ceramics research program is directed at the chemical synthesis, crystal growth, materials processing and structure development for new and improved ceramic materials for energy related applications. Of particular interest are structure-property relations for ferroelectric, piezoelectric, pyroelectric and electrooptic ceramics in both single crystal and polycrystalline form. A goal is to develop new synthetic methods for the preparation and processing of advanced electric ceramics. To this end a molecular building block approach has been developed for the synthesis, densification and crystallization of oxide materials at greatly reduced temperatures. The chemical method allows for the integration of functional ceramics with semiconductors. The research has been successful in that several sensing, transducing and memory devices have been fabricated.

HIGHLIGHTS

The chemical processing of electrical ceramics offers greater control of purity, stoichiometry, doping level, homogeneity and reactivity than can ever be achieved by conventional mixed-oxide processing. Moreover, if chemical bonds can be induced a the molecular level in solution between the constituent ions, mixed-metal oxide complexes can be formed as molecular precursors to ceramic materials. These mixed-metal oxide complexes, or building blocks of associated structures, are the novel precursors currently under investigation for electrical ceramics. Highlights of our recent work are in the $PbTiO_3$-$PbZrO_3$ system.

Recent work on the FTIR characterization of $Pb(Zr,Ti)O_3$ (i.e., PZT) precursor solutions has identified that careful control of precursor chemistry, especially the control of formation of esters and their eventual elimination (by reflux and distillation), resulted in solutions which yielded PZT ceramics with reproducible and consistent properties. In addition, it was determined that phase and microstructure development could be related to precursor chemistry, which was extremely important for

the fabrication of reliable electrical ceramics. Single-phase perovskite layers with uniform microstructures resulted from ester-free solutions which were found to be suitable for integrated ferroelectric applications.

FUTURE

Future research will continue on the molecular building block approach to ceramic synthesis, and determine pathways by which structure evolves on densification and crystallization. We plan to grow heterometallic metallo-organic precursor crystals (with more than two cations, e.g., Pb, La, Zr, Ti, Sn for piezoelectric, pyroelectric and electrooptic devices) and explore chemical methods for low temperature crystallization (e.g., 200°C). Low temperature crystallization gives rise to nanostructures and we expect to discover unusual properties (e.g., superparaelectricity) at these fine features and scale. An emerging area of our research is the effect of size and scale on electrical properties. Research will continue on the crystal growth of field-responsive materials, by melt, flux and hydrothermal methods. Materials under investigation, include, potassium titanyl phosphate ($KTiOPO_4$) and lithium triborate (LiB_3O_5). The asymmetric phosphate and borate groups give rise to polar structures with high eccentricities and second harmonic generation capability. The large nonlinear electrooptic coefficients and anisotropies could be suitable for phase matching applications.

SIGNIFICANT ACCOMPLISHMENT

Synthesis and Properties of Electrical Ceramics

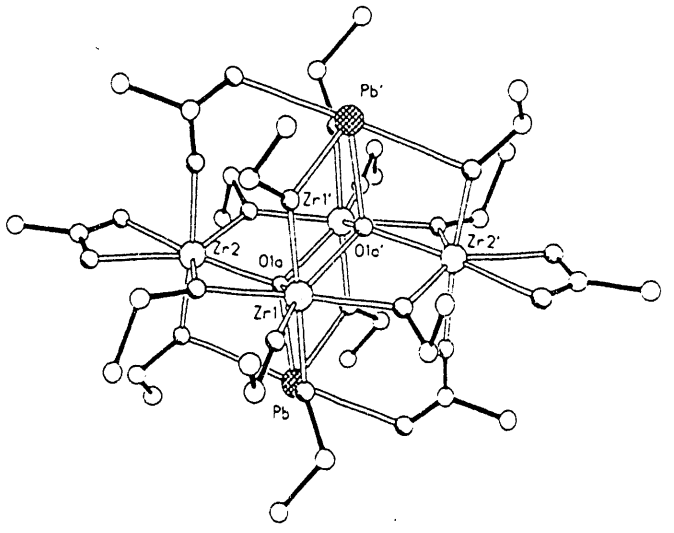
Scientific Achievement:

In our studies on precursor chemistry and phase stability in the PZT we identified two new metallo-organic oxo compounds. When a solution of zirconium and titanium ethoxides was heated in refluxing ethanol and combined with an ethanol suspension of $Pb(OAc)_2$ of the prescribed stoichiometry, a clear solution formed within minutes at room temperature. Analysis indicated the formation of heterometallic species with the complete consumption of $Pb(OAc)_2$. From the reaction mixture, two white crystalline solids were separated and characterized. ^1H NMR spectroscopy confirmed one of these species (**2**) to be a recently discovered compound $[PbTi_2(m_3\text{-}O)(OOCH_3)(OCH_2CH_3)_7]_2$ determined by other research in our group. The other compound (**1**) was a new species, which contained lead and zirconium in a 1:2 ratio as determined by elemental analysis.

Formulation and structural characterization of compound **1** was achieved by growing single crystals and XRD refinement. It was determined that the new molecule had a formula $[PbZr_2(m_3\text{-}O)(OOCH_3)_2(OCH_2CH_3)_6]_2$ and adopted a $M_2M'_4$ dimeric structure. A perspective drawing of the molecule (without hydrogen atoms) is shown. The two halves of the molecule are connected by one bridging acetate ligand, one oxo- ligand, and two bridging ethoxy groups. Alternatively, the structure can be viewed as two up-side-down "$PbZr_3(m_3\text{-}O)$" tetrahedra fused at a hypothetical Zr1-Zr1' edge. It is noteworthy that $PbZr_3(m_4\text{-}O)(OAc)_2(OPr^i)_{10}$ has recently been reported and compound **1** is related to it by elimination of two $Zr(OEt)_4$ molecules upon dimerization. In fact, the lead atoms in both compounds have a penta-coordination geometry. In addition, the average value for the various types of metal-oxygen bonds lengths are similar. However, a major difference does exists in that each zirconium atom in $PbZr_3(m_4\text{-}O)(OAc)_2(OPr^i)_{10}$ has six surrounding oxygen atoms while in compound **1** the zirconium atoms are hepta-coordinated. The difference in zirconium coordination number in the two compounds may arise from the different steric crowdness each type of alkoxy group exerts at the metal and the requirement of metal cations for maximum space filling in its ligand sphere.

The discovery of an oxo-ligand in $[PbZr_2(m_3\text{-}O)(OAc)_2(OEt)_6]_2$ is in good agreement with the observation that reactions of $Pb(OAc)_2$ and $Ti(OR)_4$ or $Zr(OR)_4$ lead to spontaneous formation of oxo-ligands by elimination of ester or ether molecules from acetato and alkoxy ligands. The loss of a molecule of diethyl ether from two ethoxy groups may explain the origin of the oxo-ligand

Crystal Structure of $[PbZr_2(\mu_3\text{-}O)(OOCCH_3)_2(OCH_2CH_3)_6]_2$



Crystal system: Triclinic; Space group: $P\ \bar{1}$;
a = 11.572(3) Å; b = 11.920(4) Å, c=12.455(4) Å; α = 61.84(2) °, β = 89.30(2) °, γ = 65.03(2) °; V = 1335.0(7) Å^3; Z = 1;
R = 0.052, R_w = 0.060.

in compound **1** since all acetate groups are retained in the bimetallic species.

Significance:

The discovery of two new compounds (**1** and **2**) in the ethoxide-based system may be significant for the compositional heterogeneity reported by others for PZT dielectrics prepared by this particular chemical route. A Zr-precursor in 7-fold coordination may lead to the formation of a pyrochlore structure, whereas a Ti-precursor in 6-fold coordination would yield the perovskite structure. The subsequent presence of a Zr-rich second phase would cause a deterioration in properties due to the non-ferroelectric nature of the pyrochlore structure. This was not observed in our previous work on a carefully prepared methoxyethoxide based system, but has been reported by others for the ethoxide system. The role of alkoxide precursors on phase stability and properties of heterometallic ceramic systems (e.g., PZT) is extremely important. Future research is directed at this general topic, and how structure evolves in sol-gel processing.

Performer: David A. Payne, University of Illinois at Urbana-Champaign.

A. A. ROCKETT

Atomic-Scale Mechanisms of Vapor-Phase Crystal Growth

GOALS

This program seeks to develop an understanding of the atomic-scale processes which determine the surface and bulk structure, morphology, and defects in thin films growing from the vapor phase.

HIGHLIGHTS

Our current research focuses on showing how the surface morphology and lattice defects in crystals are related to the kinetics of deposition and diffusion of adatoms. This includes fundamental work relating individual diffusion events to the nucleation of new monolayers of atoms and studies with direct application to forming high-performance insulators and to production of improved solar cells.

We have developed a model of epitaxial growth which includes three approaches optimized for performance on three time scales. These have been applied to the Si(100) surface to show how atom diffusion dynamics affects the morphology of the deposited film. For example, we have shown that sites for nucleation of amorphous Si during low temperature epitaxy should occur near the edges of steps on the (100) surface. We have also shown that the growth of the type-A step on Si(100) should be limited by the rate of nucleation of chains of atoms on the step edge while the type-B step should grow at a rate limited by the flux of atoms reaching the step. Hence, when the atomic mobility is high the type-B step should grow much faster than the type-A step.

$CuInSe_2$ is one of four major candidate materials for use in large area solar cell arrays. Our research is aimed at understanding and controlling the development of morphological and structural defects and in demonstrating the relationship of these defects to device performance. During FY92 we have demonstrated that application of the deposition conditions used for epitaxial $CuInSe_2$ to growth of polycrystalline material leads to an increase in grain size. Transmission electron microscopy studies we have initiated this year have shown that the density of threading dislocations in our epitaxial layers decreases with film thickness, as expected. This should allow solar cells with varying dislocation densities to be fabricated and tested, showing the effect of dislocations on cell performance.

$Si_{1-x}Ge_x$ alloys are becoming increasingly critical components in state-of-the-art semiconductor devices. Unfortunately, methods for forming high performance dielectrics on Ge and $Si_{1-x}Ge_x$ are not yet available. We have shown that exposure of Ge to ultraviolet light in air, generating ozone (O_3), at room temperature accelerates oxidation significantly with respect to the rate at elevated temperatures in pure O_2. The oxidation is diffusion-limited for all oxide thicknesses measured and, unlike thermal oxidation, results in the desired phase, stoichiometric GeO_2. We have shown the rate limiting step for native oxide formation and high temperature oxidation to be O_2 decomposition. For the UV/ozone process the reaction is limited by the rate of diffusion of O_3 through the oxide and, hence, is relatively fast. Removing the oxide is also critical to device processing and wafer cleaning. We have shown that GeO_2 desorbs from the surface of Ge at 410 °C and have analyzed the desorption kinetics quantitatively.

FUTURE DIRECTIONS

With a characterization of O_3 oxidation of Ge well underway, we have begun to examine oxidation of the more critical $Si_{1x}Ge_x$ alloys using the same UV/ozone process. We will perform a similar investigation of the reaction and desorption kinetics of the resulting oxides and attempt to demonstrate a method for producing the oxide without the commonly observed segregation of Ge to the alloy/oxide interface. We have preliminary indications that this can be accomplished by reducing the ozone treatment temperature. We plan to apply the methods developed for this study to other surface reactions involving $Si_{1x}Ge_x$ such as the formation of silicides.

SIGNIFICANT ACCOMPLISHMENT

A Quantitative Analysis Technique for Conducting Thermally-stimulated Desorption in an X-ray Photoelectron Spectrometer

Scientific Achievement:

Thermally stimulated desorption is normally conducted by heating a specimen and observing the desorbing species with a mass spectrometer. The desorption mechanism and its effect on surface chemistry are then inferred from the products evolved and the temperature at which desorption occurs. By contrast, conducting this experiment in an X-ray photoelectron spectrometer provides information on the chemistry of the remaining film. We have developed a quantitative procedure for determining the desorbing flux as a function of temperature and have applied this analysis to the desorption of GeO_2 from Ge. A desorption spectrum acquired by photoelectron spectroscopy and converted using this method to a flux vs. temperature spectrum is shown in the figure.

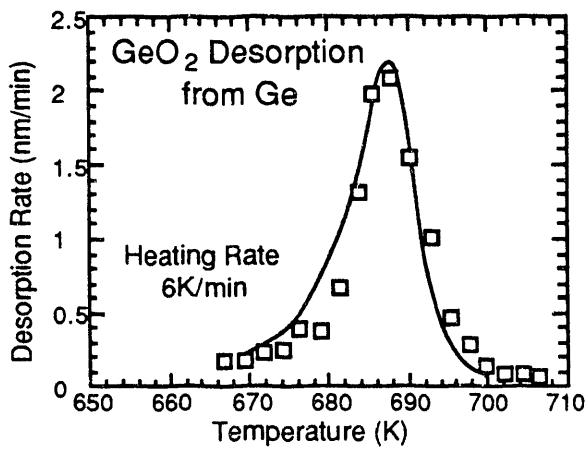


Figure Caption: GeO_2 desorption from Ge based on X-ray photoelectron spectroscopy data. The Ge does not change valence during the desorption thus the GeO_2 is not converting to GeO. Squares indicate points derived from the data, the solid line is a theoretical fit from which the desorption activation enthalpy was determined.

Significance:

The processes of adsorption and desorption of molecules from surfaces are critical to both thin film growth and surface catalysis. Adsorption processes have commonly been studied by photoelectron spectroscopy. However, desorption is more difficult to analyze quantitatively. The technique we have demonstrated allows quantitative analysis of the desorption process and permits the formalisms developed previously for thermally stimulated desorption to be applied directly to the results. It extends the conventional desorption technique to much lower desorption rates where the process is much closer to equilibrium than in conventional mass-spectrometer-based experiments.

Performer: A.A. Rockett, University of Illinois at Urbana-Champaign

C. F. ZUKOSKI

Processing Monodispersed Ceramic Powders

GOALS

The goal of this program is to develop a fundamental understanding of the chemical and physical processes which limit the fabrication of advanced ceramic materials. In particular, the program focuses on gaining an understanding of i) methods of controlling the morphology of ceramic precursor powders prepared from solution precipitation reactions, ii) powder and suspension properties required to process green bodies with low flaw densities and low sintering temperatures and iii) wet processing techniques for sub 50 nm oxide powders.

HIGHLIGHTS

Fabrication of low flaw density green bodies requires dense particle packing prior to sintering. Process history can dramatically alter compact microstructure and thus improve or degrade green body quality. In a series of studies aimed at elucidating the role of shear on particle packing, the links between shear rate and microstructure in dense suspensions have been explored. Microstructure determinations were carried out using optical visualization and small angle neutron scattering (SANS) at the Cold Neutron Reactor Facility at NIST in Gaithersburg. A phase diagram has been established as a function of shear rate and volume fraction showing how shear alters the steady state microstructures of dense suspensions and detailing the volume fraction/ shear rate range where processing can occur.

In separate studies, the formation of uniform 10-50 nm gold particles has been investigated. For particles formed by the reduction of auric acid with citrate, the first particles observed have diameters greater than several hundred nanometers. As the reaction proceeds, the particles decrease in size and at the end of the reaction the sol has a very narrow size distribution. The origin of this peculiar "growth" mechanism has been elucidated through a series of detailed kinetic studies carried out at the University of Illinois and a collaborative study with Prof. F. Griezer and the University of Melbourne where we have established that the large particles seen early in the reaction are the result of a weak agglomeration of small gold particles. These particles are kept out of a primary van der Waals minimum by the adsorption of citrate and auric acid which act as steric stabilizers. In addition, the competitive binding of these charged species determines the colloidal stability of the growing particles such that over the course of the reaction where auric acid is consumed, the particle surface potential increases and the agglomerates fall apart. These studies involved a novel use of an Atomic Force Microscope to determine the interaction potential of gold surfaces in the presence of electrolytes and demonstrate the importance of colloidal stability in determining precipitate morphologies.

FUTURE DIRECTIONS

Links between suspension microstructure and rheological properties of dense suspensions will continue to be explored where details of the flow properties will be correlated with microstructural behavior. In addition a new series of studies has been initiated investigating the microstructure and flow properties of dense suspensions containing a bimodal mixture of spheres in collaboration with H. Hanley and G. Straty at NIST in Boulder, Co. These studies involve determination of partial structure factors of the large and small components of the mixture in SANS studies in conjunction with rheological characterization.

Methods of processing sub-50 nm metal oxide particles will be explored with the goal of preparing dense compacts of these materials for sintering and mechanical studies. Currently we are investigating how to prepare compacts through osmotic dewatering techniques and have been successful at preparing shaped compacts of 10 nm zirconia particles at green body volume fractions in excess of 0.5. Future studies will include detailing the role of osmotic forces in dewatering suspensions of 1-10 nm particles, the sintering properties of the resulting compacts and the mechanical properties of the resulting ceramics.

SIGNIFICANT ACCOMPLISHMENTS

Non-equilibrium Phase Diagram for Sheared Suspensions

Scientific Achievement:

The influence of process history on suspension microstructure is of growing significance in the development of methods for controlling flaw density in green body fabrication. Our studies have been aimed at establishing the links between rheological response and steady state microstructure in dense suspensions. We have generated, for the first time, a complete non-equilibrium phase diagram of charge stabilized colloidal particles as a function of shear rate and volume fraction. These studies covered a volume fraction range from below the equilibrium order/disorder phase transition up to close packing. At volume fractions above the equilibrium order/disorder phase boundary, four distinct phases are observed. At rest, we observe a random registered stacking of close packed layers which lie parallel to the walls of the rheometer. At any small but finite shear rate, this long range orientational order is lost and a polycrystalline phase (PC) is formed. As the shear rate is raised a sliding layer structure (SL) emerges. An amorphous (A) microstructure is seen at high shear rates. The PC and SL microstructures and the SL and A microstructures coexist over a range of shear rates and the transitions in microstructure are reversible on lowering the shear rate. Our studies suggest there is a shear rate above which no long range order is observed in the suspension at any volume fraction. In addition, detailed rheological experiments demonstrate that the PC to PC/SL boundary is associated with a discontinuous reduction in viscosity while the SL/A to A transition is associated with shear thickening for volume fractions greater than 0.5

Significance:

The ability to alter microstructure through variation in shear history has profound implications in generating low flaw density ceramics. As different microstructures are typically locked into the sample when shear is stopped, how a powder compact is prepared will dictate the location of phase boundaries and thus where flaws will be located. Establishing the links between shear rate and microstructure thus allows processing windows for dense suspensions to be established. In addition, by developing the scaling relationships of critical shear rates and stresses on volume fraction, mechanisms of non-equilibrium phase transitions can be evaluated. Future studies will extend rheological and microstructural studies to include particle size and continuous phase viscosity thus providing a broad picture of nonequilibrium phase behavior.

Performer: C. F. Zukoski, University of Illinois at Urbana-Champaign.

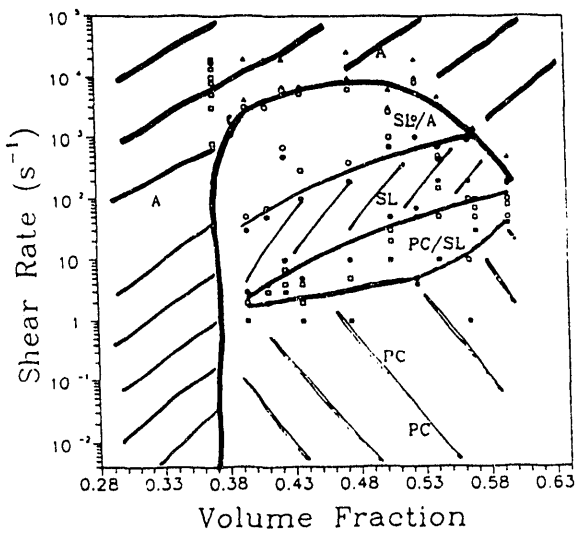


Figure caption: Non-equilibrium phase diagram at sheared colloidal suspensions consisting of 250 nm charge stabilized spheres suspended in 10^{-3} M NaCl. At rest suspension orders at a volume fraction near 0.38. The various phases identified are polycrystalline (PC), Sliding layer (SL) and amorphous (A). PC and SL phases coexist over a range at volume fractions and shear rates (PC/SL) as do SL and A phases (SL/A).

E.4.a RESEARCH SUMMARIES FOR RADIATION EFFECTS KC-02-01-04

I.M. ROBERTSON

Radiation Effects in Materials

GOALS

The focus of this program is to provide a fundamental understanding of the microstructural changes that are produced in materials bombarded with energetic particles. Specifically, in metals the formation of vacancy loops from displacement cascades as a function of ion dose, ion mass, ion energy and irradiation temperature are being investigated and in semiconductors the crystalline-to-amorphous transition and the amorphous-to-crystalline transition caused by icn implantation are being studied.

HIGHLIGHTS

The vacancy defect population produced in a series of solid solution Cu-Ni and Ag-Pd alloys by heavy ion irradiation has been investigated. These alloys were selected as they form solid solution alloys over the entire composition range and, as the masses of the constituents are similar the cascade dynamics should be independent of the alloy composition. Thus the effect of the melting temperature of the alloy and the heat removal by the electronic system on the loop formation probability can be examined in a systemic manner. The molten zone model for loop formation predicts that the vacancy retention factor, which is defined as the product of the defect yield and the number of vacancies in a loop of average size, is related inversely to the melting temperature and the heat removal rate. In the Cu-Ni system it was found that energy dissipation through the electronic system played a stronger role in determining the loop formation probability than the melting temperature. Although a similar trend was expected in the Ag-Pd system, the results showed no strong correlation between the vacancy retention factor and the inverse of either the melting temperature of the alloy or the power removed by the electronic system.

Radiation Induced segregation has been studied in random solid solutions of Ni-Al and Ni-Si and in the ordered $L1_2$ alloys, Ni_3Al and Ni_3Si. The Ni_3Al alloy proved to be unusual in that no RIS to the surface was detected by AES. Elevated temperature, *in situ* irradiations, in the HVEM-Accelerator facility at ANL showed that a complex dislocation structure persisted in this alloy. By contrast, in the binary NiAl alloy no dislocation structure was detected. This suggests that the lack of RIS to the sample surface is a consequence of the complex internal sink structure that persists in this alloy. This explanation is currently being tested. In conjunction with this effort in Ni_3Al is a study correlating the disordered zones to the vacancy loop population as a function of ion mass, ion energy, ion dose and irradiation temperature.

The crystalline to amorphous transition induced by heavy-ion bombardment of $Al_xGa_{(1-x)}As$ alloys is being investigated. We have shown that the resistance of these alloys to direct impact amorphization increases with increasing Al content. Even alloys with 20 % Al are more resistant to direct impact amorphization than pure GaAs. The AlGaAs alloys are driven amorphous at higher ion doses. The reason for the need of the high dose is not understood but may reflect differences in amorphization mechanisms in these alloys. Information on this fundamental damage state is needed if ion mixing in these systems is to be better understood and fully utilized.

FUTURE DIRECTIONS

We will continue to study the fundamental aspects of loop formation from heavy-ion generated displacement cascades. A major effort in the next year will be to determine the nature (vacancy or interstitial) of these loops. The loop nature has recently been brought into question because of computer simulation results of low energy ion damage. This is a critical issue and has wide ranging implications to our modeling and understanding of radiation damage.

A new effort focusing on the embrittlement problem has been initiated. The work will involve a study of the interaction between matrix dislocations and thermally produced Cu precipitates in model alloy systems and how the grain boundary chemistry controls the grain

boundary deformation. The model alloys have been obtained and are currently being heat treated to produce the BCC Cu precipitates.

SIGNIFICANT ACCOMPLISHMENT

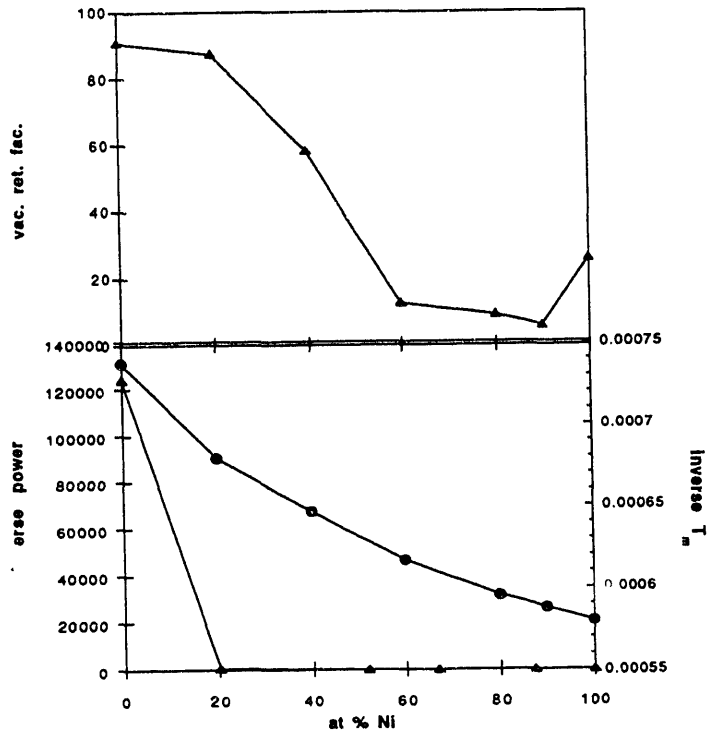
Experimental evidence supporting the molten zone model for loop formation.

Scientific Achievement:

Our experimental work on the formation of vacancy type defect clusters from displacement cascades has provided tests for models describing the process of vacancy loop formation. From the different models that have been proposed, the one that provides a self-consistent explanation of the wide range of experimental results is the molten zone model. This model was developed from the molecular dynamic computer simulation studies in which the displacement cascade showed features of melting, cooling and crystallization. Direct experimental verification of these features is difficult because of the time scales involved (10^{-11} sec). However, it is expected that, if such a model is correct a number of material parameters (melting temperature, heat removal rate through the electron and phonon system, impurities) and irradiation parameters (ion mass and energy, irradiation temperature) will affect the number and size of vacancy loops formed. For example, the model predicts that in systems where the cascade dynamics are similar the loop formation probability will be higher in the material with the lower melting temperature and that the loop formation probability will decrease as the cooling rate increases.

We have shown, through *in situ* TEM irradiations, that decreasing the irradiation temperature decreases the loop formation probability and the loop size. Typically, the loop formation probability is reduced by about 50 % when the irradiation temperature is decreased from 300 to 30 K.

By selecting suitable alloy systems, the role of the melting temperature of the alloy and the effectiveness of heat removal through the electronic system has been investigated. The vacancy retention factor (defect yield x average number of vacancies in a loop) is compared with the inverse of the melting temperature and power dissipated through the electronic system in Cu-Ni alloys in Figure 1. In this system, the heat removed through the electronic system appears to play a significant role in determining the loop formation probability. A similar conclusion was drawn from our study of Ni-Cr data. In the Ag-Pd system, no strong correlation was found.



The change in the loop formation probability (i.e. the microstructural development) as a function of ion dose has been studied. It was found that the defect production rate decreased as the ion dose increased. Detailed examination of defect structures showed that pre-existing loops could be annihilated or caused to coalesce by the continuing irradiation. These effects explain the observed decrease in the loop production rate. The effect of the irradiation on the preexisting loop population is easily understood if the molten zone of the new cascade destroys the preexisting defect. Currently, a probability based model is being developed to predict the change in the loop production rate as a function of ion dose.

By considering the effectiveness of the heat removal mechanisms, the change in the melting temperature with alloy content, and changes in the energy density profile and the interstitial position by solute effects, the molten zone model has been successful in explaining , in a consistent manner, a wide range of experimental results. No other loop formation model has been able to explain all of these results in a consistent manner.

Significance:

The formation of vacancy defect clusters from displacement cascades has important consequences for the subsequent microstructural development under ion and fast neutron irradiation. Furthermore these defects may play a role in processes such as void swelling, radiation hardening and radiation creep. Understanding the underlying mechanisms controlling the formation of these defect structures is clearly important to understanding damage development in reactor environments.

Performer: I.M. Robertson, University of Illinois at Urbana-Champaign.

R.S. AVERBACK and C. P. FLYNN

Fundamental Studies of Irradiation Effects in Tailored Crystals

GOALS

This new project seeks to elucidate fundamental mechanisms of radiation damage in solid matter. The unique feature of the program is the ability to grow single crystal materials that are structured at the atomic level by molecular beam epitaxy to provide model systems for radiation damage experiments. Thermal spike behavior, radiation-enhanced diffusion, the role of interfaces in phase evolution, and sputtering are being investigated. Elucidation of these radiation effects in oxide ceramics is a primary concern.

HIGHLIGHTS

Work in the initial phase of this project has started on the task of understanding irradiation effects in oxides at a fundamental level. To this end we have selected MgO as a prototype, and have developed methods for growing high quality single films by molecular beam epitaxy. A new achievement is a method by which buried layers of $Mg^{18}O$ can be created in $Mg^{16}O$ with various depths and thicknesses suitable for tracer diffusion experiments. The new method is economical in tracer material as growth is achieved using a Mg molecular beam with $^{18}O_2$ tracer trapped at low pressure in the MBE chamber with the vacuum pumps isolated. The resulting quality of crystal growth appears competitive with the MBE MgO of the remaining tailored material. A parallel goal of creating buried tracer layers with Mg isotopic doping by means of ion beam methods has proved extremely difficult, and success in this aspect of the program is not expected for some time to come. Instead we are developing the ability to create rocksalt $Zn_xMg_{1-x}O$ buried layers in MgO so that the mixing processes on the Mg sublattice can be monitored by Zn diffusion, in addition to those on the O sublattice now made accessible by isotopic doping.

Our goal of understanding defect behavior on the two sublattices of oxides, both in the presence and absence of irradiation fields, has been initiated with studies of ^{18}O tracer self diffusion on the O sublattice of MgO. Interdiffusion profiles are analyzed from SIMS data acquired in the MRL Center for Materials Microcharacterization. The initial results reveal that over a very wide range of diffusion temperatures the oxygen diffusion is an order of magnitude slower than the best data from bulk samples. While the high purity of the MBE material offers one possible explanation of this important difference, alternative factors central to the defect behavior also enter. In particular, defect populations near the outer surfaces and other defect sinks in ionic salts are strongly perturbed by poorly characterized Debye-Huckel screening effects. The population distortions that occur near the outer surface in conventional experiments may be largely absent in the present research because our tracer layer is buried under perfect overgrown MgO to a selected depth which can be 1 μm or more. Experiments of this type promise future measurement of the screening distributions themselves on both sublattices near surfaces. The potential for extension to similar measurements of defect mobility in the presence of radiation fields is self evident and preliminary studies have been carried out. Radiation-enhanced diffusion (RED) of ^{18}O has been measured in MgO using the SIMS methods outlined above, and that RED was shown to become important only above 900 °C. These measurements are the first direct measurements of RED in an oxide ceramic.

FUTURE RESEARCH

The initial phases of this research will examine the diffusion properties of both anions and cations in MgO, both in the presence and absence of a radiation field. The roles of primary recoil spectra, electronic excitation and interfaces on diffusion will be examined. Sink action at interphase boundaries will also be a primary topic of study. The role of electron-phonon coupling on the thermal evolution of displacement cascades will be investigated using an approach that combines molecular dynamics computer simulations and measurements of black body radiation from irradiated surfaces.

E.5. SIGNIFICANT ACCOMPLISHMENTS FOR KC-02-01

SIGNIFICANT ACCOMPLISHMENT

Correlation of STM, AFM and Surface X-ray Scattering Structures of Monolayers on Electrode Surfaces

Scientific Achievement:

We have used the three available *in situ* structural techniques -- Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and Surface X-ray Scattering (SXS) -- to characterize monolayers of Bi on Au(111) electrode surfaces. We have demonstrated that all three give the same structures in the same potential regions. The figure shows the (2 x 2) - Bi overlayer on Au(111) as determined by a) SXS, b) AFM, and c) STM. This is the first proof that the probe techniques -- STM and AFM -- provide true images in metal-on-metal systems. This is also the first time an open metal-on-metal system has been observed with SXS.

Significance:

A major question in Scanning Probe Microscopies such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) concerns the representativness of images. This is especially true in the electrochemical environment where we have observed open (not close packed) structures of metals on other metals. These metal-on-metal structures, which are without precedent in the Ultra High Vacuum (UHV) environment, act as catalysts for a variety of electrochemical processes. Bi monolayers especially act as catalysts for efficient reduction of H_2O_2 to H_2O. Until this work there was significant uncertainty about whether the structures observed with the AFM and STM were, in fact, truly representative of the real atomic arrangement on the electrode surface. Our demonstration, for the first time, that all three *in situ* structural techniques -- STM, AFM, and SXS -- give exactly the same structures of Bi on Au(111) allows us to proceed with characterization of this and other catalytically important surfaces.

Performer: Andrew A. Gewirth, University of Illinois at Urbana-Champaign and Benjamin M. Ocko, Brookhaven National Laboratory.

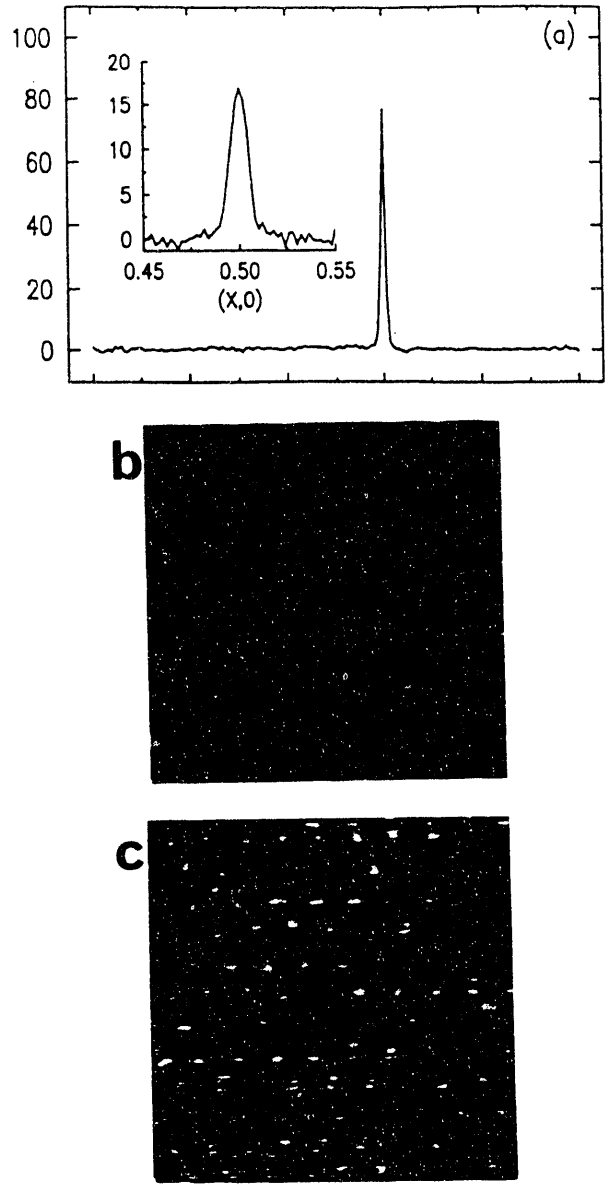


Figure caption: Electrodeposited (2x2)-Bi adlattice on Au(111) as determined by three different *in situ* structural techniques. a) Surface X-ray Scattering diffraction shows a peak at (1/2, 1/2) in reciprocal space consistent with a (2x2) adlattice. b) AFM and c) STM images of the (2x2) structure.

F. RESEARCH SUMMARIES FOR SOLID STATE PHYSICS

F.1.a EXPERIMENTAL RESEARCH KC-02-02-02

THEODORE L. BROWN

Synthesis and Characterization of Organometallic Liquid Crystal Polymers

GOALS

The goals of this program are to:

(a) Prepare reactive intermediates of organometallic compounds adsorbed on oxide surfaces, such as silica and alumina, via flash photolysis at low temperatures.

(b) Study the interconversions of photochemically-generated intermediates, their reactions with the surface and with added substrates or reagents, employing FTIR or UV-visible spectroscopy.

(c) Build models on the basis of this and related experimental work for the mechanisms of catalysis of important reactions by adsorbed organometallic compounds.

(d) Design new more selective and efficient heterogeneous catalytic systems.

HIGHLIGHTS

The study of adsorbed organometallic compounds is a new effort. During the past year we have initiated design and construction of the apparatus necessary to carry out the proposed work. The funds for a new step-scan FTIR instrument have been acquired, the instrument has been ordered, and should be in operation by January, 1993.

During the past year we have brought to near-completion work on the synthesis and characterization of organometallic liquid crystalline polymers. New side chain homopolymers and copolymers containing organometallic functional groups have been synthesized, but proved not to be mesogenic.

FUTURE DIRECTIONS

The objectives of the new work are to study the photochemical properties of organometallic compounds on oxide surfaces. The analytical techniques to be employed are primarily (a) flash photolysis, using both lasers and xenon flash lamps; (b) FTIR for identification of intermediates, and for transient detection, particularly at low temperatures; (c) uv-visible detection of the spectra and time dependencies of transients.

The properties of metal carbonyl compounds adsorbed on oxides reveal the important roles of the surface as a reactant medium. Surfaces may constrain the dimensionality of the reacting system, in that reactions may occur only between adsorbed species, or between the adsorbate and surface atoms or groups. The surface generally modifies the chemical behavior of the adsorbate through the forces that bind it to the surface. The surface may also behave as an acid, base or oxidation/reduction reagent toward the adsorbate.

Our plans for the forthcoming year are to initiate detailed flash photolytic studies of the following systems of adsorbed carbonyls:

A. $Mo(CO)_6$ on γ-Al_2O_3 or SiO_2

Flash photolysis provides an ideal tool for examining the successive reactions of $Mo(CO)_6$ on γ-Al_2O_3. We will adsorb $Mo(CO)_6$ on appropriately activated γ-Al_2O_3 , at room temperature or lower, to ensure that there is no significant loss of CO. Flash photolysis will lead to loss of CO. We can observe the resulting transient species, the spectra of which are known from solution studies, to determine the kinetics of reaction with the surface. We will search for competition of gas phase CO with the surface for binding to intermediates, and probe the question of how the extent of hydroxyl group coverage of the surface (determined by the conditions of preparation) affect the product distributions and kinetics. We will also study the photochemical behavior of $Mo(CO)_3$(ads).

B. Photochemical properties of $Mn_2(CO)_{10}$

$Mn_2(CO)_{10}$ is interesting as a prototype for metal carbonyl clusters, having just a single metal-metal bond. Photolysis of $Mn_2(CO)_{10}$ adsorbed on g-Al_2O_3 could, in analogy to its behavior in solution, lead to either CO loss or homolysis of the metal-metal bond. The flash photolysis experiment will enable us to determine which processes occur, and in which time domain.

Loss of CO upon photolysis yields $Mn_2(CO)_9$, which could be expected to bind strongly to the substrate via the vacant coordination site on Mn. Homolysis of the Mn-Mn bond gives rise to formation of a pair of $Mn(CO)_5$ radicals:

$$Mn_2(CO)_{10} + hn \rightarrow 2Mn(CO)_5$$

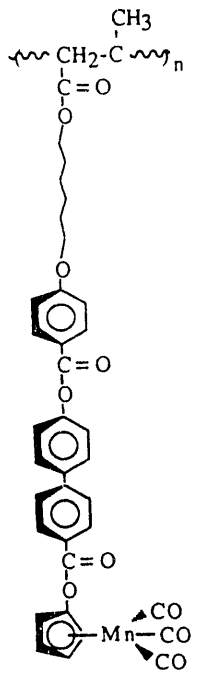
The time-dependence of the spectra attributable to the radicals will provide information on the dynamics of their interactions with the surface and with one another.

SIGNIFICANT ACCOMPLISHMENT

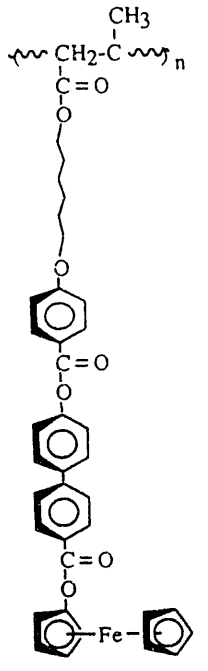
Synthesis of New Side Chain Polymers

Scientific Achievement:

The most significant achievement during the past year has been the syntheses of new side chain homopolymers and copolymers containing organometallic functionalities. Two new homopolymers, shown below as I and II, were prepared. These are the first examples of organometallic-containing side chain polymers designed for mesogenicity. In addition, copolymers with a vinyl precursor terminated with OH rather than the organometallic functional group were also prepared.



I



II

Significance:

The new polymers are reasonably stable thermally. They proved not to be mesogenic, nor were the vinyl precursors from which the polymers were formed mesogenic. Apparently, the organometallic functionality interferes with liquid crystal formation because the organometallic groups lack the high aspect ratio and flat steric character characteristic of mesogenic functional groups. We are pursuing further characterization of the new materials, which may have interesting optical and mechanical properties.

Performer: T.L. Brown, University of Illinois at Urbana-Champaign.

DAVID G. CAHILL

Microscopic Mechanisms of MBE Crystal Growth Assisted by Low Energy Ions

GOALS

A wide variety of methods for the synthesis and processing of thin film materials utilize the interaction of low energy ions with surfaces. Ion bombardment of surfaces modifies the surface structure, chemistry and kinetics. The objective of our research is to identify and quantify how the surface physics and chemistry are altered by inert and reactive gas ions and to investigate the use of low energy ion bombardment in the synthesis of thin film materials with metastable crystal structures. We directly observe the important atomic-scale processes using a scanning tunneling microscope installed in the Molecular Beam Epitaxy Laboratory.

HIGHLIGHTS

Our principal experimental tool, a scanning tunneling microscope (STM) operating in ultrahigh vacuum, has been installed in the Molecular Beam Epitaxy Laboratory. We designed and constructed an STM analysis chamber and systems for sample transfer and vibration isolation. These systems maintain compatibility with the 3" sample blocks used by the seven interconnected molecular beam epitaxy growth chambers and therefore samples can be transferred directly from any of the growth chambers to the STM system without leaving the ultra-high vacuum environment. The vibrational noise level in the laboratory is high but we have succeeded in reducing the amplitude of the vibrations between the sample and the probe-tip to below 0.2 Å peak-to-peak in the important frequency range above 10 Hz.

We have designed, constructed, and tested a differentially pumped source for low-energy ions. This source delivers >1 mA of ion current with ion energies as low as 40 eV. This source is currently being installed directly on the STM analysis chamber and will allow us to maintain surfaces in ultrahigh vacuum conditions during ion bombardment.

FUTURE DIRECTIONS

During the next year, we will begin our investigations of ion-surface interactions with an emphasis on xenon and hydrogen ion bombardment of silicon surfaces. We will quantify the rates of surface defect formation as a function of xenon ion energy and explore the possibility of preferential sputtering of surface adsorbates. The reactions between semiconductor surfaces and activated hydrogen species is vital to a wide range of processing and growth technologies for electronic materials. We are particularly interested is observing the modification of surface geometric and electronic structure produced during the reaction of energetic hydrogen ions with the Si(001) surface.

TAI-CHANG CHIANG

Semiconductor Surfaces and Interfaces

GOALS

This research is a study of the growth behaviors, the resulting atomic structure, and the electronic properties of surfaces, interfaces, overlayers, and multilayer structures that are of scientific and technological interest. The goal is to obtain a fundamental understanding of the general crystal growth behaviors, the various effects involved in materials synthesis, and the properties of lower-dimensional systems and novel quantum structures. State-of-the-art experimental techniques are employed, including molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) for sample preparation, synchrotron-radiation photoemission for band structure and core level studies, scanning tunneling microscopy (STM) for real-space inspection of the surface, electron diffraction and Auger spectroscopy for sample characterization, and grazing-angle X-ray diffraction for structural studies.

HIGHLIGHTS

(1) Si and Ge are the most important and most widely used semiconductor substrate materials in fundamental research involving prototypical systems and in many applications. We have examined the CVD growth of Si on Ge(100) using disilane as the source gas. This growth process is of industrial importance and of scientific interest because of its simplicity. In our experiment, we investigated the room temperature adsorption of disilane, the reactions and decomposition of the adsorbed molecules at various temperatures, the combination and coalescence of surface radicals, and the growth of multilayers. A fairly complete picture of the growth process, with atomic detail, has emerged from this study. These results form an interesting comparison with our studies of the MBE growth of Si on Ge. (2) Using X-ray diffraction techniques, we have examined the interfaces formed between C_{60} overlayers and Si(111)-(7x7), Si(100)-(2x1), and Ag(110):Cs-(1x2) substrates. In the case of Si(111) and Si(100), the (7x7) and (2x1) reconstructions are well preserved – a rather surprising result. For Ag(110):Cs-(1x2), the (1x2) reconstruction is suppressed by the C_{60} coverage. These results are discussed in terms of the interaction between C_{60} and the substrate surface. This research is partly driven by an interest in understanding the fundamental interactions at an interface and the development of novel capping (coating) materials.

FUTURE DIRECTIONS

This research will focus on atomic-resolution studies of surface and interface phenomena. We will continue the investigation of the CVD growth and atomic layer epitaxy of Si on a variety of substrates. The role of the terminating hydrogen during the growth and the effects of strain, reconstruction, and alloying will be investigated in detail. X-ray diffraction techniques will be employed to examine the growth processes in real time. We will continue to improve and refine our experimental techniques and develop new approaches for a more precise control and characterization of material properties. For example, we are developing a state-of-the-art X-ray diffraction system for use at the 7 GeV storage ring of the Advance Photon Source which is under construction with DOE support.

SIGNIFICANT ACCOMPLISHMENT

Atomic Behavior of CVD Growth of Si on Ge Using Disilane

Scientific Achievement:

Scanning tunneling microscopy (STM), core level photoemission spectroscopy, and electron diffraction techniques were employed to study the CVD epitaxial growth of Si on Ge(100)-(2x1) using disilane (Si_2H_6) as the source gas. We examined the initial chemisorption, dissociation, and pyrolytic reactions of individual disilane molecules on the surface, and observed the evolution of the chemical states through the formation and decomposition of various hydride species on the surface (SiH_3, SiH_2, SiH, and GeH). Also observed were the formation of clusters and islands on the surface, island coarsening, step flow, intermixing and indiffusion of Si, and the multilayer growth of Si

via atomic layer epitaxy. This study, based on a combination of spectroscopic, microscopic, and diffraction techniques, provides a detailed, step-by-step description of a prototypical CVD growth process on a well characterized surface.

Significance:

One of the critical issues in surface science and engineering is a fundamental understanding of the atomic processes involved in the preparation of surfaces and thin films. This topic of research is relevant to an important area of advanced materials synthesis and processing. Our study exemplifies the use of a multi-technique approach, with an energy and spatial resolution sufficient to distinguish individual atoms and different chemical states, to gain a detailed understanding of a prototypical CVD process, which is also of interest to industrial applications.

Performer: Prof. Tai-chang Chiang, University of Illinois at Urbana-Champaign.

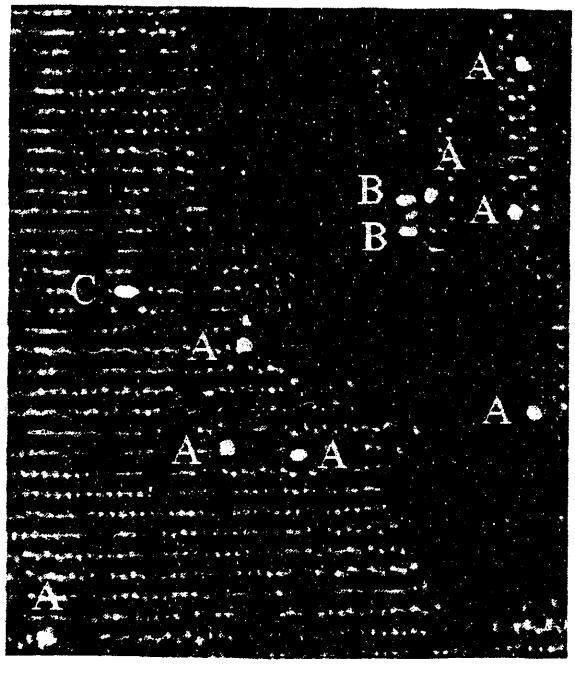


Fig. 1. 210x250 $Å^2$ STM image of Ge(100)-(2x1) exposed to 0.02 L of Si_2H_6. Three bonding configurations of disilane fragments on top of the substrate dimer rows are observed. A and B: two SiH_3 aligned along the dimer row and dimer bond, respectively; C: two SiH_2.

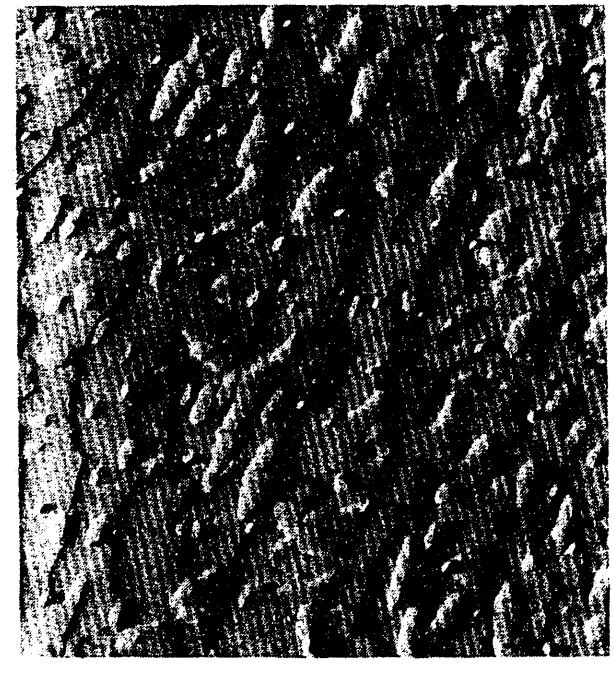


Fig. 2. 3,700x4,000 $Å^2$ STM image of Ge(100) exposed to 5-L disilane and annealed to 720 K. The hydrogen has desorbed, and the Si (1/2 monolayer) has diffused into the substrate. Many monolayer islands are seen on terraces between atomic steps.

S. L. COOPER

Optical Studies of Dilute Magnetic Semiconductor Epilayers and Heterostructures

GOALS

Recent advances in the fabrication of high quality II-VI dilute magnetic semiconductor (DMS) films and heterostructures provide an opportunity to study the effects of low dimensionality and artificial environment on the unusual spin interactions in these materials. In this program, we are studying the effects of impurity type, artificial structure, and quantum confinement on (1) the exchange interaction, (2) the electronic and vibrational properties, and (3) the spin and charge dynamics of Zn(Mn,Co,Fe)Se epilayers and superlattices.

HIGHLIGHTS

In the past year, we have used magneto-photoluminescence and reflectivity measurements to study magnetically-induced type I to type II band alignments in ZnMnSe/ZnSe quantum wells. Carriers confined to the ZnSe layers at zero-field in these systems become confined in the ZnMnSe layers at small fields, as evidenced by an enhanced magneto-optical response of the band-edge states for H>0. For low concentrations of Mn, we have also observed the formation of a "spin superlattice," in which holes and electrons of different spin states are confined to alternating layers in the ZnMnSe/ZnSe quantum wells. We are planning time-resolved optical experiments to explore the charge dynamics exhibited by different spin and charge configurations. We have also obtained evidence for the formation of a two-dimensional bound magnetic polaron in ZnMnSe/ZnSe quantum wells, wherein a magnetic alignment of Mn impurities is stabilized at the ZnMnSe/ZnSe interface through an exchange interaction with band edge electrons.

Finally, we have used spectroscopic ellipsometry to study the effects of the exchange interaction on the Γ- and L-point band gap energies in Zn(Mn,Co,Fe)Se epilayers. These studies are the first examination of sp-d exchange interaction effects on electronic bands away from the zone center. A simple model describing the effects of sp-d exchange between the magnetic impurity and the band edge has been developed in order to explain the strong dependence of band energies on the magnetic impurity type and concentration.

FUTURE DIRECTIONS

The future direction of the Zn(Mn,Fe,Co)Se/ZnSe quantum well research will primarily involve using time-resolved Raman scattering and photoluminescence measurements to explore the spin and charge dynamics of these materials. For example, we plan to examine the different spin relaxation times of the electrons and holes in the spin superlattice, and to study the effects of quantum confinement, concentration, and magnetic species on these relaxation times. Time-resolved studies will also be used to explore the influence of the exchange interaction on the lattice and electron dynamics.

We also intend to extend our ellipsometric studies of epilayers to studies of quantum well structures. At issue are the effects of low dimensionality on the electronic structure and the consequences of confinement on the strength of the exchange interaction between the magnetic impurities and states at the band edge.

C. P. FLYNN

Growth and Properties of Novel MBE Materials

GOALS

In this project we explore the mechanisms of epitaxial growth, using molecular beam epitaxy, in order to synthesize new materials, structured on an atomic length scale, for novel scientific and technical applications. A global understanding of growth mechanisms is sought with the goal of achieving a predictive framework that reveals what stable and metastable structures are accessible by synthesis using molecular beams. Ongoing research largely concerns metallic and ceramic oxide materials, their heteroepitaxy, interface and surface phases, and structures grown with selectable tilt.

HIGHLIGHTS

We have followed up last year's exploration of extraordinarily perfect films of Nb grown by MBE on sapphire by broader investigations of similar phenomena in several metals. In addition to Nb, we have discovered rocking curves at a resolution limited width below 0.007° also for samples of V, Cr, and Au grown on Al_2O_3. These correspond to structural coherence lengths of several microns. This perfection competes with semiconductors and is unmatched for metals. In certain samples where the sapphire substrate exhibits a multipeaked rocking curve caused by mosaic, the identical pattern appears for the epitaxial metal also. This establishes beyond serious question the fact that the high perfection of the metal is acquired directly from the sapphire substrate. In the case of Nb it is possible by means of H additions to enhance to sharp structure at the expense of residual broad structure from defective regions. Indeed by incorporating H during growth the sharp line has been increased to half the total intensity. This is not the case with V, where growth in H apparently results in extensive hydride formation and a spoiled crystal. The case of V is of further special interest. Figure 1a shows how an x-ray rocking curve can be fitted very well by superposed broad and sharp component lines. Figure 1b shows in addition how the fractional area of the sharp component increases to nearly 100% for a film about 400Å thick. At this point the V planes apparently all are precisely aligned with those of the sapphire substrate. We are interested in future opportunities for increasing this thickness, and in the possibility of using these extraordinarily aligned metals as templates for new structures.

Much of our atomic resolution research on metal-ceramic interfaces has come to maturity this last year. This work follows x-ray investigations in which we have found that the bcc metals V, Mo and Ta conform to same 3D relationship with sapphire reported in our earlier Nb work. Thus the orthogonal Nb planes (110), (111) and (211) grow on the orthogonal sapphire planes $(11\bar{2}0)$, (0001) and $(1\bar{1}00)$ with azimuths that make a single 3D orientational relationship between the two lattices. In collaboration with Rühle's group at Stuttgart we have in earlier studies confirmed our x-ray conclusion by means of high resolution electron microscopy studies of the interfacial regions. An important new result of these interface studies is that the Nb and Al_2O_3

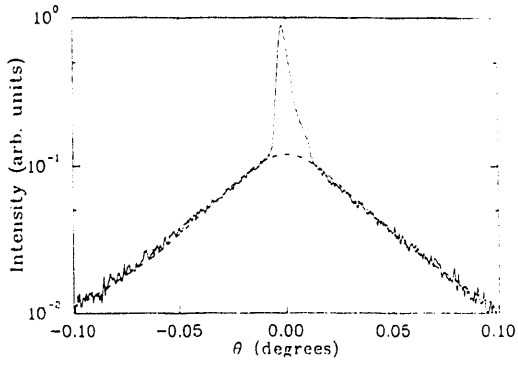


Figure 1a.

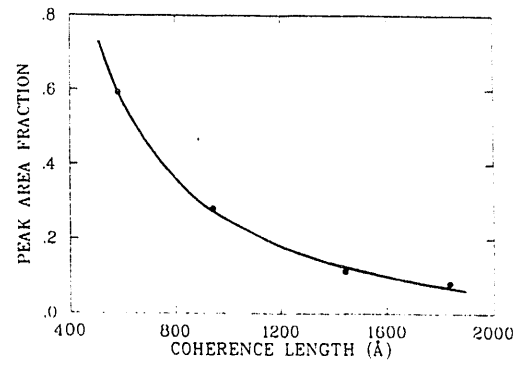


Figure 1b.

lattices also occupy the same translational relationship when grown in different epitaxial orientations, at least for the cases of the prism plane and the R plane. This research is leading to knowledge of the detailed atomic locations at the interface, and hence to a microscopic explanation of the unique 3D relationship in this series of epitaxial systems.

A second important result is that the misfit dislocations near the interface in the Nb in all cases have the Burger's vector $\frac{1}{2}$<111>Nb and that the line direction simply adjusts so that the dislocations lie in the right direction in the interface. The misfit dislocations are thus not always pure edge dislocations, and the Burger's vector in many cases is not parallel to the interface.

The 3D relationship leaves the Nb (001) plane tilted by about 2.8° around Nb <110> from Al_2O_3 $(1\bar{1}02)$, and indeed we find that the (100) planes of the bcc metals do grow with tilts comparable to this prediction. By x-ray studies in the case of V, however, we find generally larger tilts that depend on the growth temperature (see Fig 2) in a way that currently remains unexplained. These tilted materials have subsequently been employed as substrates for studies of the interface between V and MgO.

We find that MgO (001) grows well on V (001) with MgO <100> || V <110>. In addition the MgO grows with a tilt larger than that of the V substrate by a factor of about 1.4. We explain

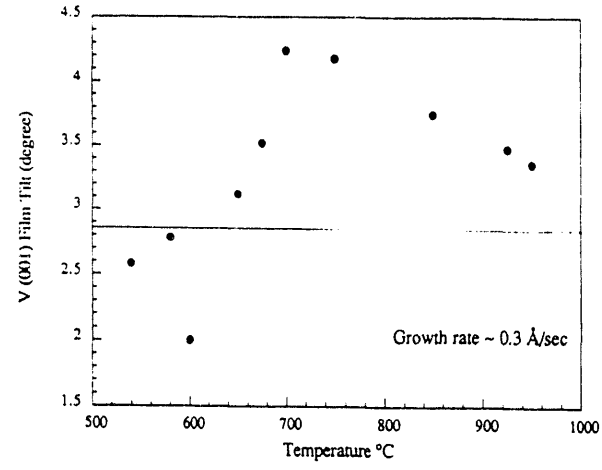


Figure 2

this unique behavior by a "flexible sheet" model of the interface in which the increased MgO tilt exceeds the V tilt by the ratio of the MgO plane thickness to that of V, which is about $\sqrt{2}$ for this 45° interfacial structure. The way the tilt and its inhomogeneity emerge for long and short interfacial terraces is clarified in Fig 3. In keeping with our flexible sheet model we find that V grows back on the tilted MgO with precisely its former tilt, so that the growth is transitive. As a result, superlattices of alternating MgO and V may be grown with indefinitely many periods without progressive deterioration. The interfacial behavior is currently being studied at atomic resolution in collaboration with Pirouz and coworkers at Case Western.

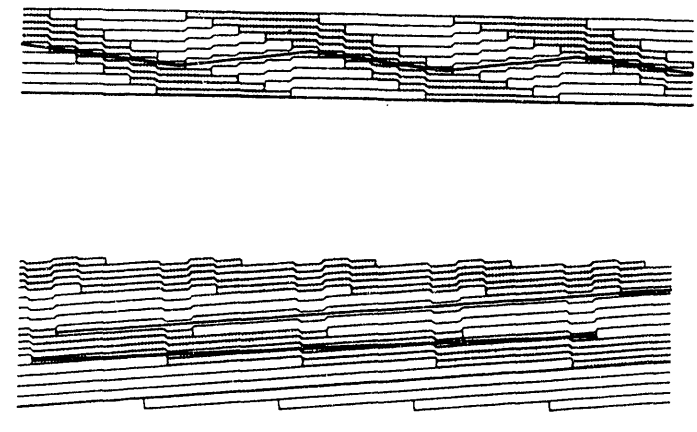


Figure 3. Flexible sheet models of superlattices synthesized by step-flow growth when one species gives thicker layers than the other, shown here with a ratio 2:3. In the upper figure the growth increments are much less than the terrace width and in the lower figure, as in our experiments, the terraces are much narrower than the growth.

Program on Point Defects in Semiconductors

GOALS

The goal of this research was to see if ultrasonic measurements could be used to determine the configuration and dynamics, or the symmetry and lattice distortion magnitudes, of EL2 centers in GaAs. No relaxation or diaelastic effects were found between 1.6 and 300K, and the project was redirected to develop a defect model for liquid and amorphous materials.

HIGHLIGHTS

The fact that no diaelastic effect was found in a specimen provided by the Berkeley Weber group of GaAs containing 0.4 ppm of EL2 centers after illuminating with white light at 20K and annealing to 150K is more surprising than the fact that no relaxation peaks were obtained. Most point defects have diaelastic susceptibilities $a_{ij} = d \ln C_{ij}/dc \sim 30 \pm 10$. A susceptibility change ~3 could have been detected in these measurements on transforming the defect either by photoionization at 20K or annealing at 150K, even if the relaxation only occurred above room temperature. This implies that the metastable excited state of EL2 differs from the ground state mainly by small electronic-induced distortions rather than by finite thermally-induced atomic displacements. Larger defect concentrations would be required to detect this effect and measure the symmetry of the susceptibility.

A model for the amorphous and liquid states of simple matter has been developed according to which these materials are crystals containing a few percent of interstitials. An analytic expression for the Gibbs free energy as a function of temperature, pressure, shear stress, and concentration is derived, from which all thermodynamic properties of the material in each of the crystalline, liquid or amorphous states, as well as their changes on melting, are obtained. The tunneling entity providing the two-level system behavior found for low temperature properties is identified as the interstitalcy configuration. The model gives a sound physical basis for the Lindemann law of melting, and provides many testable propositions.

Some of the most commonplace and universal properties of condensed matter, such as melting and the structure and thermodynamic properties of amorphous materials, have been mysteries for many years. The empirical Lindemann relation, often described as the most characteristic law describing melting, has hitherto had no basic physical foundation. Amorphous materials have been the object of intense and extensive study over the past thirty years, but there has been no simple model for the tunneling entity needed to account for many of the basic properties of these materials. Amorphous materials have been widely studied both because of the scientific interest in their structure, and because of the many important applications for such materials. The interstitalcy model provides a unified view of the structure and thermodynamic properties of the crystalline, amorphous and liquid states of simple condensed matter.

FUTURE DIRECTIONS

Support for this project was terminated in 1992.

SIGNIFICANT ACCOMPLISHMENTS

A Defect Model of Liquids and Amorphous Materials

Scientific Achievement:

The thermodynamic properties of FCC cubic metals predicted by the interstitialcy model are found to apply to a much wider class of materials than to FCC metals. The microscopic model of interstitialcies in FCC metals leads to a phenomenology from which the thermodynamic properties are obtained. However, the phenomenological aspects of the model don't depend on the microscopic model, but only on three essential features: 1) The shear modulus softens with defect concentration, 2) low frequency resonance modes exist, and 3) there is orientational degeneracy to the defect configuration. These qualities are known experimentally to be universal properties of amorphous materials. The second and third properties have been

noted before by Buchenau, Malinovsky, and Pohl.

Significance:

The fact that the phenomenological aspects of the model leads to experimentally known universal properties of amorphous materials, taken together with the fact that the model provides the first derivation of Lindemann's law from basic principle, means that the model applies to a wide class of materials. This has been illustrated by discussing the specific heat of a wide range of materials for all temperature including particularly the liquid state for the first time, as well as the relationship of its behavior near the glass temperature to that found at low temperatures. The model thereby provides a framework which not only unifies the properties of a given material between different condensed matter states, but also between different classes of materials.

Performer: A.V. Granato, University of Illinois at Urbana-Champaign.

RICHARD M. MARTIN

Theory of Solids, Surfaces and Heterostructures

GOALS

The goals of Professor Martin's research program are to develop theoretical methods to describe the electronic structure of solids and apply them to the calculation of properties of materials, including structures and electronic properties of crystals, surfaces and interfaces.

HIGHLIGHTS

1. We are developing new Quantum Monte Carlo (QMC) methods to study the many-body electron problem in solids and have applied these methods to the two-dimensional electron gas. This is the basic model for electrons in semiconductor quantum wells and is closely related to the electronic problem in the planar CuO superconductors. The new features we have included are "backflow" correlations between electrons, which we have shown to give important contributions to the correlation energy. Although backflow is a well-establish concept described by Feynman and others (the motion of one electron causes a reverse flow field of the other electrons), there have never been quantitative calculations which can be done by Monte Carlo methods. A paper will be submitted soon describing our new results for the ground state energy of the 2-d electron gas as a function of density. In addition, we are studying the excited states to make predictions for Fermi liquid parameters; we have preliminary results on the effective mass which has been a source of great controversy with different theoretical methods giving qualitatively different results in the past.
[Y. Kwon, J. Yu, and in collaboration with Prof. D. M. Ceperley]

2. We have completed work on our new approach in the theory of pseudopotentials which includes many-body correlation effects of the core electrons. Such accuracy is important for current theoretical work because calculations for valence electrons by many-body methods have reached such sophistication that their accuracy is now limited by the ways in which the core electrons are treated. We have completed two papers (submitted for publication) describing the theoretical

calculations on atoms and presenting tabulated "quasiparticle pseudopotentials" which can be used by others. An application of these potentials has now been carried out by E. L. Shirley, partly done under this contract, which shows that the bands of important semiconductors, such as GaAs, are affected by several tenths of eV's, which is extremely important for understanding the bands at the level needed for electronic devices.
[E. L. Shirley]

FUTURE DIRECTIONS

The directions Professor Martin plans to pursue in the near future are studies of the structures and electronic properties of two-dimensional layered systems and surfaces. We plan to study both the fundamental model of the homogeneous system relevant for 2-d electron systems that can be produced in semiconductors and models with two-dimensional periodic structure, relevant for the systems such as the square planar CuO layered materials. We also plan to study other materials with exciting new structures, such as the solids formed from carbon C_{60} Buckyballs. In the studies of Buckyballs, we will use simplified models of the electronic bands and interball interactions to attempt to understand their novel properties which are just unfolding, e.g., the relation of the orientation order-disorder to the metallic nature and superconductivity in the doped systems. Our long term goal is to be able to calculate quantitatively the nature of defects and artificial structures in semiconductors and novel materials, such as the transition metal oxides and new structures of carbon.

SIGNIFICANT ACCOMPLISHMENT

Theory of Solids, Surfaces and Heterostructures

Scientific Achievement:

We have completed our work to develop a systematic method which will allow electronic calculations on solids to take into account correlations of the valence and core electrons. In our approach, full many-body core-valence calculations done on atoms can be used to define effective potentials that can be employed in molecular and solid state calculations. We term the "quasiparticle pseudopotentials." We have calculated such potentials for many atoms and have shown that there are improvements over previous single particle (local density or Hartree-Fock) potentials. The most important improvements are for 3d transition metals and the s and p states in post-transition elements such as Ga and Ge. These results of large calculations are included in the thesis of E. L. Shirley and two papers which are submitted give tables of our new "quasiparticle potentials" which can be used by others in calculations on molecules and solids. In work done partly at UIUC and partly at UC Berkeley with Prof. S. G. Louie, Shirley has now carried out new calculations of the bands in GaAs, which differs from previous calculations by several tenths of an eV. This is the best calculation ever done for a such a semiconductor, and predicts important changes in the gaps and shapes of the conduction bands from previous theoretical work.

Significance:

Because of recent developments in many-body methods (Quantum Monte Carlo and diagrammatic expansion "GW" methods) it is now possible to accurately determine properties of valence electrons including all many-body effects. The key limitation for the accuracy of such calculations is the role of core electrons. However, all work up to now has used only single particle (local density or Hartree Fock) methods to treat core electrons. We have shown this leads to serious errors in some very important cases, in particular 3d states crucial to transition metals and important semiconductors such as GaAs. Nearly exact calculations on many atoms and the Na_2 molecule have shown the results are significant improvements over all previous pseudopotentials and all other ways of treating core electrons. Recent work of Shirley (done partly at UIUC) has shown that the effects in GaAs and Ge are on the level which is crucial for device-level predictions.

Our new potentials can be used in place of previous potentials and can be used as either norm-conserving pseudopotentials or as effective potentials added in all-electron calculations. They can be included directly in many-body approaches such as quantum Monte Carlo and Green's function quasiparticle methods.

Performers: R. M. Martin, University of Illinois at Urbana-Champaign.

HADIS MORKOÇ

Synthesis of High Quality Semiconductor/Insulator Structures

GOALS

This research program is predicated on the use of state of the art deposition equipment to produce and analyze semiconductor/insulator stacks, which have important commercial significance, without ever exposing any of the interfaces to air. Semiconductor/Insulator structures based on both compound and elemental semiconductors are under investigation. Among the semiconductors investigated are Si, Ge, GaAs, InP and binaries and ternaries based on these materials. Among the insulators are SiO_2, Si_3N_4, and Ge_3N_4. The versatility of our approach allows ultimate control and the inclusion of the interface heterojunction most conducive for the lowest defect density and maximum stability. Potential applications include solar cells and passivation for long term stability and longevity of a variety of artificial structures. Collaborations with the National Renewable Energy Laboratory and with Prof. Murray Gibson of MRL provide for a comprehensive analysis of these unique stacks.

HIGHLIGHTS

As evidenced by ubiquitous nature of the insulator SiO_2, the SiO_2/Si insulator/semiconductor interface has proven extremely fruitful. Outside of this particular combination however, insulator/semiconductor structures so far have not been nearly as successful. The absence of such structures has dwarfed the applications of novel insulator/semiconductor stacks based on semiconductors with greater performance potential. While the present interest in the Si/SiO_2 system is to explore synthesis schemes producing oxides with hot electron buoyancy, the focus in other semiconductor systems , which can be characterized as nascent, is on the achievement of low interface defect density and stability. For example, despite years of effort, though data scatter, the compound semiconductor dielectric interfaces have been notoriously defect ridden. With our unique deposition scheme and novel semiconductor stacks which facilitate the transition between the semiconductor and the insulator, we have already demonstrated interfaces with interface defects that would have been unbelievable a few years ago.

Electrical, time-resolved optical, and structural analyses are employed to support our efforts to optimize the deposition conditions. Electrical analysis, both charge analysis and current conduction, will be used to gauge the quality of interfaces and the findings will be correlated with time resolved optical measurements and transmission electron microscopy images. Our long term goal is to attain very stable interfaces with defects in the low 10^{10} cm^{-2} eV^{-1} range in systems based on semiconductors InP, GaAs, and Si . Stability of these interfaces on compound semiconductors present formidable obstacles. We are, however, very optimistic as the results obtained so far are already indicative of interfaces with low interface defects and promising stability. The structures produced - though the project is in its infancy - have shown extremely small drift over a 10 hour period.

FUTURE DIRECTIONS

Having established, to a first order, the MBE growth conditions, particularly the surface with which the semiconductor growth is terminated, interface heterostructure, insulator deposition conditions, and the growth environment, we will turn attention to systematic investigation of these structure in an effort to understand the underlying science. Along with the science, we are eager to begin exploring the nature of the interfaces with electrical, optical and other microprobes. The samples required for microprobe analysis, and for time resolved luminescence measurements for determining the minority carrier lifetime will be diligently and systematically prepared. In parallel, particularly as our understanding of the issues advances, we will undertake detailed interface characterization by electrical means. Recently developed characterization schemes, see article by Mui et al on the new equivalent circuit model, for investigating electrical properties of high quality interfaces which employ deposited insulators will be utilized. We are equipped to fabricate the required structures for these measurements. The semiconductors Ge, SiGe, GaAs, and InGaAs and the dielectrics SiO_2, Si_3N_4, and Ge_3N_4 , with the appropriate combination of each of the semiconductors mentioned, will be prepared and investigated. To reiterate, the combination of MBE and a

UHVCVD fitted with a 1 kW Electron Cyclotron Resonance source will be employed for the deposition. The equipment is already located in the EpiCenter and has been functional for several years in its entirety.

SIGNIFICANT ACCOMPLISHMENT

Synthesis of High Quality Semiconductor/ Insulator Structures

Scientific Achievement:

The emphasis in this program has been the synthesis of dielectric-semiconductor heterostructures encompassing elemental as well as compound semiconductors of commercial importance. In the elemental semiconductor arena, we have achieved high quality SiO_2/Si Metal Oxide Semiconductor (MOS) structures at low temperature (~ 300°C) using a plasma assisted CVD process. Silane and oxygen are the source gases. Nearly ideal Capacitance-Voltage curves have been obtained for MOS capacitors with oxide thickness of 150 - 500Å. The interface trap density for these devices is the in the low 10^{10} eV^{-1} cm^{-2} range and the details were covered in the past report. In this reporting period, however, we have concentrated our efforts in the elemental semiconductor area on Ge.

We have made significant advances toward improving the dielectric compound semiconductor composite stack. The emphasis again was placed on the investigation of synthesis conditions leading to minimum interface and bulk defects. The semiconductors selected for this particular investigation were GaAs and InGaAs. While we have at our disposal the capabilities of depositing, in situ, Si_3N_4 or SiO_2, we have chosen Si_3N_4 /Si on GaAs and Si_3N_4 /Si on InGaAs. The minimum interface density was reduced from last year's $1x10^{11}$ eV^{-1} cm^{-2} to an incredible value of $3x10^{10}$ eV^{-1} cm^{-2}. This result which represents a major breakthrough, has far reaching implications for solar cells and many other applications where surface passivation and the alleviation of instabilities with time are essential.

Time resolved photoluminescence has been employed to study the surface recombination velocity of GaAs in cooperation with Drs. Rick Ahrenkiel and D. Levi of the National Renewable Energy Laboratory in Golden, CO. Preliminary results show that with a Si_3N_4 /Si stack as a passivation layer, GaAs surface recombination velocity decreases to about one third of that of the free surface. Due to differences in the types of samples required for capacitance measurements and time resolved luminescence decay measurements, the conditions leading to minimum interface defects have not been investigated with the time resolved probes yet. This is one of the priorities to be explored in the new period.

Significant reduction of interface state density was achieved with the assistance of hydrogen during growth of pseudomorphic Si on GaAs. Si_3N_4/Si/GaAs capacitors investigated have shown an overall reduction of the interface state density to as low as $3x10^{10}$ eV^{-1} cm^{-2}, which rival the characteristics of the SiO_2/Si system. The reduction of interface state density is most evidenced by much improved CV characteristics. The frequency dispersion and the hysteresis are very small, which implies that the amount of fast interface state and slow interface states is significantly reduced.

In collaborations with Prof. Gibson, plan view TEM and high-resolution electron microscopy have been carried out on these Si_3N_4/Si/GaAs capacitors to study the mechanism responsible for the reduced interface state density and reduced surface recombination velocity. It was found that the insertion of a Si interlayer greatly decreases the roughness at Si_3N_4 and GaAs interface and therefore significantly reduces the interface state density.

Si_3N_4/Si/$In_{0.53}Ga_{0.47}As$ interfaces are also being studied for possible applications in Solar Cells. From conductance measurements, the fast interface trap density of annealed samples is of the order of 2.4×10^{11} cm^{-2} eV^{-1}. Such a low value of interface trap density results in small frequency dispersion. The amount of slow traps is also small, evidenced by a small hysteresis.

Due to the deleterious nature of oxygen in the presence the germanium, Si_3N_4 has been used for the insulating material of MIS devices which contain germanium. Prior to investigating Si_3N_4/Ge MIS structures, the quality of the Si_3N_4 was determined by investigating Si_3N_4/Si MIS diodes.

After establishing the overall robustness of the Si_3N_4 films, these films were used as the insulating material in Si_3N_4/Ge MIS structures. A thin pseudomorphic silicon interlayer was deposited by a CVD process on the Ge surface in an effort to improve the electrical quality of the Si_3N_4/Ge interface. It is important to note that the Si interlayer and the Si_3N_4 are deposited in the same Ultra-High Vacuum CVD chamber and so the Si_3N_4/Si interface is virtually free of contamination. Capacitance-Voltage and Conductance-frequency (G - w) measurements indicate that the minimum interface trap density in these device is below 10^{11} eV^{-1} cm^{-2}. Our results using these devices compare favorably with the best results reported in the literature. We also observed that the hysteresis can be reduced dramatically by utilizing a Si interlayer. This fact suggests that the quality of nitride near the interface is maintained when deposition takes place on the thin Si interlayer, in contrast to the situation when Si is absent.

Using *in situ* techniques, we have also investigated the properties of Si_3N_4/Si_xGe_{1-x} MIS structures. By depositing the Si_3N_4 on a pristine, MBE-grown Si_xGe_{1-x} surface we can minimize the presence of oxygen at the interface. The is desirable since the oxides of germanium are know to be of extremely poor quality both electrically and in terms of stability. Our results suggest that the interface trap density is insensitive to the presence of a Si interlayer up to 100Å in thickness. This result differs from the case when SiO_2 is used in a similar manner.

Recently, we have established that fairly high quality Ge_3N_4 thin films can be grown in our laboratory. Historically, Ge_3N_4 has suffered from poor bulk properties. However, Ge_3N_4 is of interest since it can, at least in theory, serve as the insulator material for both Ge and GaAs MIS devices. This fact, coupled with our encouraging results obtained using our growth apparatus to deposit Si_3N_4 (with which Ge_3N_4 can be combined to form a composite insulator), suggests that Ge_3N_4 is worthy of further investigation. Only a few layers have been grown and this project is in its infancy.

Performer: Hadis Morkoç, University of Illinois at Urbana-Champaign.

THOMAS B. RAUCHFUSS

Synthesis of Organometallic Polymers

GOALS

This program examines the synthesis of new polymeric materials. Of particular interest are the synthesis of novel monomers and the invention of new methods for polymerization. Targeted materials are those with novel electronic/photonic/magnetic properties.

HIGHLIGHTS

Polymers represent one of the richest sources of new materials for device applications (electrical conductors and photonics) and as energy storage components such as batteries. The covalent attachment of metals to organic polymers gives rise to a family of materials which display a particularly wide range of exciting properties. For these reasons our research focuses on organometallic polymers. The past year has been dedicated to understanding the new polymers poly(ferrocenylenepersulfides). The following key results have been obtained:

1. We have shown that solvents dramatically affect the polymerization of ferrocene trisulfides with regards to the polymerization rate and the polydispersity of the products. Polar solvents such as DMF are optimal. It was discovered that poly(*n*-butylferroceneylenepersulfide) prepared in this new way is insoluble but swellable. The new methods are allowing us to systematically examine the polymerization of many precursors (e.g. selenides instead of sulfides).

2. The influence of stereochemistry on the polymers has been partially tested. We have prepared both the mono- and di(t-butyl)ferrocenetrisulfides. These have been obtained via regiospecific syntheses and both have been subjected to polymerization. Interestingly the di-substituted derivative polymerizes only poorly.

3. We have prepared two crosslinking agents wherein the ferrocene monomer contains two trisulfide groups. Spectroscopic characterization showed that these hexasulfides exist in conformers, and this isomerization was examined. The hexasulfides homopolymerize to

give highly crosslinked (Fe:S ratio is 1:4) solids. Preliminary results show that *partially* crosslinked materials have different physical properties.

4. Chiral, dimethylaminosubstituted monomers were prepared. They have the formula $(C_5H_3CHRNMe_2)(C_5H_4)FeS_3$ (R = Me, H).

5. Progress is being made in the preparation of cluster monomers. The water soluble cluster $(C_5H_4CO_2H)(C_5H_5)Fe_4(CO)_4$ has been synthesized.

FUTURE DIRECTIONS

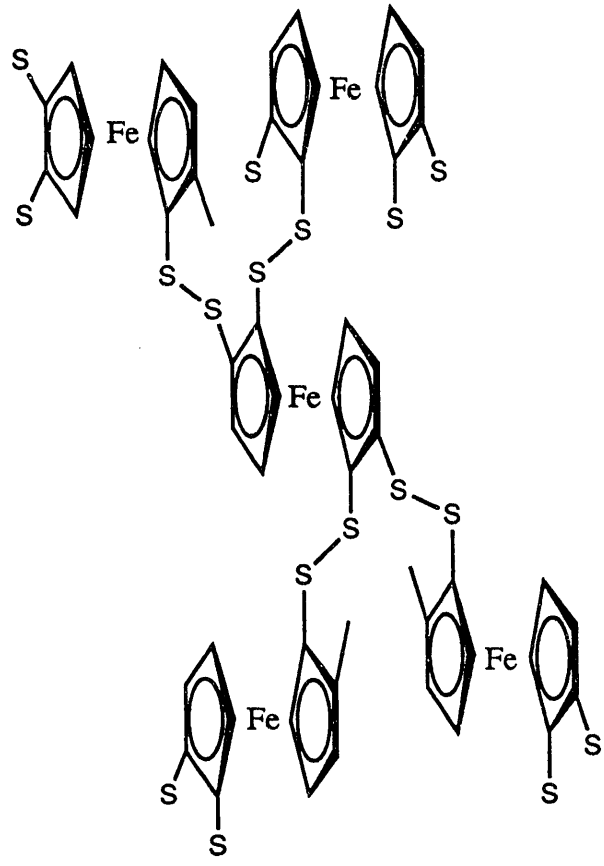
Light scattering measurements are just underway in C. Zukoski's lab on the new organometallic polymers. This will allow us to publish a detailed account on ferrocenylene persulfide polymers. Using the crosslinking agents prepared this past year, we are optimizing the synthesis of crosslinked persulfide copolymers. We also expect to capitalize on our recent studies on solvent effects to examine the polymerization of selenium and chiral dimethylamino monomers. Plans have been made for the synthesis of polymers based on dibenzene chromium. The properties of $(C_5H_4CO_2H)(C_5H_5)Fe_4(CO)_4$ will be more fully examined and the corresponding thiol will be prepared and incorporated into polymers.

SIGNIFICANT ACCOMPLISHMENT

"Organic pyrite," a novel 3-D organometallic iron sulfide network polymer has been prepared.

Scientific Achievement:

The doubly functionalized monomer $Fe(C_{10}H_6)S_6$ features two polymerizable S_3 centers attached to iron via cyclopentadienyl linkages. This species is of interest as a precursor to a three-dimensional network of iron atoms interconnected by S_2 units comparable in some ways to the structural pattern in the inorganic semiconductor iron pyrite (FeS_2). Using phosphorus reagents, the monomer $Fe(C_{10}H_6)S_6$ was converted into the polymer $\{Fe(C_{10}H_6)S_4\}_n$ (see figure).



Structure of $\{Fe(C_{10}H_6)S_4\}_n$

The corresponding butyl derivative $\{Fe(BuC_{10}H_5)S_4\}_n$ has been also been prepared. This highly crosslinked polymer readily forms gels. Its solubility allows further characterization by NMR, gel permeation chromatography, optical spectroscopy, and soon, light scattering.

Significance:

Network polymers of well defined local architecture are difficult to prepare in a soluble, processible form. Especially challenging are those containing metals. Such species are of interest for applications in photolithography, charge storage, and electrical conductors. The organometallic network polymer described in this report represent a new type of 3-D solid that utilizes methods that are being extended to other metals and other linking groups.

Performer: T. B. Rauchfuss, University of Illinois at Urbana-Champaign.

Properties of Crystalline and Liquid Condensed Gases

GOALS

The goals of Professor Simmons' research program are a) to discover and explore unusual phenomena in quantum crystals and other novel solids prepared from condensed gases, and b) to measure key properties of prototype materials, over a very wide range of conditions, to directly confront sophisticated calculations of these properties. Properties of interest include single-particle translational and rotational dynamics, characteristics of point defects, impurity-matrix physical interactions, atomic and molecular mobility and disorder, and the equilibria and dynamics of structural phase transformations.

HIGHLIGHTS

Analyses of two comprehensive series of deep-inelastic neutron scattering (DINS) studies were completed. Direct measurements of the translational momentum distributions produced precise values a) of the single-particle kinetic energy, $\langle E_k \rangle$, of pure Ar and b) of para-H_2 as dilute substitutional guest in an Ar host. In both cases, the temperature dependence, $\langle E_k(T) \rangle$, was determined and values for the ground state, $\langle E_k(0) \rangle$, were obtained. The pure Ar work showed, for the first time, that DINS can produce $\langle E_k(T) \rangle$ values even for massive atoms, for which practical problems of limited spectrometer resolution had heretofore prevented accurate results. Ar is a test case, for which considerable evidence from coherent inelastic neutron scattering is available and for which many theoretical models have been constructed. The DINS results agree with other precise experiments, and in addition provide unique evidence about low-temperature lattice anharmonicity in crystal Ar. For substitutional para-H_2, the DINS results are surprising. They show that the para-H_2 $\langle E_k(T) \rangle$ follows that of the host very closely at <u>all</u> T, not just toward the high-temperature limit where classical equipartition of energy rules. Contrary to previous expectation from variational calculations, which account for IR and Raman internal spectral features of the guest para-H_2, the "local mode" frequency is far lower than expected.

Synchrotron x-ray studies of crystalline helium were continued, both at Brookhaven NSLS Beamline X-14A and at HASYLAB, Hamburg (this in collaboration with the group of Dr. E. Burkel of Munich). At NSLS we studied x-ray Debye-Waller effects for the first time in fcc ^{4}He. At HASYLAB we obtained <u>inelastic</u> x-ray scattering for the first time from any condensed helium, in this case both hcp and fluid ^{4}He. These studies used our special Be sample cell, good to pressures up to 0.4 GPa, which we have thereby proved to have low background for <u>both</u> inelastic and elastic x-ray studies on very weakly-scattering systems.

FUTURE DIRECTIONS

Synchrotron x-rays will be used to study atomic vibrations, point defects, structures and phase separation in ^{4}He and ^{3}He crystals and mixtures. We will continue x-ray <u>inelastic</u> scattering studies in collaboration with the University of Munich at HASYLAB, Hamburg, Germany (on a wiggler line), and at ESRF, Grenoble, France (on an undulator line). We also will continue our development, for use at the Argonne APS, of techniques for crystalline condensed gases, especially since aspects of work in this project have come up against severe limitations of eV neutron inelastic scattering, including formidable neutron absorption by ^{3}He. A DINS collaboration at ISIS Rutherford-Appleton Lab, England, will continue.

Our unique helium dilution-refrigerator laboratory facilities for simultaneous pressure and x-ray study of defect excitations in crystalline ^{3}He and ^{4}He will be applied to exploration of possible exotic collective phenomena at low crystal densities.

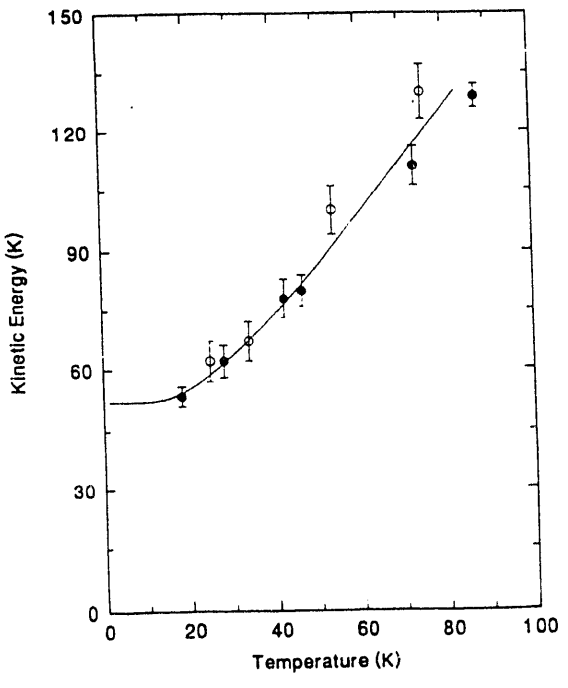
SIGNIFICANT ACCOMPLISHMENT

Kinetic Energies Versus Temperature in Prototype Host-Guest System

<u>Scientific Achievement:</u>

Kinetic energies in a prototype crystal host with a substitutional guest have been directly measured for the first time, over the complete range of temperature from quantum ground-state up to classical conditions. The host was fcc argon, for which many theories of its dynamical behavior have been constructed, and the dilute guest was para-hydrogen, for which both

theories and extensive spectroscopic data are available. For ground-state (low-temperature) conditions, a) for the host argon the results yield a direct measure of crystal lattice anharmonicity where previously only indirect inferences from experiment were available, and b) for the light guest para-hydrogen (5% of the host mass) the result is surprisingly small. The figure shows the results; filled circles are the argon, open circles the para-hydrogen. The line is a theory for the host kinetic energy. At high temperature the kinetic energies are equal, as expected (but never before shown) from classical equipartition of energy. But at low temperatures, they are also equal, whereas usual expectation has been that such a light impurity will have a very high-frequency local mode of oscillation. The frequency is indeed higher than that of the host, but quantitatively much less than sophisticated variational theory predicts, a theory which otherwise successfully predicts many details of the internal molecular energetics. Re-examination of usual expectations is indicated.



Significance:

Materials are needed for uses over extreme ranges of pressure and temperature. The single-particle dynamics of materials is often important for properties such as atomic diffusion and disorder, the kinetics of phase transformations, and thermal properties. Further, research on the energetics of molecules and radicals has often employed an inert host, such as solid argon, for stabilization of a dense system for spectroscopic study. Such conditions may be simulated by computer, but to be significant the simulations depend upon accurate interatomic potentials and realistic models. Otherwise, microscopic phenomena present in the simulations and macroscopic behavior of the models may not correspond to actual performance of the materials. To test such concepts, direct confrontation between simulations and experiment is required on prototype systems over the widest possible ranges of physical conditions. For single-particle dynamics, the most direct test is measurement of the momentum distributions through deep inelastic scattering of neutrons from a pulsed spallation source, a method first broadly applied by this Illinois group.

Performers: R.C. Blasdell, M.A. Fradkin, K.W. Herwig, R. O. Simmons and S.-X. Zeng, University of Illinois at Urbana-Champaign

C. P. SLICHTER

Nuclear Magnetic Resonance in Solids

GOALS

Professor Slichter conducts fundamental studies of solids and surfaces, principally by magnetic resonance. The current effort is divided equally between supported catalysts of Group VIII metals (Ru, Rh, Pd, Os, Ir, Pt) and high temperature superconductors. Specific topics are: (1) Surfaces: Chemical reactions related to C-C bond scission of simple hydrocarbons, diffusion rates of molecules on surfaces, nature of alkali metal promoters; (2) High T_c Superconductors: normal and superconducting state NMR properties and comparison with those of conventional (Bardeen, Cooper, Schrieffer) superconductors, to help explain why the transition temperatures are so high.

HIGHLIGHTS

(1) Surfaces

(a) Reactions of acetylene adsorbed at low temperatures. We have used ^{13}C-^{1}H spin echo double resonance to follow the chemical species formed by adsorption of ^{13}C enriched acetylene at 195K, followed by annealing to progressively higher temperatures up to 400 K. Initially, a mixture of HCCH and CCH_2 is formed. As the annealing takes place, we observe formation of CCH and CCH_3.

(b) We have initiated reaction studies following changes in molecular structure versus time at fixed temperature to augment results of annealing studies.

(2) Superconductivity

(a) We have carried out the first studies of proton NMR in single crystals of superconductor $(ET)_2$ Cu $(NCS)_2Br$. We find that in the superconducting state there is a strong enhancement of the relaxation rate at about $T_c/2$ (Tc=normal to superconducting transition temperature). We have shown that the peak arises from motion of fluxoids by studying how the relaxation rate depends on orientation of the magnetic field relative to the crystal axes.

(b) We have shown that in the superconducting state the ^{17}O nuclear spin-lattice relaxation rate of planar O in $YBa_2Cu_3O_7$ depends on the strength of the applied static magnetic field. We have thus obtained for the first time the zero field limit of the ^{17}O relaxation rate in $YBa_2Cu_3O_7$. This is the quantity needed for comparison with theory.

(c) At low temperatures, in the superconducting state, both the ^{17}O and ^{63}Cu nuclear relaxation rates go as T^3 with temperature T, suggesting that the orbital pairing is d-state.

(d) By variation of the orientation of the static field relative to the crystal axes, we have shown that the dependence of relaxation rate on magnetic field strength arises from fluxoid motion.

(e) We have measured the Gaussian component of the transverse relaxation rate of ^{63}Cu in the planes of $YBa_2Cu_3O_7$, and used it to draw conclusions about the real part of the static electron spin susceptibility c'(**q**, o) at wave vector **q**.

(f) We have studied the ^{63}Cu nuclear quadrupole relaxation rate of $La_{2-x}Sr_xCuO_4$ up to 900K for various values of x from 0 to 0.15.

FUTURE DIRECTIONS

Continuation of studies of both metal surfaces (catalysts) and high T_c materials. Surfaces The studies are largely focused on studying reaction rates (C-C scission, diffusion, promoters), and modeling them through reaction equations. High T_c Superconductors Continuation of efforts to understand the normal and superconducting properties of $YBa_2Cu_3O_7$. Studies of organic superconductors will continue.

SIGNIFICANT ACCOMPLISHMENT

Determination of spin and orbital pairing of the superconducting state of $YBa_2Cu_3O_7$

Scientific Achievement:

The Slichter group has employed ^{63}Cu, ^{17}O, and ^{89}Y nuclear magnetic resonance (NMR) of the 93K superconductor $YBa_2Cu_3O_7$ to obtain detailed information about the electrical and magnetic properties of various atomic constituents of the material. By this means his group has found results in the superconducting state which according to two theoretical groups appear to determine both the spin and orbital pairing of the ground state.

Previously, measurements of the Knight shifts of the Cu atoms in both chains and planes by the Slichter group had shown that the superconductor had spin singlet pairing but could not decide on the orbital pairing. Recently, their experiments on spin lattice relaxations may have determined the orbital pairing as well.

The relaxation rate of the Cu nuclei of the CuO_2 planes depends on the orientation of the magnetic field with respect to the crystal axes. In the normal state, the anisotropy in this rate is independent of temperature, but the Slichter group finds that in the superconducting state, the anisotropy varies with temperature. This result was quite unexpected. Recently, two theoretical groups (Lu and Pines at Illinois, Bulut and Scalapino at Santa Barbara) have shown that the data can be explained if one assumes the superconducting state has so-called d-state pairing.

In the course of these studies, the Slichter group found that the relaxation time in the superconducting state of the ^{63}Cu nuclei in the CuO_2 planes depended on the strength of the applied magnetic field. These experiments suggested that the same might be true for the ^{17}O nuclei. They have now shown that this is true, and have determined the temperature dependence of the rate in the limit of weak applied fields, the quantity needed for comparison with theory.

Both the ^{63}Cu and ^{17}O relaxation rates at low temperatures go with temperature T as T^3. This dependence is that expected for orbital d-state pairing. Thus, the evidence now is strong that for $YBa_2Cu_3O_7$, the superconducting pairing is an orbital d-state and a spin singlet.

Significance:

The pairing state of a superconductor depends on the mechanism of superconductivity. Mechanisms depending on coupling of electrons to lattice vibrations, the classic BCS mechanism, lead to spin singlet but orbital s-waves. Some spin dependent mechanisms lead to spin-singlet but orbital d-states. The results of the Slichter group appear to be explainable within a generalized BCS approach, but suggest that the orbital pairing is d-state, hence that the mechanism of superconductivity is not the electron-lattice coupling of BCS.

Performer: C.P. Slichter, University of Illinois at Urbana-Champaign.

SAMUEL I. STUPP

Field Responsive Polymers and Organometallic Materials

GOALS

This program studies the synthesis and properties of organic and organometallic solids which order in response to electric or magnetic fields and develop useful physical properties as a consequence of this interaction. A phenomenon of great interest in the program is the formation of noncentrosymmetric organic structures in electric fields leading to second order nonlinear optical properties. One of our objectives is to gain a basic understanding of how molecular architecture impacts on the stability of configurations with large nonlinearities.

HIGHLIGHTS

This past year our research centered around the new photonic material discovered earlier in our program which generates a second harmonic beam from an infrared laser of intensity greater than that of $LiNbO_3$ and poled polymers. We reported before that this compound self organizes from the liquid crystalline state into macroscopic photoactive crystalline domains without requiring the energy of an external poling electric field. We discovered this year that the compound is obtained from the chemical reactor in a polycrystalline form that converts spontaneously to photoactive crystals of different unit cell through a solid-solid phase transition. Macroscopic particles containing hundreds of crystals transform at 115°C to a few co-aligned board-shaped crystals that generate a strong signal of green light. Electron diffraction analysis of the active phase characterized it as a monoclinic crystal in which molecules are oriented nearly parallel to the surface normal of the board-shaped crystals. Second harmonic signals were found to vary as the flat crystals were rotated about an axis perpendicular to the laser beam. This suggests that conjugated aromatic groups parallel to the principal molecular axis are linked to the observed second harmonic activity. The strong dipole moment associated with the nitrile group of this molecule is perpendicular to the molecular axis and an analogous molecule without the nitrile substituent was synthesized this year in our laboratory. Measurements on the new compound indicate that the strong dipole might be involved in the self organizing nature of the crystals but not in their nonlinear optical activity. This conclusion is in fact based on synthesis and nonlinear optical measurements of several model compounds and also on studies of the photonic material that combine computer molecular modeling with electron diffraction data. We also carried out this year measurements of thermally stimulated discharge which revealed that a significant electric current is generated as the photoactive crystals melt into a liquid crystalline fluid. The measurements indicate that the self organized crystals store electrical polarization amounting to 3 micro-coulombs per cm^2. This polarization may result in piezo- or pyroelectric behavior in these photoactive crystals. We have preliminary evidence that this material and other related compounds can also generate third order nonlinear optical signals. At the moment we are trying to understand the chemical response of these materials to the high energy radiation sources used as incident beams for third harmonic generation.

FUTURE DIRECTIONS

Efforts are underway to analyze the wavelength dependence of nonlinear optical activity in the chiral oligomer discovered recently. We are particularly interested in the ability of this compound to double the frequency of laser beams in the visible range of the spectrum. This could be particularly important in various technological applications in information systems that rely on light as opposed to electric current and also for technologies in which semiconductors with band gaps in the visible regions are to be coupled to radiation sources. An effort will be initiated this year in a different direction involving the synthesis of precursors for molecular objects such as tube-shaped or rod-shaped polymers containing conjugated structures. The conjugated nature of these structures may lead to molecular objects having semiconducting or third order nonlinear optical properties.

SIGNIFICANT ACCOMPLISHMENT

Solid-Solid Phase Transition of a Photo-active and Electro-active Material

Scientific Achievement:

Figure 1a shows electron micrographs and electron diffraction patterns describing the solid-solid phase transition of a compound with molecular structure shown in 1b. The transition transforms polycrystalline particles to aligned and transparent board-like crystals that generate a strong signal of green light from an infrared laser beam. Figure 1b shows the molecule in minimum energy conformation as obtained by computer molecular modeling using the diffraction data as a guide to find the local minimum.

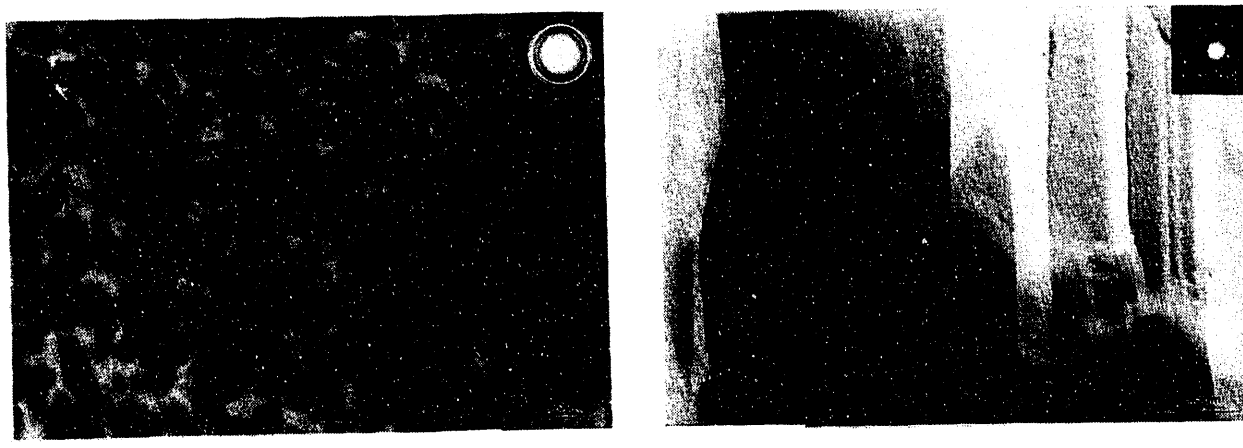


Figure 1 (a)

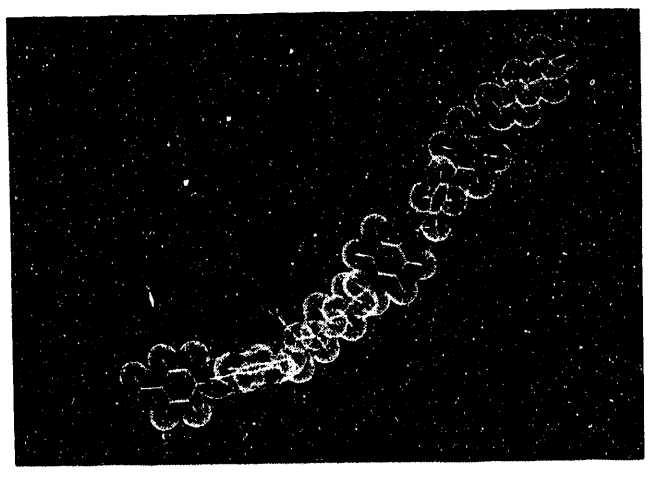


Figure 1 (b)

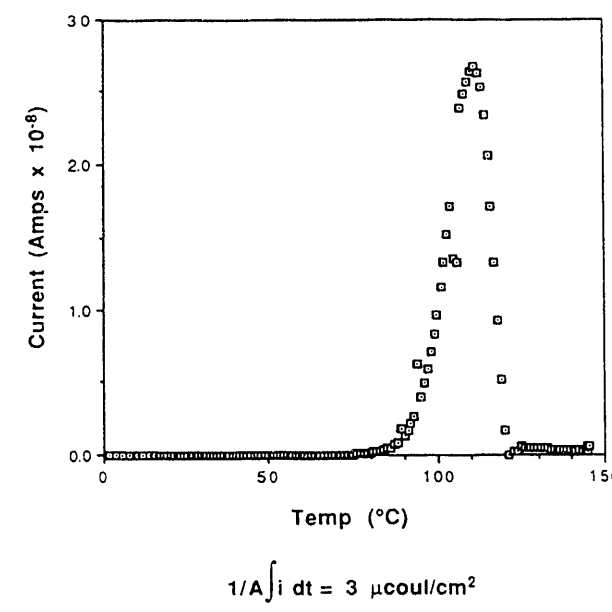


Figure 1 (c)

Measurements obtained this year indicate that the self organized crystals store a significant amount of electrical polarization in their noncentrosymmetric configuration, amounting to 3 micro-coulombs per cm^2 (see figure 1c). We have preliminary evidence that this material and other related compounds can also generate third order nonlinear optical signals.

Significance:

New materials of the type synthesized in our laboratory could find application as frequency doublers of laser beams and also as media for optical switches. This last possibility is based on the fact that significant changes in refractive index are observed in these materials when exposed to electric pulses. The new materials may contribute to the development of powerful computers which utilize strong optical signals and less electric current or new telecommunication systems. The magnitude of electrical polarization associated with the polar crystals of this material offers potential for multiple functions including piezoelectric and pyroelectric activity. The electric current generated by this material during thermal discharge is easily three to six times greater than that in other known organic ferroelectric materials.

Performer: Prof. S.I. Stupp, University of Illinois at Urbana-Champaign.

KENNETH S. SUSLICK

Metalloporphyrins as Field Responsive Materials

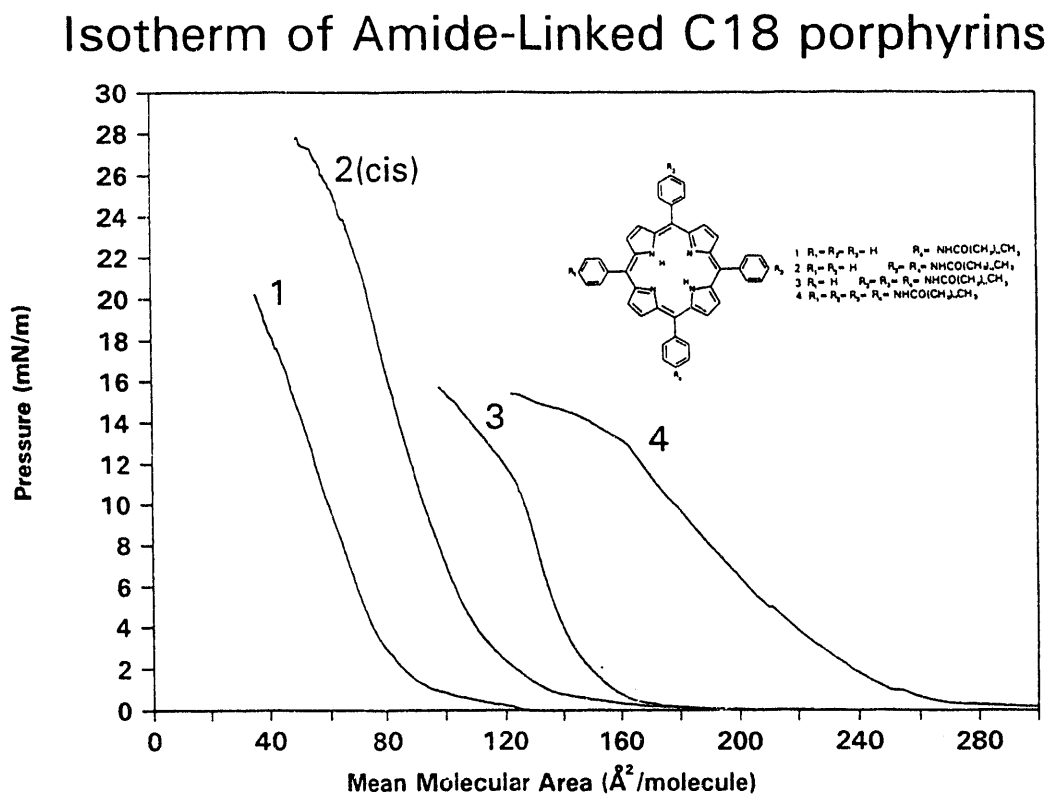
GOALS

Metalloporphyrins and related macrocycles provide an extremely versatile synthetic base on which to design physical and chemical properties. Molecular engineering in this field has had dramatic success in the synthesis of reversible O_2 binders, shape selective catalysis, and the synthesis of one-dimensional conductors and semiconductors. The use of porphyrinic arrays in the photosynthesis reaction center and antennae has led to intensive study of energy transfer in synthetic systems. However, investigation of their field-responsive properties has been extremely limited. The goal of this research effort will be the exploration of metalloporphyrin assemblies as field responsive materials, particularly as ferroelectrics and as non-linear optical devices.

HIGHLIGHTS

Due to their potential applications for optical communications, data storage, and electrooptical signal processing, molecules with non-linear optical (NLO) properties have been extensively investigated. We have synthesized, isolated, and characterized the first use of porphyrins or related macrocycles as non-linear optical materials. We have extended the concept of the use of aromatic systems with both electron donating and withdrawing substituents as organic NLO materials. And most recently, in collaboration with Professor P. Bohn, we have developed a set of Langmuir-Blodgett film-forming porphyrins with NLO properties. These porphyrins form self-assembling monolayers on water surfaces that align the porphyrins roughly parallel to the interface. A graph of the isotherm of monolayer formation is shown below.

As part of our interest in porphyrins and metalloporphyrins as field responsive materials, we have synthesized a series of "push-pull"



porphyrins containing both donor and acceptor substituents and have examined their NLO properties by the EFISH (electric-field induced second harmonic generation) technique in collaboration with a research group at the du Pont Company. The enhancements in molecular hyperpolarizabilities in previous organic systems have relied on donor-acceptor interactions along one-dimensional pathways; our porphyrinic compounds are prototypes of donor-acceptor interactions in *two* dimensions. The molecular hyperpolarizabilities of these porphyrins are substantial, comparable to some of the better previous organic NLO materials.

FUTURE DIRECTIONS

Our efforts continue to be a combination of synthetic chemistry, with full spectroscopic and crystallographic characterization of pure isolated solids, together with examination of new materials for their ferroelectric and optical dichroic and nonlinear optical behavior. To this end collaborative efforts for such characterization have now been established with the research group of Professor Bohn, a participant in the UIUC MRL, and with Dr. G. R. Meredith and his group at duPont Central Research. Our most active efforts during this next year will be on the development of thin films of self-assembled monolayers of our metalloporphyrin as non-linear optical materials in the near-infrared (where porphyrins do not absorb).

SIGNIFICANT ACCOMPLISHMENT

New Films of Non-linear Optical Materials

<u>Scientific Achievement:</u>

We have succeeded in preparing a new class of thin films of organic non-linear optical (NLO) materials made from metalloporphyrins, materials closely related to the central units found in both photosynthesis and in the oxygen carrying protein hemoglobin. These thin films are based on the Langmuir-Blodgett principle of an organic liquid floating on water, for example the sheen of gasoline on a water puddle. As part of our interest in porphyrins and metalloporphyrins as photoresponsive and field responsive materials, we have synthesized a series of "push-pull" porphyrins containing both donor and acceptor substituents. These materials have substantial hyperpolarizabilities and exhibit excellent NLO properties. We have extended this by adding long greasy molecular chains to our push-pull porphyrins and used these chains to self-assemble films on a water interface. We can transfer these films to glass or

other surfaces where they may be made part of an electro-optical device.

Significance:

Materials with non-linear optical (NLO) properties have been extensively investigated because of their extensive applications for optical communications, data storage, and electrooptical signal processing. Such materials for example can convert infrared light into visible light by second harmonic generation.

The design and synthesis of *molecular* species capable of responding to applied electrical, magnetic, or electromagnetic (i.e., light, radio waves, etc.) fields will eventually lead to the practical development of a new class of "nano-electronic devices", so-called because of their even smaller size than present semiconductor-based microelectronics.

Performer: K.S. Suslick, University of Illinois at Urbana-Champaign.

J.P. WOLFE

Carrier Transport in Quantum Wells – Picosecond Imaging

GOALS

The main goal of this project is to characterize the relaxation and diffusion of electronic energy in a semiconductor quantum well following intense picosecond optical excitation. To achieve this, we have developed time- and space-resolved methods based on optical absorption and photoluminescence. We seek to understand the physical processes by which highly excited carriers lose their excess kinetic energy and move in the plane of the quantum well, which has a typical thickness of 10 to 20 nanometers.

HIGHLIGHTS

Continuing work in this project examines the lateral diffusion of carriers in semiconductor quantum wells of GaAs by combining picosecond pulse-probe techniques with spatial imaging.

Because the lifetime of photoexcited carriers in these quantum wells is only about 1 nanosecond, extremely high time and spatial resolution is required to observe the carrier propagation before electron-hole recombination occurs. Our results, based on picosecond imaging with two synchronously pumped dye lasers in a pulse-probe arrangement, have uncovered interesting dependences of the diffusivity on the excitation power and crystal temperature. Use of a tunable pump beam has enabled us to change the excess kinetic energy imparted to the photoexcited electron-hole pairs, and we have reported unusual dependences of the ambipolar diffusion of electronic energy on wavelength and temperature.

This year we have also developed a photoluminescence imaging system with 50 picosecond time resolution and less than 5 micrometers spatial resolution. Using this apparatus and a 10 nm quantum well, we have observed a spectral feature ascribed to biexciton luminescence (two electrons and two holes in a bound complex). The emergence of this feature is accompanied by a large increase in the diffusivity of the nonequilibrium carriers.

FUTURE DIRECTIONS

These unique experimental tools will be used to study the thermodynamics and motion of highly excited excitonic phases in photoexcited quantum wells. We will attempt to determine the origin of the rapid anomalous diffusivity observed at high excitation levels and short times. In addition we are examining the in-plane transport and energy relaxation in double quantum wells. In those systems the optical -- and presumably transport -- properties are modified by an applied voltage bias normal to the planes, which acts to separate the electrons and holes.

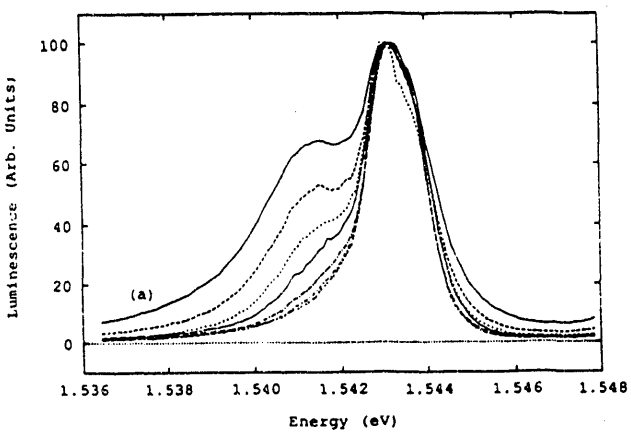
SIGNIFICANT ACCOMPLISHMENT

Thermodynamics of excitons and biexcitons in a GaAs quantum well.

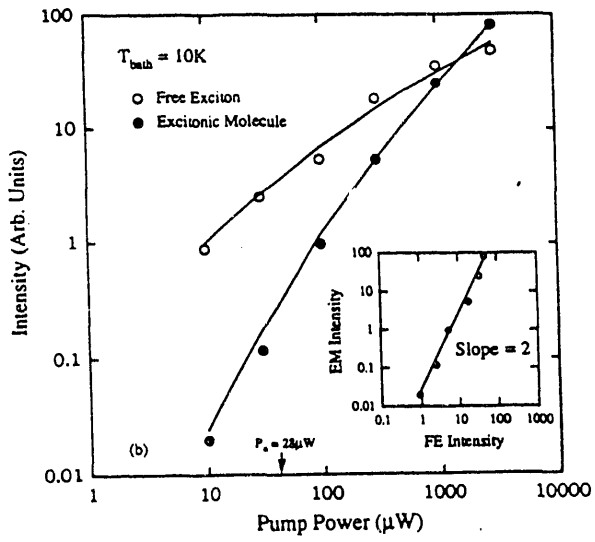
Scientific Achievement:

Intense photoexcitation of a semiconductor produces a "gas" of excited electrons and holes which in principle can bind together to form a variety of complexes. The elementary bound particle (analogous to atomic hydrogen and consisting of a single electron-hole pair) is the exciton. At extremely high densities the excitons ionize to form an electron-hole plasma which has been studied by many workers. At intermediate densities excitonic complexes may occur, although in bulk GaAs there is no definitive observation of such particles. Confinement of excitons in GaAs quantum wells increases the interparticle binding energy and affords an opportunity to observe these complexes. Indeed, two previous studies have noted a new spectral feature which may be associated with a biexciton (two electrons and two holes). We have observed a similar feature in a 10 nm GaAs quantum well and performed time- and space- resolved experiments to gauge the properties of the new particle.

Careful spectral deconvolution reveals that the density of the new particle varies closely as the square of the excitonic density, strongly supporting the biexciton interpretation and indicating that under these pulsed conditions the two species achieve a thermodynamic equlibrium. The photoluminescence intensities obey the predictions of simple rate equations for this two-component gas and give the relative densities of the species. When the biexciton population is dominant, a striking increase in the diffusion rate of the gas is observed. The origin of this remarkable effect is presently unknown and will be one of the principal goal within the next granting period.



(a) Time-integrated luminescence spectra showing the growth of excitonic molecule with increasing excitation density.



(b) Plot of free exciton (FE) and excitonic molecule (EM) intensities as a function of excitation density. Solid lines are from rate equation theory.

Performer: J.P. Wolfe, University of Illinois at Urbana-Champaign.

F.2 SIGNIFICANT ACCOMPLISHMENTS FOR SOLID STATE PHYSICS KC-02-02-02

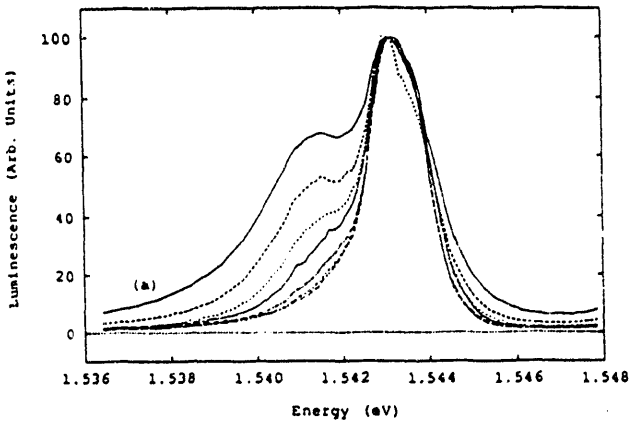
SIGNIFICANT ACCOMPLISHMENT

Thermodynamics of excitons and biexcitons in a GaAs quantum well.

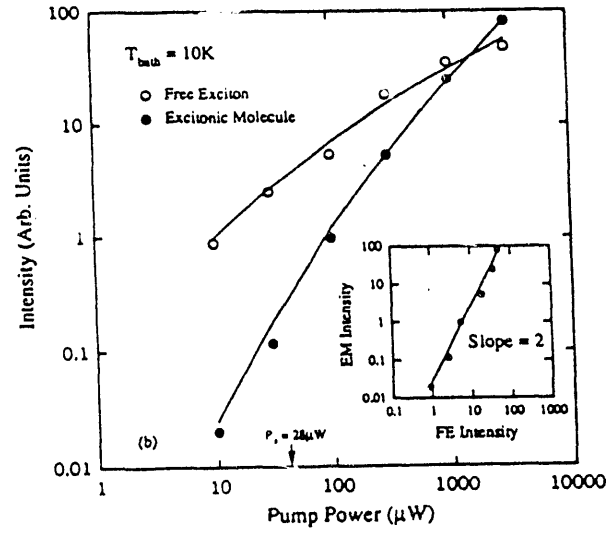
Scientific Achievement:

Intense photoexcitation of a semiconductor produces a "gas" of excited electrons and holes which in principle can bind together to form a variety of complexes. The elementary bound particle (analogous to atomic hydrogen and consisting of a single electron-hole pair) is the exciton. At extremely high densities the excitons ionize to form an electron-hole plasma which has been studied by many workers. At intermediate densities excitonic complexes may occur, although in bulk GaAs there is no definitive observation of such particles. Confinement of excitons in GaAs quantum wells increases the interparticle binding energy and affords an opportunity to observe these complexes. Indeed, two previous studies have noted a new spectral feature which may be associated with a biexciton (two electrons and two holes). We have observed a similar feature in a 10 nm GaAs quantum well and performed time- and space- resolved experiments to gauge the properties of the new particle.

Careful spectral deconvolution reveals that the density of the new particle varies closely as the square of the excitonic density, strongly supporting the biexciton interpretation and indicating that under these pulsed conditions the two species achieve a thermodynamic equilibrium. The photoluminescence intensities obey the predictions of simple rate equations for this two-component gas and give the relative densities of the species. When the biexciton population is dominant, a striking increase in the diffusion rate of the gas is observed. The origin of this remarkable effect is presently unknown and will be one of the principal goal within the next granting period.



(a) Time-integrated luminescence spectra showing the growth of excitonic molecule with increasing excitation density.



(b) Plot of free exciton (FE) and excitonic molecule (EM) intensities as a function of excitation density. Solid lines are from rate equation theory.

Performer: J.P. Wolfe, University of Illinois at Urbana-Champaign.

G. RESEARCH SUMMARIES FOR MATERIALS CHEMISTRY

G.1.a RESEARCH SUMMARIES FOR CHEMICAL STRUCTURE KC-02-03-01

H. G. DRICKAMER

High Pressure Studies of Molecular and Electronic Phenomena

GOALS

The object of this research is to study the effect of pressure on the electronic and vibrational energy levels of molecules in condensed phases, to characterize and understand electronic and molecular phenomena, and to test theories concerning these phenomena. The ultimate goal is to provide a better understanding of the physical and chemical properties and processes of condensed phases, especially crystalline and amorphous solids, and to develop useful materials.

HIGHLIGHTS

During the past year the major accomplishments in the application of pressure tuning spectroscopy by the Drickamer group are as follows:

(1) A study has been initiated of molecules which can have two different geometries in the excited state (e.g., planar and twisted). From high pressure luminescence intensity measurements it has been possible to characterize the steps in the twisting process and to separate the different rotations in molecules which can undergo two or more twists. These molecules are widely used as probes of the polymerization process and of polymer structure as well as potential switching devices.

(2) From high pressure measurements of luminescent peak location, intensity and lifetime it has been possible to establish the cause of the very different luminescence efficiencies in pairs of similar organometallic ions, e.g., $Ru(bpy)_3^{+2}$ and $Ru(bpy)_2(py)_2^{+2}$ [bpy - bipyridine, py = pyridine]. These molecules are important in photocatalysis, electro-luminescence, chemiluminescence and energy transfer.

(3) A thermoluminescence study of mixed crystals of doped $Zn_xCd_{1-x}S$ has been completed and accepted for publication. No more thermoluminescence studies are planned in the immediate future. Six papers have appeared and one is submitted.

(4) Studies of energy transport have been initiated and preliminary results obtained for coumarine - 138 as donor and Rhodamine B as acceptor in polyacrylic acid polymer (PAA).

(5) The collaboration with L. R. Faulkner on high pressure electrochemistry includes a study of microelectrodes and of electrodes coated with quaternized polymers or adsorbed organic molecules. Two papers have appeared, one is in press and two are in preparation.

(6) A collaboration has been initiated with the Luminescence Dynamics Laboratory in Physics (Enrico Gratton, head). A high pressure rig has been developed which interfaces with their pulsed laser facilities and will permit lifetime measurements in the one nano second range or faster to over 100 kbar.

FUTURE DIRECTIONS

(1) It is planned to pursue extensively the study of materials which can have two or more geometries in the excited state. To date we have used molecules which emit only from the planar orientation. Measurements are being initiated on molecules which emit from a twisted state or from two states simultaneously. So far four polymeric media have been used: PMMA (polymethylmethacrylate). PVCl (polyvinylchloride), PVAc (Polyvinylacelate) and PS (polystyrene). It is planned to extend our investigation to other media. In particular there were observed some anomalies as yet unexplained in PS, so it is desirable to use other nonpolar but highly polarizable media, e.g., polyvinylnaphthalene. It is also planned to obtain the temperature coefficient of the luminescent efficiency at various pressures to establish the height of the barrier to transfer between configurations (see (2) below).

(2) A vacuum cryostat has been obtained and the interior has been modified to accommodate a high pressure cell. A program of calibration of the temperature control is being

initiated. The ability to measure the temperature coefficient of the luminescent efficiency (and lifetime) will be valuable for both the study of flexible dye probes of polymers ((1) above) and for the energy transfer studies ((3) below).

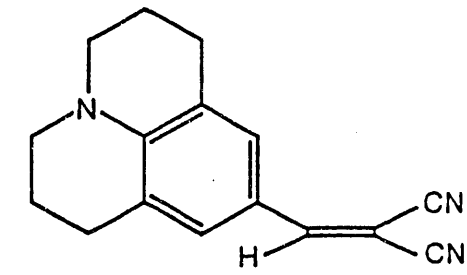
(3) An extensive investigation of energy transfer between organic molecules in polymeric matrices has been started. Preliminary results for coumarine 138 as a donor with Rhodamine B as an acceptor in PAA (polyacrylic acid) reveal large and scientifically significant pressure effects. It is planned to extend these studies to other donor-acceptor pairs and other media. Also it will be desirable to investigate pressure effects where the donor and/or the acceptor is attached to the polymer chain. The collaboration with the Luminescence Dynamics Laboratory is important for this project.

SIGNIFICANT ACCOMPLISHMENT

High Pressure Study of Molecules with Two Excited State Geometries

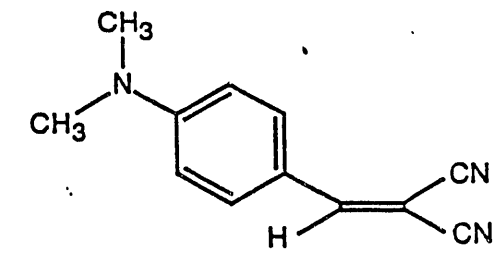
Scientific Achievement:

Molecules which can assume two or more configurations in the excited state are widely used as probes of polymerization mechanisms, polymer structure etc. The structure of two such molecules, julolidinemalononitrile (JDMN) and dimethylaminobenzilidenemalononitrile (DMABMN) appear in Fig 1a. On both molecules the malononitrile group can twist, but for DMABMN the $(CH_3)_2N$ group can also rotate. In none of the papers involving these molecules as probes are the characteristics or the relative importance of one or more twists at one atmosphere investigated or discussed. Both molecules show low emission intensity at 300k and 0 kbar with DMABMN < JDMN. Emission efficiencies vs pressure relative at 0 kbar are shown for DMABMN in Fig 1b. JDMN shows similar behavior with a considerably smaller increase.



JDMN

a



DMABMN

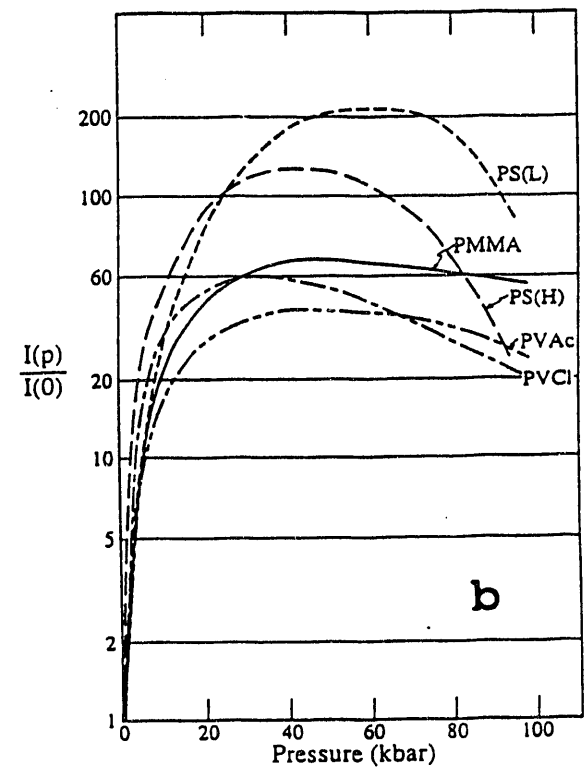


Fig 1 (a): Structure of JDMN (julolidine malononitrile) and DMABMN (dimethylamino-benzilidine malononitrile).
(b) Intensity change with pressure for DMABMN in various polymers (relative to 0 kbar value).

Fig 2 shows a schematic CC diagram along the angle of twist coordinate. The solid line potential wells represent 0 kbar. The non-radiative dissipation of energy can be expressed

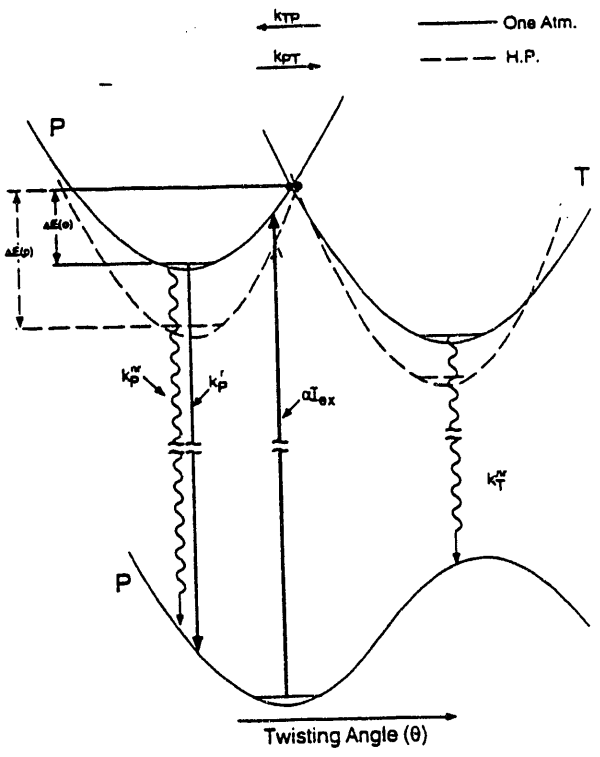


Fig 2. Schematic configuration coordinate diagram. Solid potential wells represent 0 kbar, dashed wells represent high pressure.

in terms of two coefficients k_p^{nr} and k'_{nr} where the former is the ordinary non-radiative rate from the planar state and k'_{nr} is a combination of coefficients:

$$k'_{nr} = \frac{k_{PT}}{1 + \frac{k_{TP}}{k_{nr}^{T}}} \qquad (1)$$

(The terms are defined in Fig 1b.)

The intensity decrease beyond the maximum can be explained in terms of k_p^{nr} and the energy gap law. (PS exhibits some anomalies not yet completely explained.) k'_{nr} is the quantity of interest for describing the steep initial rise in intensity up to the maximum. It can be evaluated from:

$$k' = \frac{k'_{nr}(p)}{k'_{nr}(o)} = \frac{\frac{\Phi_o}{\Phi_p} - \frac{\Phi_o}{\Phi_{max}}}{1 - \Phi_o} \qquad (2)$$

where Φ_o, Φ_p and Φ_{max} are the quantum yields at 0 kbar, at pressure p and at the maximum respectively. In Fig 3a ln k' is plotted vs pressure for JDMN in PVCl and PVAc. The other media gave similar plots. From the linearity it seems that a single process may control.

In general, one can write

$$k' = \gamma \exp\left(-\frac{"\Delta G"}{RT}\right) \qquad (3)$$

where, if a single rate process dominates $\gamma = \frac{k_B t}{h}$ and "ΔG" = $\Delta G^{\neq}$. The free energy difference between the initial state and the transition state. If one is dealing primarily with an equilibrium between two states $\gamma = 1$ and "ΔG" = ΔG_{eq}. In the first case the pressure derivative of ln k' yields $\Delta V^{\neq}$ the volume change upon activation, while in the second case one obtains ΔV_{eq} between the two excited states.

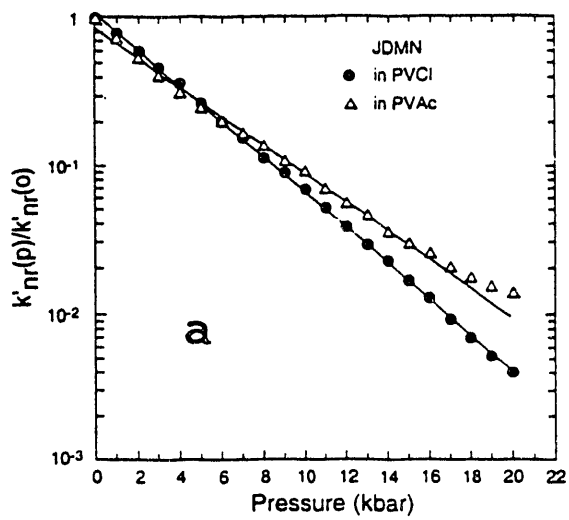


Fig 3 (a) $k' = \frac{k'_{nr}(p)}{k'_{nr}(o)}$ vs pressure for JDMN in PVAC and PVCl.

In Fig 3b ln k' is plotted vs the energy of the emission peak. The lines represent the change in energy necessary to give the observed change in ln k'. The fact that the lines and the points coincide except for PS at low pressure implies that the increase in quantum yield is due entirely to the decrease in k_{PT} because of the increase in the barrier height, i.e. that the second term in the denominator of eq. (1) is negligible for the malononitrile twist. The situation at elevated pressure is represented schematically by the dashed line potential wells in Fig 2. ΔV^{+} = 4 - 5 cc/mol depending on the medium.

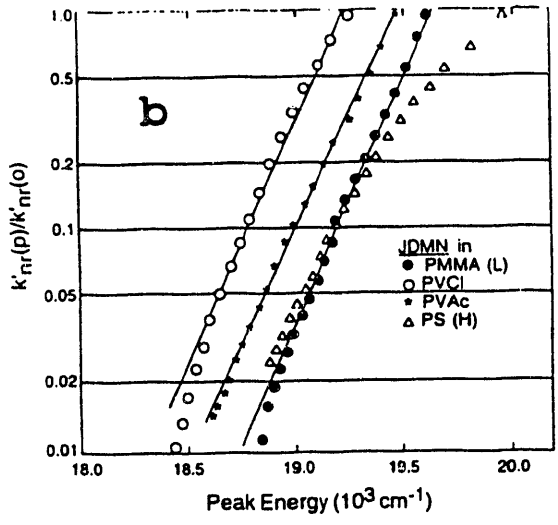


Figure 3(b). ln k' vs emission peak energy for JDMN in various polymers.

In Fig 4a ln k' is plotted vs pressure for DMABMN in PVCl and PVAc. Other media yield similar plots. The data can be well fit by two straight lines extending over several orders of magnitude, which implies that one twist governs at low pressure while the other dominates at higher pressure. Fig 4b exhibits a plot of ln k' vs peak energy. At lower peak energies (higher pressures) the data coincides with the energy change necessary to give the observed change in ln k' as for JDMN in Fig 3b. Thus the process which dominates at higher pressures must be the malononitrile twist, governed by the change in k_{PT} as for JDMN. For DMABMN, $\Delta V^{\neq}$ = 3-3.5 cc/mol. The volume of activation need not be identical for the rotation of a given group on different molecules.

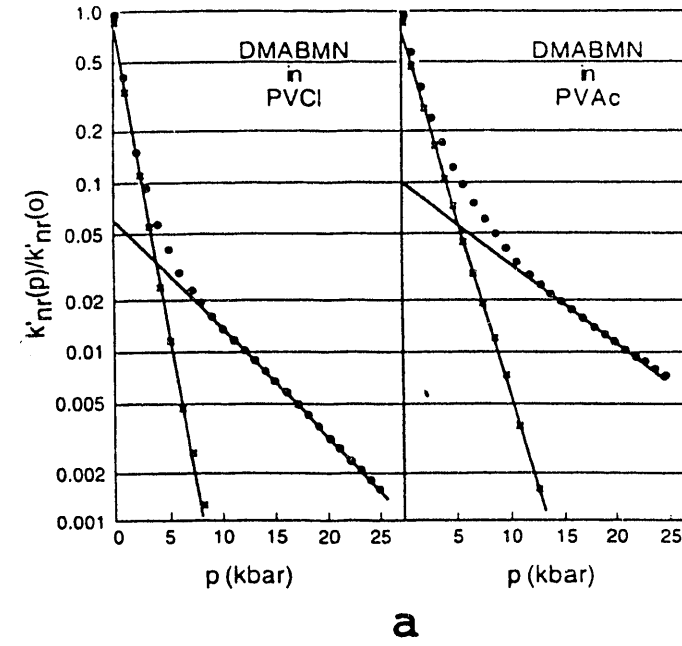


Fig 4 (a). ln k' vs pressure for DMABMN in PVAc and PVCl.

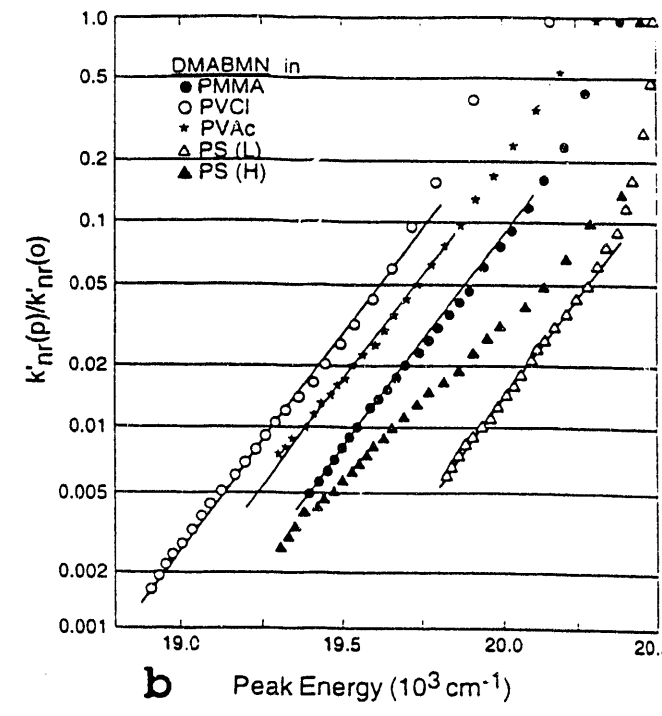


Fig. 4(b). ln k' vs emission peak energy for DMABMN in various polymers.

The process which dominates at low pressure cannot yet be characterized definitively. There are several possibilities all with some degree of ad hoc character: (1) the second term in the denominator of eq.(1) could be large at 0 kbar and decrease with increasing pressure giving a larger decrease in k_{PT} than that provided by the peak shift; (2) the potential wells (dashed lines) of Fig 2 could move with pressure to have the same effect on k_{PT}; (3) the second term in the denominator of eq. 1 could be large at all pressures, then

$$k' \cong \frac{k_{PT}}{k_{TP}} k_T^{nr} = K_{eq} k_T^{nr} \qquad (4)$$

Since k_T^{nr} is assumed small

$$\frac{\partial \ln k'}{\partial p} = \frac{\partial \ln K_{eq}}{\partial p} + \frac{\partial \ln k_T^{nr}}{\partial p} \cong$$

$$\frac{\partial \ln Ke_q}{\partial p} = -\frac{\Delta V_{eq}}{RT} \qquad (5)$$

For DMABMN $\Delta V_{eq} = 15 \pm 2$ cc/mol depending on the polymer. This is $7 \pm 1\%$ of the molar volume, a not unreasonable value.

Performer: H.G. Drickamer, University of Illinois at Urbana-Champaign.

G.2.a RESEARCH SUMMARIES FOR CHEMISTRY OF MATERIALS AND SURFACES KC-02-03-03

R. G. NUZZO

Mechanistic and Synthetic Studies in the Chemical Deposition of Thin Film Materials

GOALS

It is the objective of our research to investigate the mechanistic bases of materials growth and processing involving reactive chemistries occurring on surfaces. Our primary aims are twofold. First, we wish to understand how molecular level processes come to shape the character of solid state materials. Second, we seek to use these insights to guide the development of altogether new ways to prepare and fabricate materials.

HIGHLIGHTS

We have made significant advances in several areas in this the first full year of our efforts conducted under the sponsorship of the DOE. Each is summarized below.

In collaboration with Professor G. Girolami, we have developed and characterized mechanistically a new approach to the growth of alloy thin metal films by OMCVD that involves a new class of reactive gas solid interaction. The process we have discovered is based on a highly selective transmetallation, a process in which the ligands are transferred from an organometallic precursor to a substrate metal atom which then subsequently desorbs in the form of a stable complex. Our most completely characterized system at present involves the selective growth of Pd/Cu alloys from the reaction of Bis-hexafluoroacetylacetenoate Palladium(II) ($Pd(hfac)_2$) on copper substrates. In this particular system, palladium is deposited and the copper etched (in the form of $Cu(hfac)_2$) at temperatures above 350 K. The kinetics, structure-property correlations, and ligand exchange mechanisms of this process has been explored by a variety of experimental techniques.

Also in collaboration with Girolami, we have developed a new reagent (trans-(pyridine)(ethylene)$PtCl_2$) for the chemical vapor deposition of platinum which yields elementally pure films even in the absence of hydrogen as a reducing agent. This is the first example of an elementary deposition chemistry for this metal that does not require a co-reactant gas to deposit high quality metal films. We have also developed a new MOCVD process for the deposition of technologically important material PtSi using several different Pt source gases. This process is far from optimized (impurity contents run to as high as 10 atom %). To advance this technology will require us to build a new CVD apparatus capable of handling the necessary feed gasses; this effort is currently in progress. The chemistries outlined above involved the study of the surface mediated decompositions of literally dozens of organometallic complexes in a specially constructed UHV apparatus. Significant efforts were spent investigating the mechanisms by which the large organic ligands associated with these precursors are transformed on a platinum surface. During these studies, we discovered a series of reactive chemistries on platinum which have significant implications for the mechanistic bases of the catalytic reforming of hydrocarbons. We have characterized in ultrahigh vacuum the reactions which convert cycloalkanes of varying size to benzene via coupled dehydrogenation and ring contraction reactions. For example, we have been able to determine all the intermediates and the energetics associated with the high yield conversion of cyclooctane to benzene and acetylene on Pt(111) in a well defined UHV setting. We have also characterized well defined examples of olefin hydrogenation reactions which occur under the limits of low pressure. Very few such reports exist in the current literature.

We also have explored the growth and etching of Cu_3Si. This material figures centrally in the catalyzed synthesis of the precursors of organosilicone polymers and has been suggested as material for application in advanced devices. We have been able to grow high quality thin films based on the reaction of SiH_4 on Cu single crystal surfaces. Most importantly, we have identified spectroscopically all the Cu/Si-H_x (x=4-1) intermediates involved in this process and determined their stability as a function of both temperature and coadsorbate (Si and H) coverages. We have also studied the etching of

this material by hydrogen. The reaction of this material with hydrogen atoms yields SiH_4 at remarkably low temperatures (<160K). We are currently exploring the nature of the hydrogen surface diffusion processes which appear to be involved in this facile gas-solid etching chemistry.

FUTURE DIRECTIONS

In the next year we will attempt to perfect the growth chemistries for PtSi as well as begin a detailed investigation of the catalyzed etching of compound solids by atomic hydrogen. We will continue to explore the structure rate correlations of hydrocarbon reforming on Pt surfaces with a specific focus being given to the energetics involved in the activation of the C-H bonds of adsorbates bound to this metal.

SIGNIFICANT ACCOMPLISHMENT

Mechanisms of Metal Alloy Thin-Film Growth by Reactive Transmetallation

Significant Achievement:

In collaboration with G. Girolami and graduate student W.-B. Lin, a new method for preparing alloy thin films has been explored. The reaction of bis(hexafluoroacetyl-acetenoate)Pd(II) on Cu surfaces has been found to lead to the selective deposition of Pd metal. The deposition of this metal occurs by a reaction mechanism in which the ligands of the Pd complex (hfac) are transferred to the metal surface and become bound to Cu surface atoms. At temperatures above 350 K significant desorption of $Cu(hfac)_2$ into the gas phase occurs. The deposition involves a mechanism which has not been observed before. The most salient feature involved in this process is the facile transfer of the ligands to Cu and the efficiency of the recombination process which liberates the Cu species even in the low pressure limit. The mechanism is selective, depositing Pd only on Cu. The chemistry is thus directly applicable to the growth of Pd/Cu alloys in a spatially defined way. Pd/Cu alloys are currently employed as part of the hierarchical metallization of VLSI devices. There exist no methods other than physical deposition and subsequent patterning for the deposition of these materials. Selective Cu deposition is a well advanced technology and the newly discovered reactions suggest a possibility for forming alloys via substrate specific gas phase reactive alloying.

The mechanism involved in the present case has been studied in depth and a good understanding of the process has been obtained. Salient microscopic features of this intriguing reaction are described below.

$Pd(hfac)_2$ has a large reactive sticking probability on Cu. At temperatures as low as 100K the ligands are activated on the substrate and the Pd(II) atoms of the complex reduced to the zero valent state. Between 100 and 300K a coverage dependent tilt-phase transition occurs in the surface bound ligands. Our current belief is that this transition involves the reorientation of the hfac ligands from a flat, lying down geometry to one involving the orientation of the O-C-C plane along the surface normal direction. In the presence of an adsorbate flux corresponding to a surface pressure of at least 10^{-5} torr and at temperatures of the order of 400K or above, two of these latter ligands combine with a single Cu surface atom to form adsorbed $Cu(hfac)_2$. This latter event is the rate limiting step of the process as the desorption of $Cu(hfac)_2$ is facile at this temperature. The transmetallation reaction operates in a kinetic window in which the hfac ligands are stable on the surface. We have demonstrated this by independently preparing these same adsorbate overlayers in the absence of Pd and showing that their thermolytic decomposition occurs at much higher temperatures. The reversible etching of Cu by the free ligand, H-hafc, has also been observed. We are currently modeling the temperature dependent spectral data (principally reflection absorption infrared spectroscopy) which defines the ligand orientations and the results of reactive molecular beam-surface scattering studies to extract more detailed understandings of the structural dependences and kinetics of the most elementary molecular processes involved in this unique reaction.

Performer: Ralph G. Nuzzo, University of Illinois at Urbana-Champaign.

KENNETH S. SCHWEIZER

Microscopic Theories of the Structure and Phase Transitions of Polymeric Materials

GOALS

The overall goal is the development and application of novel molecular scale statistical mechanical theories of the equilibrium properties of polymeric materials. A unified microscopic approach to calculating the thermodynamics, structure, conformation, and phase transitions of polymer melts and alloys is being pursued. A common theme is to both understand structure-property-phase behavior relationships of existing materials, and also develop chemically realistic predictive methods of use for designing new macromolecular materials.

HIGHLIGHTS

Our general off-lattice integral equation theory (Polymer Reference Interaction Site Model, "PRISM") of polymeric liquids has been further developed and applied in three important directions.

1) A new PRISM theory of polymer blends has been formulated and applied which explicitly accounts for chain connectivity at all levels of the theory. Extensive comparisons of the theoretical predictions for simple isotopic-like blends with recent small angle neutron scattering measurements and computer simulation studies have documented the high accuracy of the novel statistical mechanical approximations. The theory has also been systematically applied to "real chemical" polymer mixtures in which the two species differ in many respects, e.g. chain stiffness, molecular weight, attractive potentials, etcetera. The fundamental nature of the calculated phase diagrams are found to depend very sensitively, and in a nonlinear manner, on all the single chain structural aspects, the detailed nature of the intermonomer potentials, and thermodynamic state. The insights obtained suggest new molecular strategies for intelligently controlling miscibility and phase structure in polymer alloys. Detailed applications to polyolefin blends and random copolymer alloys have been initiated.

2) The PRISM theory with the new statistical mechanical approximation scheme mentioned above has been generalized to treat periodic block copolymer materials which undergo microphase separation. Extensive numerical studies of simple diblock copolymers have revealed a rich array of "fluctuation" phenomena associated with strong interchain correlations which are in accord with recent small angle scattering measurements.

3) The first successful microscopic theoretical calculation of the equation-of-state of alkane and polyethylene liquids has been performed by combining the PRISM theory of melts with chemically realistic modeling of single chain conformation and intermolecular forces. Excellent quantitative agreement between theory and experiment has been demonstrated, and the new approach can be applied to more complex hydrocarbon materials such as branched polyolefins.

FUTURE DIRECTIONS

A comprehensive numerical and analytical study of the relationships between chemical architecture, interchain forces and blend phase diagrams will be carried out with the goal of establishing novel, molecular-level strategies for controlling alloy miscibility. Specific applications will be made to isotopic polyethylene blends being studied experimentally at Oak Ridge National Laboratory, and mixtures of randomly branched polyolefins being studied at Exxon. Programs will be initiated to extend and apply the PRISM blend theory to treat the unusual and poorly understood lower critical solution temperature(LCST) phenomena in polymer mixtures, and also phase-separating blends near surfaces. Further development and application of the "self-consistent" version of PRISM theory will be pursued which, for the first time, will allow an *ab initio* calculation of conformation in polymer mixtures. Generalization of the PRISM approach to treat branched polymers, particularly star-branched molecules, will also be carried out. Finally, a program will be initiated to develop suitable interchain potentials, and statistical mechanical methods based on the PRISM theory, to treat condensed phases of electroactive conjugated polymers.

SIGNIFICANT ACCOMPLISHMENT

New Microscopic Theory of Multiphase Polymeric Materials

Scientific Achievement:

All prior microscopic integral equation theories of polymer mixtures were very recently shown to predict an incorrect scaling of the critical temperature with chain length. This lead us to reconsider in a fundamental way the statistical mechanical approximations inherent to molecular fluid theory. A family of new closure approximations have been invented which consistently account for chemical-bonding mediated correlations. The resultant new PRISM theory has been shown to be both qualitatively and quantitatively reliable by comparison with experiments and computer simulations on isotopic-like polymer blends. The new theory has been employed to begin to map out the complex , nonadditive influences of local chemical structure, global chain architecture, intermolecular forces and thermodynamic state on polymer alloy phase diagrams. In addition, the theory is unique in the sense that local packing information is also obtained which allows a microscopic interpretation of both wide and small angle scattering measurements.

Significance:

Multiphase polymeric materials are of major scientific and commercial application importance. Although the primary question is often one of miscibility, the properties, composition, morphology, and thickness and strength of interfaces in the phase-separated state are all intimately related to the thermodynamics of mixing in the melt. The new blend PRISM theory allows one to explore, for the first time, "cause-and-effect" at a molecular level. New strategies for molecular structure modification to either promote or hinder phase separation in polymer mixtures are emerging. The theory has been generalized to another important class of materials: microphase separating block copolymers, and also provides a fundamental framework for treating related self-assembling macromolecular materials, e.g. ternary mixtures, block copolymer/binary blend mixtures, polymer gels and networks, and ionomer materials. The theoretical breakthrough also has major consequences for small or intermediate-sized(e.g., surfactants) molecular fluids which undergo ordering and/or phase separation due to attractive forces. Finally, the new PRISM theory provides the foundation for understanding surface segregation and adsorption phenemona in multicomponent molecular and/or polymeric fluids.

Performer: Kenneth S. Schweizer, University of Illinois at Urbana-Champaign.

Nonlinear Optical Probes of Surface Chemical Dynamics

GOALS

Professor Seebauer's investigations are intended to examine the chemical dynamics of thin film deposition, particularly of semiconductors. Surface second harmonic generation (SHG) is being developed as a probe of surface diffusion and of adsorption kinetics near atmospheric pressure. Being a photon-based method instead of an electron or ion-based technique, SHG is relatively nonintrusive and avoids some of the severe surface perturbations that are often encountered with other methods. Special focus lies in performing experiments under real processing temperatures and pressures. Much of the chemical dynamics under such conditions is unknown because of the lack of suitable methodology.

HIGHLIGHTS

This past year has seen the full development of Optical Second Harmonic Microscopy (SHM) as a quantitative tool for measuring the surface diffusion of adsorbates. This milestone represents the first quantitative use of SHG for spatially resolved imaging of adsorbate layers. An initial step concentration profile of adsorbate is obtained using a molecular beam source combined with a retractable mask on the surface. After heating the sample to relax the step, the resulting profile is imaged by SHM with a resolution of 5μ and a precision of 0.02 monolayers.

A detailed study of Sb on Ge(111) has been completed this year, representing the most systematic examination of surface diffusion on a semiconductor yet published. Sb is an n-type dopant of Ge whose incorporation may be controlled by surface diffusion. Sb is also used as a surfactant in Si/Ge growth.

The results were explained semiquantitatively with a new vacancy diffusion model developed by Professor Seebauer this past year. In this model, the adsorbate diffuses over a substrate surface layer which is itself quite mobile and contains many vacancies. The energy and entropy of formation of these vacancies form the primary contributions to the diffusion parameters.

FUTURE DIRECTIONS

Professor Seebauer intends to continue these surface diffusion measurements on Ge and other substrates using other adsorbates in order to confirm important elements of the vacancy diffusion model. In particular, the model predicts that surface diffusion may be affected by substrate doping and by photon illumination. Such effects have never before been observed quantitatively. In addition, Professor Seebauer intends to use SHG to probe the adsorption kinetics of gases that interact weakly with surfaces, such as molecular H_2 on Si or Ge.

SIGNIFICANT ACCOMPLISHMENT

Development of a Vacancy Model for Surface Diffusion at High Temperature

Scientific Achievement:

A thorough, quantitative investigation of the surface diffusion of antimony (Sb) on germanium (Ge) has been completed using the newly-developed technique of Optical Second Harmonic Microscopy (SHM). As shown in the accompanying figure, the activation energy E_{diff} for surface diffusion remains constant at 2.0 eV, but the pre-exponential factor D_o decreases from roughly 10^4 to 10^2 cm^2/s as the surface coverage, q, increases. These results may be explained semiquantitatively by a new model developed in this laboratory based on vacancy-mediated diffusion. The coverage dependence arises through an islanding mechanism in which immobile islands of Sb pin down the otherwise mobile Ge surface layer. The model predicts that the presence of a near-atmospheric pressure ambient should not significantly affect the diffusion parameters because they are dominated by the thermodynamics of vacancy formation. The first quantitative measurements of surface diffusion under such conditions (100 torr of helium or 5 torr of argon) have confirmed this prediction.

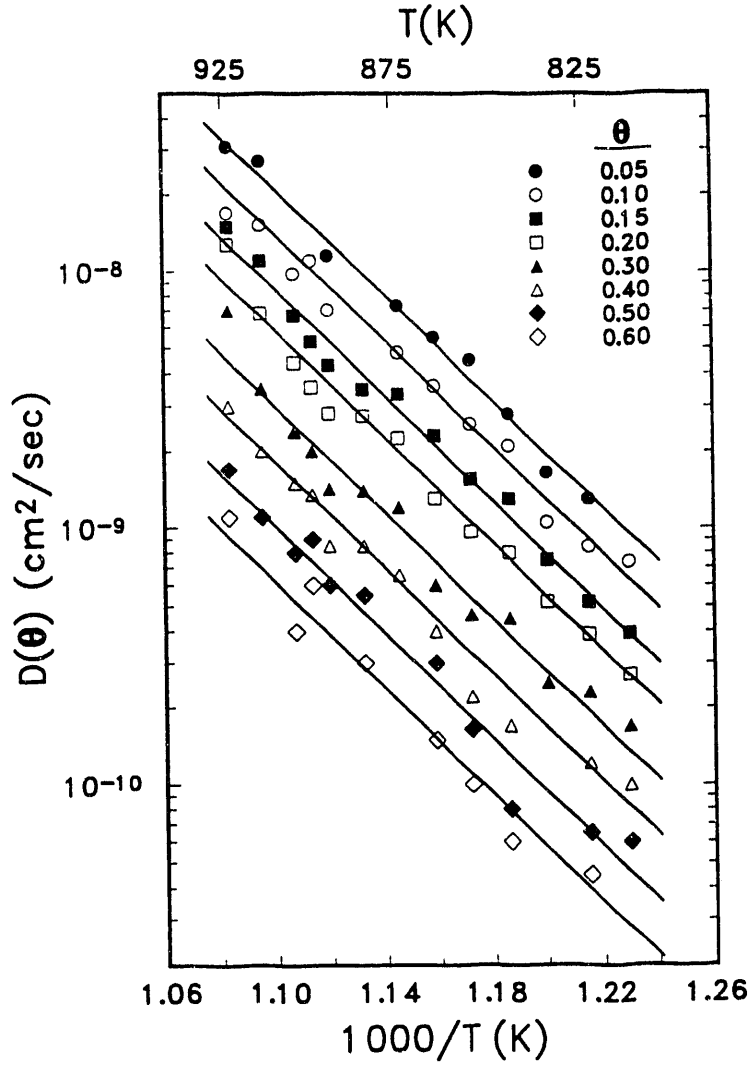


Figure Caption: Arrhenius plots of Sb diffusivity D on Ge(111) as a function of fractional coverage q. Constant slope indicates constant E_{diff}, but the intercepts D_0 decrease dramatically with q.

Significance:

Reliable measurements of surface diffusion on semiconductors are practically nonexistent because most available methods either damage the surface or measure diffusion too indirectly to be reliable. However, surface diffusion is a critical step in the chemical mechanism for thin-film deposition. Slow diffusion results in highly defected, poor-quality material. Particularly lacking are surface diffusion measurements at the temperatures characteristic of thin-film growth; most measurements are performed at much lower temperatures. Our method of SHM has allowed us to look at surface diffusion under processing temperatures and has shown that the fundamental mechanism for surface mobility can change under these conditions. Furthermore, the model predicts that surface diffusion may be influenced by such process parameters as substrate carrier concentration and photon illumination. This suggests that additional control and enhancement may be possible during processing.

Performer: E.G. Seebauer, University of Illinois at Urbana-Champaign.

G.3 SIGNIFICANT ACCOMPLISHMENT FOR MATERIALS CHEMISTRY KC-02-03

SIGNIFICANT ACCOMPLISHMENT

New Microscopic Theory of Multiphase Polymeric Materials

Scientific Achievement:

All prior microscopic integral equation theories of polymer mixtures were very recently shown to predict an incorrect scaling of the critical temperature with chain length. This lead us to reconsider in a fundamental way the statistical mechanical approximations inherent to molecular fluid theory. A family of new closure approximations have been invented which consistently account for chemical-bonding mediated correlations. The resultant new PRISM theory has been shown to be both qualitatively and quantitatively reliable by comparison with experiments and computer simulations on isotopic-like polymer blends. The new theory has been employed to begin to map out the complex , nonadditive influences of local chemical structure, global chain architecture, intermolecular forces and thermodynamic state on polymer alloy phase diagrams. In addition, the theory is unique in the sense that local packing information is also obtained which allows a microscopic interpretation of both wide and small angle scattering measurements.

Significance:

Multiphase polymeric materials are of major scientific and commercial application importance. Although the primary question is often one of miscibility, the properties, composition, morphology, and thickness and strength of interfaces in the phase-separated state are all intimately related to the thermodynamics of mixing in the melt. The new blend PRISM theory allows one to explore, for the first time, "cause-and-effect" at a molecular level. New strategies for molecular structure modification to either promote or hinder phase separation in polymer mixtures are emerging. The theory has been generalized to another important class of materials: microphase separating block copolymers, and also provides a fundamental framework for treating related self-assembling macromolecular materials, e.g. ternary mixtures, block copolymer/binary blend mixtures, polymer gels and networks, and ionomer materials. The theoretical breakthrough also has major consequences for small or intermediate-sized(e.g., surfactants) molecular fluids which undergo ordering and/or phase separation due to attractive forces. Finally, the new PRISM theory provides the foundation for understanding surface segregation and adsorption phenemona in multicomponent molecular and/or polymeric fluids.

Performer: Kenneth S. Schweizer, University of Illinois at Urbana-Champaign.

H. FACILITIES OPERATION

About thirty Central Facilities of various types and sizes are operated by the Materials Research Laboratory for the support of the research program. The size and complexity of these range widely; from the very extensive Center for the Microanalysis of Materials to single instrument facilities. Operations of these facilities are coordinated and their financing is related to the usage and need for the facility by each of the MRL research programs. A manual describing each of the facilities and means of access is available and is widely distributed.

The method of central facility operation at the MRL has major advantages. It allows sharing of instrumentation by many users and increases the intellectual interactions between the users. The provision of expert scientists to work with the users improves efficiency and the quality of the science. Open, easy access to the facility allows all members of the MRL to utilize techniques appropriate to the science being carried out.

The Center for Microanalysis of Materials

The Center for Microanalysis of Materials recently completed its first decade of operation. During this period it has evolved and developed into a comprehensive facility for the microstructural and microchemical analysis of materials. The Center will continue to evolve to meet the changing needs of its users during the next period in order that its remarkable success in supporting the DOE materials science research programs be continued.

The primary role of the Center is to contribute to the DOE research and other materials research programs through the provision of resources for micro-characterization. In order to do this, the Center must maintain, support and develop the instruments and instrumentation and provide the expertise for training and consultation.

Central to the philosophy of the Center is the idea that its users - the PI's and their students - should be able to move freely from one microanalytical technique to another as the research needs change. More than that, that it should be possible for the techniques to be used in combination when the complementary nature of the information obtained makes this desirable. Another central theme is the hands-on availability of a variety of instrumentation coupled with the expertise of the professional employees of the Center. This allows free access and training for students and Research Associates and provides the ability to optimally select the best characterization instruments.

The three threads that combine to give the Center its unique strength are the breadth of the instrumentation, the strength of its staff and its accessibility.

Equipment Changes

The MRL, with support from DOE, has manifested its commitment to the Center for Microanalysis of Materials by providing the renewal and upgrading of equipment needed to keep the Center operating at the state of the art. Since the Center operates a large set of instruments this upgrading must be continued year by year in order to provide the best resources to the research programs.

An important aspect of this renewal funding is the way in which the MRL has been able to use the funds provided by DOE to leverage additional funding from other sources. Typically the DOE funding can be leveraged by a factor of two, but it is the critical, catalytic component that makes the rest possible.

The following paragraphs describe the major changes in 1992.

The new SIMS unit, the CAMECA 5f, has been installed, and is almost fully operational. This instrument provides both microscope and microprobe SIMS imaging.

A Backscattered pattern detector system (EBSP) has been installed on the Zeiss 960 scanning electron microscope. This system greatly increases the power of crystallographic analysis available to SEM users. A major use has been for texture analysis of thin films and of ceramics.

In addition to the major items listed above, this year has seen a continued effort to improve the infrastructure of the Center with the purchase of

some smaller, but significant items. The most important of these is a badly needed turbopumped evaporator which replaced one which was thirty years old.

Personnel Training

An important National need that is being addressed by the Center is the training of personnel to a high level of expertise in broad areas of materials characterization. This is a matter of particular importance because different instruments and techniques fulfill complementary roles in materials characterization. Optimum results can be achieved only by a combination of techniques.

An advantage of locating the Center in a major materials sciences community on a university campus is that graduate students taking MS and PhD research degrees have the opportunity to gain the necessary broad experience by being exposed to the instruments and technical expertise located at the Center. Upon graduation, these trained personnel will take their skills to other government and university laboratories, and in this way the Center will diffuse sophisticated characterization expertise on a national scale. Indeed the Center has now been in operation long enough that these benefits can be seen working in practice. Both graduate students and staff of the Center have available a variety of alternative favorable employment opportunities.

In FY92 the number of users of the various techniques of Center for the Microanalysis of Materials was 747. This was a 28% increase in the training load at the Center for the Microanalysis of Materials. It is clear that the facilities and the staff of the CMM are being stretched to the limit.

User Activities

The Center provides a heavily used resource available to scientists at the MRL, at the Universities within the U.S., at National Laboratories, and in Industrial Laboratories. In the past five years, we have had outside users from 50 outside institutions, many of whom made repeated trips to use our facilities. These users include the scientists and engineers from National Laboratories, industries and universities. Particularly active use of the Center's facilities was made by researchers from Argonne National Laboratory.

Usage of instruments in the Center is very high. In the past year the usage (not counting maintenance time) of the major instruments (2,000 hours per year is full single shift use) is:

INSTRUMENT HOURS OF USE

TEMs/STEM	5073
SEMs	2989
X-Ray	5542
SAES	1947
SIMS /SNMS	1117
XPS	1441
Accelerator	986
Ion millers	6782

These are actual use times during which the instruments were engaged in useful work. Demand for these instruments is higher than indicated in the above figures, as usage is limited by the necessity for extensive maintenance and renovation as the instruments age.

Problems

The Center for the Microanalysis of Materials is considerably underfunded and understaffed considering the level and scope of its activities. A particular need is that the number of professional personnel be increased. Since the Center undertakes a very large responsibility in teaching instrument use and techniques to many of the CMM users, performs much of its own maintenance, undertakes an active technique development program which has a large research component, and since we have added new instrument responsibilities to the center, we are in serious need of additional personnel. This has been a continuing problem for the past five years. **It is essential that this be addressed as soon as possible.**

Following departures by some members of staff, replacements have been made in a way that will improve the effectiveness of Center operation and do so with a saving in costs. There remain critical needs for further resources particularly in the area of TEM and computers (especially image handling and analysis). A

need for additional manpower in the field of x-ray diffraction is also foreseen.

We would also like to add Research Associates to the Center to support the efforts in instrument science that are carried out. This would make the work of the professional staff of the Center much more effective in this field.

Carefully considered plans have been laid for continuing capital purchases based on input from the facility Advisory Committee and are being reported to the DOE as a long-term Development Plan. The Center operates about 19 major instruments, each of which has a useful life expectancy of about ten years. Funds equal to 10 - 15% of the current total replacement costs are therefore needed each year simply to maintain a steady state of up-to-date instrumentation. Development of new instruments, and expansion of the instrumentation base, will each require further new resources.

Future Plans

The MRL has submitted a Long Range Plan for the development of the Center For The Microanalysis of Materials to the DoE. The needs of the Center are fully documented in that Plan. A summary of the major equipment items required in the next few years is given below.

FY 1993

Ion Milling instrument replacement - $ 60,000
Rotating Anode X-ray Unit upgrade - $ 150,000

FY 1994

Completion of the purchase of the 300 kV STEM - $ 2,500,000
Cathodoluminescence detector - $ 150,000
Ion Milling instrument replacement - $ 60,000
Upgrade of the computer systems and software for the x-ray systems - $ 200,000
EPISEM - $ 500,000

FY 1995

Imaging system digitization - $ 350,000
Ion Milling instrument replacement - $ 60,000
Rotating Anode X-ray Source - $ 300,000
Upgrade of CM-12 Analytic TEM - $ 250,000

FY 1995

Scanning Tunneling Microscope/Atom Probe - $600,000
Ion Accelerator - $ 700,000

Space Needs

These have been completely addressed as a consequence of funds obtained from the State of Illinois and the Department of Education.

The EpiCenter (Molecular Beam Epitaxy Center)

The Molecular Beam Epitaxy Laboratory (the EpiCenter) has been operating for about four years and has been used to produce some very exciting new materials and concepts in the area of crystal growth. Facilities to supplement MBE growth with chemical beam growth based on gaseous sources have been successfully operated. The combination of MBE, GBE, and CVD growth capabilities has given us a very useful operational base on which to develop a variety of synthesis and processing systems. These new growth techniques have enabled a great improvement in the flexibility and quality of growth of tailored materials.

An on-line STM for studying the surfaces of crystals during growth has been installed and its operation is being tested.

The Center for Computation

The Center for Computation provides computer facilities for the MRL as well as providing the links to the large Supercomputing Centers used by the staff. Due to the rapid growth of computer use for simulations of the behavior of real materials and for theory development and modeling, there is an impending shortage of supercomputer capacity available to researchers in Materials Science. The MRL has installed a VAX 6310, and two VAX 6410s with vector boards and large memories to meet the needs for large batch computations. In addition, we have installed a number of large RISC computers for very fast, interactive computations and for batch jobs which require

very fast computation. While these machines are not as fast as the CRAYs, they can be configured to have large memories and in fact are comparable to Cray speeds on many types of computations. An extensive series of workstations which meet the needs of the computation intensive groups for convenient access and high quality graphics have been installed.

The Laser Facility

The Laser Facility provides access to pulsed lasers which operate in the microsecond to femtosecond range. In addition to the pulsed laser capabilities, the facility also provides Raman and non-linear optics capabilities. The facility has moved to expanded and upgraded quarters and provides a very flexible system for measuring the optical properties of solids.

The Ceramics Fabrication Facility

The Ceramics Fabrication Facility continues to operate efficiently to meet the needs of the ceramic researchers for specimen preparation. Its capabilities include a high temperature (2300 C), high pressure (60,000 psi) vacuum / atmosphere hot press and a HIP unit capable of achieving 2300 C and 30,000 psi pressure. It is also equipped with the capability if HIPing in an oxygen atmosphere. No major change in the facility occurred during this past year.

The Low Temperature Facility

Two SQUID units are operated in the low temperature facility; one of which is equipped for ultra low field operation. The demand for these units is so high that they operate on a 24 hour basis.

A vibrating specimen magnetometer is also operated by this facility and is used primarily for measurements on magnetic and paramagnetic specimens over the temperature range from 4 K to 300 K.

The Microfabrication Facility

This facility has seen increased demand in recent years as a result of increased interest in MBE crystal growth and experiments carried out with this class of materials. The Microfabrication facility has installed a JEOL SEM as a very high resolution e^- beam lithography unit. In addition the facility operates a number of PVD systems for film growth, electron beam evaporators, sputtering systems for deposition and etching, mask aligners, etc.

I. GRADUATE STUDENTS SUPPORTED BY THE MRL/DOE

Name	Anticipated Graduation Date
Abraham, Daniel	1993
Agarwal, Avinash	1994
Arnett, Michael	1996
Batzer, Robert	1994
Bonham, Scott	1994
Bui, Tho	1993
Butler, Christopher	1996
Carlisle, John	1993
Chang, Carole	1994
Charnick, Suzanne	1995
Chen, Jie	1994
Chen, Yuewu	1994
Cheon, Jin	1993
Chey, Sukjay	1996
Chow, Mei-Kam	1993
Chung, Dean	1995
Chung, Ki-Sup	1997
Clem, Paul	1996
Compton, David	1995
David, Edwin	1995
Day, Nishit	1995
Day, James	1996
Desoto, Stewart	1993
Dorsten, Jeffrey	1995
Dua, Praveen	1995
Entley, William	1995
Ferreira, Paulo	1995
Fradkin, Mark	1993
Fu, Gaoling	1997
Fujita, Isao	1994
Galloway, Collin	1994
Ghaly, Mai	1993
Gorlin, Philip	1994
Hao, Jinling	1994
Haworth, John	1995
Hollar, Eric	1996
Houser, Eric	1993
Huang, Ching-Hua	1995
Hug, John	1994
Huggins, Kevin	1996
Hunt, William	1996
Kepler, Keith	1995
Kim, James	1994
Kim, Yongil	1993
Kim, Young-Woon	1994
Klatt, Jeffrey	1993
Kwon, Yongkyung	1994
Lakeman, Charles	1995
Lau, See Yan	1995
Lee, Sang	1998
Lee, Young	1993
Liang, Shurong	1995
Lin, Deng-Sung	1993
Lin, Wenbin	1994
Little, Thomas	1996
Lordi, Scott	1994
Manheim, Edna	1993
Marquart, Todd	1994
Martindale, Joseph	1993
Menezes, Marlon	1996
Nelson, Melissa	1996
Nomura, Niki	1993
Paik, Chi-Hun	1993
Palovchik, Rebecca	1995
Papapanayiotou, Demetrius	1994
Park, B.J.	1996
Park, Changwoo	1993
Park, Jung	1996
Pohland, Oliver	1995
Pollack, Margolita	1994
Presley, Darryl	1996
Raghuraman, S.	1993
Reimer, Paul	1993
Ritley, Kenneth	1995
Roubik, Jeffrey	1993
Rudland, David	1993
Rynders, Rebecca	1993
Sabel, Dawn	1993
Sakaie, Ken	1996
Schmidt, Wolfgang	1995
Sengupta, Samit	1994
Shi, Jing	1994
Sieger, Matthew	1995
Sneddon, Douglas	1994
Son, Sehwan	1993
Spencer, Michael	1993
Tao, Rong	1995
Tien, Chee	1994
Tomasch, Gregory	1993
Turkot, Britt	1996
Twesten, Ray	1996
Van Nostrand, Joseph	1997
Van Sambeek, Andrew	1995

Walker, Kenneth	1997
Wang, Jun	1994
Wu, Jianjun	1996
Xiao, Hanzhong	1993
Xu, Wei	1994
Yoon, Howard	1993
You, Young-Hyuk	1994
You, Yu-Jian	1995

J. PUBLICATIONS

J.B. Adams

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