University of Illinois at Urbana-Champaign
Materials Research Laboratory

Progress Report for FY 1991
and
Research Proposal for FY 1992

Department of Energy
Grant DEFG02-91ER45439

October 1991

University of Illinois at Urbana-Champaign
Materials Research Laboratory

Progress Report for FY 1991

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MASTER

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MATERIALS RESEARCH LABORATORY OVERVIEW

I. SUMMARY OF IMPORTANT ISSUES

Organizational Overview

The Materials Research Laboratory at the University of Illinois is an interdisciplinary laboratory operated in the College of Engineering. Its focus is the science of materials and it supports research in the areas of condensed matter physics, solid state chemistry, and materials science. These research programs are developed with the assistance of Faculty, students, and Research Associates who are members of the Departments of Physics, Materials Science and Engineering, Chemistry, Chemical Engineering, Electrical Engineering, Mechanical Engineering, and Nuclear Engineering. The professional staff of the M.R.L. work in conjunction with these faculty, as required for the research programs. These faculty associates are chosen for their intellectual competence and creativity on the basis of proposals submitted to the Materials Research Laboratory. All proposals and the resulting programs are reviewed periodically to ensure their continuing quality; continuation of funding depends on the quality and productivity demonstrated in these reviews.

Support for the intellectual program of the Materials Research Laboratory is obtained from the Department of Energy Grant DEFG 02-91ER45439, from Cooperative Agreement DMR-86-12860/89-20538 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. Each program has specific goals and characteristics and they each complement and strengthen the others. Close cooperative relationships are also maintained with other research units on campus; notably the Coordinated Science Laboratory, the Materials Engineering Research Laboratory, the

National Center for Supercomputing Applications and the N.S.F. Engineering Research Center, as well as the academic departments.

The general organizational structure of the M.R.L. is indicated in Figure 1. Howard Birnbaum acts as the Director of the Materials Research Laboratory and reports to the Dean of Engineering. In this position, he has oversight responsibility for both the D.O.E. and the N.S.F. programs and supervises the Central Facilities of the M.R.L. The programs of the M.R.L. are under the technical leadership of H. K. Birnbaum for the D.O.E. Metals and Ceramics Program, T.C. Chiang for the D.O.E. Solid State Sciences and Materials Chemistry Program, J. Wolfe for the N.S.F./ M.R.L. Program and M. Klein for the University of Illinois part of the N.S.F. S&T Center Program.

The Executive Committee of the laboratory consists of H. Birnbaum, W. Testory, T.C. Chiang, J. Wolfe, and M. Klein and has the responsibility for advising the Director of the M.R.L. on the general policies and needs of the Laboratory. The Director of the M.R.L. coordinates its needs and opportunities with the relevant Department Heads; A. Anderson of Physics, J. Jonas of Chemistry, J. Economy of Materials Science and Engineering, T. Trick of Electrical Engineering, T. Addy of Mechanical Engineering, and B. Jones of Nuclear Engineering.

Programs of the M.R.L. reflect the best research interests of the Principal Investigators, the M.R.L. management, and the supporting agencies. In FY 1991 the D.O.E. program is broadly based on materials as indicated in Figure 2 and on areas of Materials Science as shown in Figure 3. As can be seen, the D.O.E. program achieves an excellent balance between the different classes of materials and the various scientific interests in the area of materials.

Figure 1. Organizational Structure of the M.R.L.

Figure 2. Materials Focus of MRL Research

Programmatic Changes

In the past year, we have significantly increased our efforts in the areas of synthesis of novel materials based on organic and polymeric solids. Of particular note is the effort to synthesize materials which have exciting "field responsive" properties such as non-linear optical crystals, ferromagnetic organic solids and conducting organic materials.

Ceramic and metallic synthesis has also received increased attention with the development of

novel methods of producing powders having a controlled size distribution, and the development of an understanding of how to control the flow and packing of these materials so that "defect free" ceramic materials can be developed by subsequent sintering. A great increase in the effort to produce and determine the properties of "nanophase" metals and ceramics has taken place this last year and is partially funded through the DOE initiative on Synthesis and Processing which is being directed through the Sandia National Laboratory.

Figure 3. MRL Functional Efforts

Faculty and Staff Changes

In FY 1991 and 1992 the MRL has the opportunity to make several significant additions to its faculty in areas of research of interest to the D.O.E. Professor J. Murray Gibson joined the faculty of the Physics and the Materials Science and Engineering Departments from Bell Laboratories, and will be associated with the D.O.E. program. He is focussing his efforts on the use of electron microscopy methods to study the surfaces of solids and the interactions of gases

with the surfaces. A novel UHV surface analysis instrument has been designed by him and will be installed in the M.R.L. A description of his research program is contained in Section C.1.

As a part of the new initiative on the Molecular Structure of Liquid-Solid Interfaces we began a program entitled "Molecular spectroscopy of the Solid-Liquid Interface" by Professor Paul Bohn in FY91. Professor Bohn is a member of the Department of Chemistry. In the same new initiative we began a new effort, "Atomic

Resolution Electrochemistry of Corrosion and Deposition Processes" led by Professor Andrew Gewirth of the Department of Chemistry. These programs are described in Section C.2.

Two additional opportunities have been presented to the D.O.E. program by the addition of Professor Ralph Nuzzo from Bell Laboratories and Professor Ken Schweizer from Sandia Laboratories to the faculty of the Department of Materials Science and Engineering. Professor Nuzzo is an outstanding young surface chemist whose research focuses on the interactions of organic molecules, such as polymers, with surfaces, and on the chemistry of MOCVD crystal growth processes. Descriptions of his research are included in Sections C.2.

Professor Ken Schweizer is an outstanding theorist in the field of Polymer Physics. He is proposing an effort in the area of "polymer Alloys"; an approach to rationalize the synthesis of new polymeric materials designed to have greatly improved properties. A description of his research is included in Section C.2.

Professor Faulkner has been appointed Dean of the L.A.S. College at the University of Illinois and his program was terminated in FY 91.

Hartmut Zabel's program terminated in FY 91 as he has decided to remain in Germany.

The program of Professor Anderson will be ended during FY 91 as he is retiring from the Faculty and has expressed a desire to phase out his program.

In addition to the above faculty changes, the Physics Department will be making a professorial appointment for Dr. Ian Robinson whose research interests are in the area of X-ray physics. His research program will be supported by the D.O.E. program.

We have added a new engineer, Boyd Bowdish, who is skilled in the maintenance and operation of M.B.E. equipment and who will assist in the operation of the EpiCenter.

Additional professional technicians have been added (one each) to the Center for Microanalysis of Materials and the Laser Facility.

Graduate Students

The D.O.E. research program supports the thesis research of 82 graduate students, the majority of whom are Ph. D. candidates. Of these students 23 are in Physics, 24 are in Chemistry, 25 are in Materials Science, 9 are in Chemical Engineering, and 1 is in Mechanical Engineering. The names and approximate dates of graduation are included in Section I. The D.O.E. program also supports the research of 30 post doctoral Research Associates.

During this past year 5 graduate students who have received their M.S. degrees and 24 students who have received their Ph.D.s were supported by the D.O.E. program. The majority of these students have gone on to take positions in industries and National Laboratories, while the rest have taken positions at Universities.

Technology Transfer

The past year has seen the beginning of an increased awareness of technology transfer from the D.O.E. program to industry. Professor Robert Averback has been active in the efforts to industrialize nanophase technology through the formation of a company, Nanophase Technologies Corporation, which was organized by ARCH at Argonne National Laboratory.

Professor Sam Stupp has developed a two dimensional, liquid crystal based polymer which is bonded in a manner which allows the development of three dimensional solids by stacking of the two dimensional sheets. These materials appear to have very interesting field responsive aspects, such as non-linear optical properties. This development was an outgrowth of the science supported by our Field Responsive Polymeric and Organic Materials effort.

Professors Robertson and Birnbaum have developed a level of understanding of the structure and chemistry of metal/polyimide interfaces which is of direct interest to the semiconductor packaging industry. This technology is being transferred to the Motorola and Amoco Corporations under a joint research agreement which supports their MRL/DOE program.

The research on elevated temperature subcritical crack propagation in structural materials by Professor Jim Stubbins has led to development of an interaction with SCM Metals Inc. directed

toward using these concepts to improve the properties of SCM's Glidcop alloy series, which are metal matrix composites.

Professor C. Altstetter's DOE sponsored research on the use of superionic conductors to study the

thermodynamics of O and H in metals (completed a number of years ago) has been adopted by Nippondenso Technical Center USA as the basis for an electrochemical sensor to determine the charge state of a battery.

ER F 4620.1
(7-88)

U.S. Department of Energy
Grant Application Budget Period Summary
(See Reverse for Definitions and Instructions)

OMB Approval
No. 1910-1400

Please Print or Type

Organization: UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN		Period Covering		FOR DOE USE ONLY	
		From 01-01-92 To 12-31-92		Proposal No. Award No.	
Principal Investigator (P.I.)/Project Director (P.D.): H. K. BIRNBAUM, T.-C. CHIANG		DOE Funded Person-Mos		Funds Requested By Applicant	
<small>A SENIOR PERSONNEL PVPO Co Pts Faculty and Other Senior Associates (List each separately with title. A & B show number in brackets. Attach separate sheet, if required.)</small>		<small>Ctr</small>	<small>Acad</small>	<small>Sum</small>	<small>\$</small>
1 H. K. BIRNBAUM			2.25	1.0	40,500
2 T.-C. CHIANG			2.25	1.0	23,484
3 SENIOR				24.5	217,618
4					
5					
6 (4) TOTAL SENIOR PERSONNEL					281,602
7 OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
130.5 POST DOCTORAL ASSOCIATES		366			864,923
2 (1) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)		12			17,450
3 88.5 GRADUATE STUDENTS		492			1,187,386
4 (2) UNDERGRADUATE STUDENTS					5,000
5 () SECRETARIAL-CLERICAL					
6 () OTHER					
TOTAL SALARIES AND WAGES (A + B)					2,356,361
C FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					243,855
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					2,600,216
D EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM)					
TOTAL EQUIPMENT					966,000
E TRAVEL 1 DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)					125,000
2 FOREIGN					
F OTHER DIRECT COSTS					
1 MATERIALS AND SUPPLIES					460,193
2 PUBLICATION COSTS/PAGE CHARGES					25,000
3 CONSULTANT SERVICES					
4 COMPUTER (ADPE) SERVICES					83,500
5 CONTRACTS AND SUBGRANTS					
6 OTHER MRL ADMIN., MRL FACILITIES, MRL SHOP					733,153
TOTAL OTHER DIRECT COSTS					1,301,846
G TOTAL DIRECT COSTS (A THROUGH F)					4,993,062
H INDIRECT COSTS (SPECIFY RATE AND BASE)					
MTDC 28.3%				1,139,659	
TOTAL INDIRECT COSTS TUITION-GRAD. ASST. SALARY 29.5%				350,279	1,489,938
I TOTAL DIRECT AND INDIRECT COSTS (G + H)					6,483,000
J APPLICANT'S COST SHARING (IF ANY)					
K TOTAL AMOUNT OF THIS REQUEST (ITEM I LESS ITEM J)					6,483,000
PVPO TYPED NAME & SIGNATURE H. K. BIRNBAUM <i>H K Birnbaum</i>		DATE		10/31/91	
INST REP. TYPED NAME & SIGNATURE J. J. Kameron, Director <i>J J Kameron</i>		DATE		10/31/91	
Grant & Contract Administration					

B. GENERAL PROGRAMMATIC AND INSTITUTIONAL ISSUES

B.1 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 system of the U.S.

The Department of Energy provides research support to the M.R.L. which has many of the best aspects of the D.O.E. Laboratory Program and the D.O.E. University Program. This support allows development of a unique combination of creative University faculty directed programs interfaced with Central Facilities. These Central Facilities allow development and maintenance of major, expensive equipment which is available to all members of the M.R.L. An excellent group of professional scientists maintain, operate, and develop these instruments as well as teach their use and the science associated with them to the students and Research Associates of the M.R.L. The flexible support of the D.O.E. program allows best utilization of the available funding through local management which can recognize and optimize scientific opportunities.

The M.R.L. program is about 30% of the total Materials Science and Engineering effort on the University of Illinois campus and a much larger fraction of the Materials Science effort. This size allows the M.R.L. to choose the best of the available programs, support them at an effective level, and to 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. A large number of excellent, interactive research programs are headed by the best faculty in the areas of Solid State Physics, Materials Chemistry, and Materials Sciences. A description of the MRL effort based on the types

of materials studied and on the functional areas of study is given in Figures 2 and 3 in Section I.

Coordinated efforts are being carried out in the areas of Structural Ceramics, Grain Boundaries, Interfaces and the Science of Crystal Growth, Field Responsive Polymeric and Organic Materials, and The Molecular Structure of Solid-Liquid Interfaces and Its Relation to Corrosion. 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. In the present proposal we are putting forth two additional programs for consideration by the D.O.E.: "The Science and Properties of Nanophase Materials" and "Radiation Effects in Crystals". These programs are described in Section C of this Executive Summary.

B.2. PROGRAM DIRECTIONS AND CHANGES IN DIRECTIONS

Materials Synthesis

A continuing focus of the M.R.L. is on the synthesis and characterization of new materials which are being developed and studied for the insights which they can give to basic solid state science. These include compositionally and structurally modulated materials, intermetallic alloys, novel ceramic solids, nanophase metals and ceramics, metastable semiconducting material, novel polymeric and organic materials, and the new high T_c ceramic materials. The M.R.L. offers an environment, made possible by D.O.E. support, which allows effective coupling of the solid state sciences, materials sciences, characterization methods, and novel growth methods necessary for progress in the important areas of materials synthesis.

Due to the addition of new faculty in the Departments of Physics and Materials Sciences and Engineering, and the close coupling which we have made with the faculty of the Department of Chemistry, we find that we can greatly expand our efforts in Materials Synthesis by funding the research programs of Professors Ken Schweizer and Ralph Nuzzo, described in Sections C.2.

The Molecular Beam Epitaxy Laboratory (the EpiCenter) has been operating for about two years and has been used to produce some very exciting

new materials and concepts in the area of crystal growth. We have completed the installation of facilities to supplement M.B.E. growth with chemical beam growth based on gaseous sources; allowing greater flexibility and control of the source materials. These new systems have enabled a great improvement in the flexibility and quality of growth of tailored materials. The establishment of this capability was a major undertaking as a result of the safety issues raised by these toxic gases.

Central Facilities

Improvements in the capabilities of the Central Facilities have been funded with the assistance of all of the MRL programs and of the University. Assignment of financial responsibilities to the various programs are in proportion to their anticipated use of the facility.

The Center for the Microanalysis of Materials has added a new SEM designed for general purpose use and for analytic applications. This instrument has been modified to be capable of fine line lithography; a techniques which is needed for the fabrication of structures used for scientific research.

In support of the program of research being developed by Professor J. Murray Gibson, we have ordered a new U.H.V. surface analysis instrument based on electron microscopy and incorporating other surface preparation and characterization techniques. This instrument will allow the structure of surfaces to be imaged in the electron microscope at high resolution and under controlled vacuum and gas conditions. The application of this instrument is described in Professor Gibson's program description in Section C.1.

An atomic resolution electron microscope is in the process of being installed. Professor Gibson will lead the efforts at Illinois in High Resolution microscopy. In addition to Gibson's, a number of other programs at the MRL will make use of the atomic resolution capabilities, e.g. the programs of Ian Robertson, Avi Zangvil, H.K. Birnbaum, David Payne, as well as a number of investigators supported by the MRL/NSF programs.

In connection with the hiring of Professor Ralph Nuzzo by the Department of Materials Science and Engineering, we were able to obtain a high resolution, small spot X-ray Photoelectron

Spectrometer made by Surface Sciences Corp. This unit was paid for by University of Illinois funds and from the discretionary funds of the MRL. It is being installed in the Center for the Microanalysis of Materials where it will replace a "home-made" unit with much less capability. This XPS system will complement the present XPS system in the Center and will be used for "expert" applications requiring extended access and specialized capabilities.

Funds for the installation of a PIXIE beam line and facility on the Van de Graaf accelerator have been obtained and design and installation of this equipment is underway. The PIXIE technique for quantitative analysis of materials by ion induced x-ray fluorescence will greatly enhance the analytic capabilities of the CMM.

The Center for Computation greatly upgraded its computational facilities with the installation of a series of RISC machines for computational intensive studies. These Unix based systems have very high speed computational abilities combined with access to large memories. They are excellent instruments for molecular dynamics and for materials simulations in general.

The Laser Facility has installed a non-linear optics capability which is of great interest in characterizing materials developed by our Field Responsive Organic and Polymeric Materials efforts. The pulsed laser capabilities have been improved and now extend to the femtosecond range. We have also improved our data acquisition capabilities in this facility.

Programmatic Changes

Despite severe budgetary limits, we have been able to initiate support of new programs for Professors J. Murray Gibson, Ralph Nuzzo and Ken Schweizer.

With the assistance of the new initiative funds received for the program on The Molecular Structure of the Solid-Liquid Interface we have been able to begin new programs for Professors P. Bohn and A. Gewirth.

Professor Faulkner has been appointed Dean of the L.A.S. College at the University of Illinois and his program was terminated at the end of FY 90.

Hartmut Zabel's program terminated in FY91 as he has decided to remain in Germany.

Interpass Construction

The interpass office structure located between the M.R.L. and the Coordinated Science Building (adjacent to the M.R.L.) is in the final architectural planning stage. This construction is of great importance, as it will allow us to incorporate most of our research programs in a single contiguous structure (the M.R.L., C.S.L., and Interpass buildings), and thus enhance the scientific interactions which are at the heart of the M.R.L. program. State of Illinois funding has been obtained which will allow the construction of a three story building with a basement, and the completion of two floors of offices. The Engineering College has undertaken to complete the third floor which will be used for offices for the faculty and students of the M.R.L. We still need to locate funds for the completion of the basement which is intended to house the Center for the Microanalysis of Materials. This will require about \$ 600,000 which is being requested as construction funds from the D.O.E. (see Section G.2).

B3 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 Contract DE-AC02-76ER-01198 with the Department of Energy, from Cooperative Agreement DMR-86-12860 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 D.O.E. and the N.S.F. programs and supervises the Central Facilities of the M.R.L. Mr. W. Testory is the Assistant Director of the M.R.L. The programs of the M.R.L. are under the technical leadership of H. K. Birnbaum for the D.O.E. Metals and Ceramics Program, T.C. Chiang for the D.O.E. Solid State Sciences and Materials Chemistry Program, J. Wolfe for the N.S.F./ M.R.L. Program and M. Klein for the University of Illinois part of the N.S.F. S&T Center Program. The Executive Committee of the laboratory consists of H. Birnbaum, W. Testory, T.C. Chiang, J. Wolfe, and M. Klein, and has the responsibility for advising the Director of the M.R.L. on the general policies and needs of the Laboratory. The Director of the M.R.L. coordinates its needs and opportunities with the relevant Department Heads; A. Anderson of Physics, J. Jonas of Chemistry, J. Economy of Materials Science and Engineering, T. Trick of Electrical Engineering, T. Addy of Mechanical Engineering, and B. Jones of Nuclear Engineering.

Management Changes

At the beginning of FY 1991 the M.R.L. relationship with the D.O.E. changed from a contract to a grant.

Myron Salamon stepped down as Head of the M.R.L./N.S.F. Program to return to full time teaching and research. Jim Wolfe will replace him in the position of N.S.F. Program Head, relinquishing the position of Head of the D.O.E. Solid State Sciences Program. To replace Jim, we have chosen Tai-Chang Chiang who is a Professor of Physics and has been a member of the Solid State Sciences Program for a number of years. These changes went into effect on June 1, 1991.

B.4 PROGRAM REVIEW ACTIVITIES

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 D.O.E. 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

D.O.E., 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. This procedure was used for the programs of Greg Girolami and Carl Altstetter and the results of the review will be used to determine the funding of these programs. The review of Professor Girolami's program was exceptionally favorable. The results of the review of Professor Altstetter's program are presently being collected and evaluated.

In addition to the above review procedures, the Program Heads, with the concurrence of the Director, may terminate a program for purely programmatic reasons having to do with funding, new initiatives, etc. In FY 91 the program of Professor L. Faulkner is being ended as a result of Professor Faulkner taking on additional University duties as the Dean of Liberal Arts and Sciences. The program of Professor Anderson will be ended during FY 91 as he is retiring from the Faculty and has expressed a desire to phase out his program.

A number of programs were proposed for funding to the MRL but were turned down after review. In some cases these were not of a quality suitable for D.O.E. support and in others the decision was based on the limited funds available.

C. RESEARCH SUMMARIES FOR NEW PROGRAMS FY91

C.1 KC-02-01 METALS AND CERAMICS

J.M. GIBSON

Transmission Electron Microscopy of Surfaces and Interfaces

(This program will begin in FY91)

GOALS AND FUTURE DIRECTIONS

The program will focus on the elucidation of interface and surface structure using quantitative transmission electron microscopy (TEM). This includes quantitative analysis of high-resolution images from interfaces taken in cross-section, and diffraction and imaging analysis of data from *in-situ* experiments in an ultra-high vacuum TEM.

The transmission electron microscope has been widely used in materials science, but its application in surface science has been limited by the inadequacy of the specimen vacuum. In recent years, several groups have made the effort to achieve ultra-high-vacuum conditions in the

specimen regions of the TEM, with astounding success, e.g. in the solution of the Si(111) 7×7 surface reconstruction¹. Gibson has demonstrated that atomic steps can be imaged during the oxidation of silicon², and that quantitative analysis of diffraction data can yield atomic structure of surfaces in the initial stages of oxidation³. He has also studied the mechanisms of metal semiconductor interface formation from *in-situ* experiments⁴. At the U. of I., Gibson plans to continue these studies of surface reaction and *in-situ* epitaxy, both on Si and other materials, and in the area of the fundamentals of epitaxial growth. To this end, a new surface science TEM is being developed, which will have the capability of 10^{-10} torr pressure in the specimen region, and simultaneous study with complementary surface techniques. It will be a unique capability combining medium resolution TEM and Reflection EM with fully controllable *in-situ* surface cleaning, reaction and characterization. To achieve this, more free volume will be introduced around the specimen, at the expense of resolution, which should still be approximately 20 Å. An example of the efficacy of the *in-situ* method, taken with Gibson's modified UHV microscope at Bell Labs, is shown in Figure 1. This shows a pair of surface step

Two dark-field TEM images from the same area of a thin Si (111) foil before and after *in-situ* exposure to oxygen. The image intensity changes from dark to bright when a monolayer is added to the thickness of the foil, and thus the dark/bright boundaries reveal monatomic steps on the two surfaces. Although the thickness has changed after the formation of an oxide layer in (b), causing a bright/dark contrast reversal, atomic steps have remained fixed in the same position. Therefore, step flow cannot occur during the oxidation process under these conditions (with acknowledgement to Frances Ross at Bell Labs).

images from the same area of a thin Si foil, before and after oxidation. Surface steps before oxidation are found in the same configuration at the buried interface, implying that oxidation does not occur by step flow, as proposed by Mott⁵. The method, which employs bulk-forbidden surface sensitive Bragg reflections⁶, is unique in allowing the observation of surfaces and buried interfaces without loss of detail, including the transformation of one to the other, as in oxidation.

In the area of high-resolution TEM, there will be quantitative studies of interface roughness and interdiffusion in semiconductor quantum wells, and ceramic and metal interfaces. The methods will be based on the quantitative pattern recognition methods of Ourmazd et. al.⁷, but with the significant improvement of avoiding the assumption of image linearity by using full image refinements from statistical data.

As part of both of these studies, techniques for quantitative matching of images and diffraction data will be developed, including estimation of statistical reliability and refinement. This has been successfully applied recently by Gibson in the identification of backbonded oxygen atoms by electron diffraction analysis³.

Significance:

Surfaces are very important in controlling the electronic properties of semiconductor devices, e.g. the efficiency of photovoltaics, and the corrosion and mechanical behavior of materials. Despite the massive efforts in surface science, using well-controlled surfaces in ultra-high vacuum, there is still little fundamental understanding of the chemistry and structure of real world surfaces and their processing. Typically, these are encapsulated by oxide or other layers. The transmission electron microscope is unique in permitting study of microstructure at buried interfaces without removal of overlayers. By combining this with the use of ultra-high vacuum conditions, one can continuously monitor the transition of a clean surface into an encapsulated surface, such as by *in-situ* study of oxidation or film deposition. Using a clean surface as the starting surface allows much better control, but the conditions of real world surface processing can be reproduced.

In addition, high resolution imaging of interfaces can permit new insight into buried interfaces. Viewing interfaces in the cross-section projection can give complementary information to

the plan view studies, and can be used to study systems that cannot be prepared *in-situ*.

References

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5. N.F. Mott, Proc. Roy. Soc. **A376**, 207 (1981).
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7. A. Ourmazd, D.W. Taylor, J. Cunningham and C.W. Tu, Phys. Rev. Lett. **62**, 933 (1989).

Honors

Elected Fellow of the American Physical Society (1990)

Membership of the University of Chicago
Review Committee for the Materials Science
Division of Argonne National Lab (1990-1993)

Councillor of the Materials Research Society (1990-1993)

Member of the Editorial Board of Applied
Physics Letters (1991-1994)

Invited Talks

March meeting of the American Physical Society,
Anaheim, CA

Spring Meeting of The Metallurgical Society,
Cincinnati, OH

Plenary Lecture on "High Resolution Electron
Microscopy of Semiconductor
Interfaces" at the International Conference of The
Physics of Semiconductors, Thessaloniki,
Greece (August 1990)

International Congress on Electron Microscopy,
Seattle, WA (August 1990)

Keynote Lecture on "TEM of Interfaces",
Workshop on Interfaces, Berkeley, CA
(August 1990)

Fall Meeting of the Materials Research Society,
November 1990, Boston MA

C.2 KC-02-03 MATERIALS CHEMISTRY

PAUL W. BOHN

Molecular Spectroscopy of the Solid-Liquid Interface

(This program begins in FY91)

GOALS:

In situ molecular spectroscopic probes will be used to investigate the structural chemistry of aromatic heterocyclic molecules of interest as corrosion inhibitors on various metal oxide surfaces. Properties of interest are: (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, a molecular level understanding of the relative importance of physical blocking of active corrosion nucleation sites vs. generic blocking of all surface sites is being developed. The results of these experiments will be compared with the UHV results on similar systems obtained by Wieckowski and Gellman to correlate with the macroscopic passivation behavior obtained by Alkire. 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 scale.

FUTURE DIRECTIONS

In this first year of experiments Professor Bohn will begin by characterizing the surface structure of virgin inhibitor layers on copper and iron oxide surfaces. This will be accomplished by using surface Raman scattering to probe the adsorbate-substrate binding, and then using the linear dichroism experiment to probe the supermolecular structure and orientation of the adsorbate molecules. In parallel will be the development of a sub-monolayer sensitivity fluorescence anisotropy experiment which will be used to characterize the distribution of orientations found in the structures studied. The effect that inhibitor packing has on structure and, in collaboration with Alkire, the effect on

passivation properties of the films will be studied. In addition, studies will begin of specific activator species, in collaboration with Wieckowski and Alkire. The species to be examined are those for which the equilibrium adsorption behavior and dynamics have been thoroughly studied in the absence of the inhibitor films. In FY 92 a close collaboration will begin with Wieckowski to study the adsorption of inorganic ions (halides, sulfates, thiosulfates), by performing radiochemical and SHG adsorption experiments in parallel. Initially correlations of the observations will be at unmodified single-crystal metal surfaces, followed by an examination of the effects of the inhibitor films characterized during FY 91. At the same time, for well characterized inhibitor films, Professor Bohn will begin a study of the effect of external perturbations, primarily using extremes of ionic strength, temperature, and pH, on the structure of the inhibitor films. In FY 93 work will begin on inhibitors bound to surfaces whose compositions have been specifically tailored by Alkire. The idea is to prepare surfaces with reproducible concentrations of MnS inclusions. These surfaces will be characterized from the atomic point of view by Gewirth, followed by Bohn's experiments to determine how the binding of inhibitors is affected by these inclusions. In the third year, attention will turn to additional collaborative experiments with Wieckowski on the acetylenic alcohols, phosphates and phosphonates.

Honors

Coblentz Society Award (1990)

Invited Talks

Structural Perturbations in Two-Dimensional Molecular Assemblies on Integrated Optical Structures, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, November 20, 1990.

Chemical Permeability in Polymer Multilayers on Integrated Optical Structures, Workshop on Advanced Laser Technology in Chemical Measurements, Oak Ridge, TN, November 12-14, 1990.

Probing Purposeful Structural Perturbations in Ultrathin Organic Films, IBM Almaden Research Center, San Jose, CA, October 2, 1990.

Probing III-V Materials Properties in Integrated Optical Structures, Center for Compound Semiconductor Microelectronics, University of Illinois at Urbana-Champaign, September 26, 1990.

Building the Biochip: Results from Genetic Engineering, Surface Chemistry, and Laser Spectroscopy, Hewlett-Packard Corp., Palo Alto, CA, July 11, 1990.

Biomembrane Superlattices, 3rd Annual BRDC Symposium, Peoria, IL, June 4-5, 1990.

Waveguide Linear Dichroism and Raman Depolarization Measurements for Determination of Molecular Orientation at Surfaces, Department of Chemistry, Northwestern University, May 7, 1990.

Optical Waveguides and Spectroscopy: Thin Films from 10 Å to 10 μm, 199th American Chemical Society National Meeting, Boston, MA, April 22-28, 1990.

Waveguide Linear Dichroism and Raman Depolarization Measurements for Determination of Molecular Orientation at Surfaces, Department of Chemistry, University of Minnesota, Minneapolis, MN, April 6, 1990.

Waveguide Linear Dichroism and Raman Depolarization Measurements for Determination of Molecular Orientation at Surfaces, Topical Meeting on Laser Applications to Chemical Analysis, Incline Village, NV, February 5-8, 1990.

Waveguide Linear Dichroism and Raman Depolarization Measurements for Determination of Molecular Orientation at Surfaces, Department of Chemistry, Purdue University, West Lafayette, IN, January 23, 1990.

ANDREW A. GEWIRTH

Atomic Resolution Electrochemistry of Corrosion and Deposition Processes

(This program begins in FY91)

GOALS

Research is directed toward understanding, at an atomic level, fundamental deposition and corrosion processes occurring in electrochemical environments. We focus on underpotential deposition (upd) and dissolution of metal monolayers on single crystal surfaces, the dissolution of bulk deposited metals, and on the photocorrosion of semiconductor photoelectrodes. We are interested in understanding the atomic interactions active on these surfaces that give rise to the macroscopic phenomena. To study these materials, we have developed the Atomic Force Microscope (AFM) as a tool to investigate these electrode surfaces while they are immersed in electrolyte and have demonstrated that atomic resolution images can be obtained on several close-packed metal surfaces in solution and under potential control. In the figure below, we observe by AFM the formation of monolayer steps occurring in the dissolution of bulk Cu which has been deposited on an Au(111) electrode surface.

6x6 nm Atomic Force Microscope image of the dissolution of bulk-deposited Cu(111) on a Au(111) surface obtained at a potential of +0.050 V vs $\text{Du}_2^{+}/0$ in a 0.1 M perchloric acid solution. A monoatomic step is visible at the right of the image.

FUTURE DIRECTIONS

Our ability to routinely obtain atomic resolution images of electrochemical processes on electrode surfaces enables us to begin to characterize this mostly unknown area. We will investigate the influence of differing electrolytes on electrochemical processes where we have shown previously that different electrolytes produce a wide variety of structures in monolayers of metals on electrodes. We anticipate the same rich variety to obtain during semiconductor photocorrosion processes, and this will also be characterized.

Honors:

Presidential Young Investigator Award, 1990

Invited Talks:

Electrochemical Society, Seattle Meeting, Fall, 1990.

Eastern Analytical Symposium, Fall, 1990.

RALPH G. NUZZO

Mechanistic and Synthetic Studies in Chemical Vapor Deposition

GOALS

The increasing importance of chemical vapor deposition (CVD) processes in microelectronic device fabrication is now well appreciated. Our understanding of the rich and complex surface chemistries involved in such processes remains limited, however. Our goals in this program are to study and develop new chemical vapor deposition processes. As a central feature of this effort, we will conduct in depth mechanistic examinations of reactive gas-solid interactions involved in materials growth by CVD. These studies will define the important surface mediated reaction mechanisms and energetics at a level of understanding which has relevance to, and impact on, process design and engineering. The information obtained in this program will be used to shape the development of new processes

for the preparation of materials of current or potential utility in technology.

HIGHLIGHTS AND BACKGROUND

Our most notable success has come in establishing the surface reaction mechanisms involved in the steady state growth of aluminum as effected by the exhaustive surface-mediated thermolysis of several organoaluminum reagents, including tri-isobutylaluminum (TIBA, considered as being the most the most likely source for commercialization), trimethylamine alane (TMAA), and triethylamine alane (TEAA). Studies conducted in ultra-high vacuum environments using surface sensitive spectroscopies and molecular beam-surface scattering techniques yielded kinetic parameters which quantitatively predict growth rates and, to a lesser extent, the growth morphologies seen in CVD reactors operated at significantly higher pressure (~0.5-10 torr).

The reactive sticking probability of TIBA on an aluminum surface is high (near unity). On other surfaces encountered in device fabrication, such as silicon or its oxide, adsorption occurs reversibly with only molecular desorption seen in TPD studies. The decomposition kinetics measured on clean aluminum by either TPD or scattering methods are found to be surface structure sensitive; at 500K the rate is ~5 times faster on the (111) surface than on the (100). The rate limiting step has been definitively identified as being a β -hydride elimination of a surface isobutyl group derived from the dissociative adsorption of TIBA on the surface. The origin of the autocatalysis which characterizes the steady state growth has been identified. The reaction barrier, that is the activation energy of the β -elimination, is much less than the endothermicity of the net reaction (~30 vs. ~70 kcal/mole). The significant parameter here is the stoichiometry. The decompositions of the three alkyl groups originating in TIBA are kinetically uncoupled and, thus, indistinguishable. At 500K the decomposition rate is fast and the only gas phase products formed are hydrogen and isobutylene.

Growth is epitaxial on both the (100) and (111) surfaces and the films obtained are elementally pure. At higher temperatures, we have observed that other reaction channels are accessed, foremost of these being a β -alkyl elimination of a methyl group in a surface isobutyl species. This process produces surface methyl groups which decompose to yield the carbon which is extensively incorporated into the film at these higher temperatures. Through an extensive series of studies using alkyl halides as adsorbates, the structure-reactivity profiles and thermochemical properties of alkyl groups on aluminum surfaces have been defined in significant detail.

We have also determined the surface reaction mechanisms which operate in the steady state deposition of aluminum using the two alane based sources TMAA and TEAA. These reagents, or those with very similar structures (R_3AlH_3 , $R=Et, Me$), yield elementally pure films and the growth is epitaxial on both the (111) and (100) crystal faces of the metal. As had been observed with TIBA, the metal surface displays almost unique autocatalytic activities. The kinetics of decomposition differ markedly from TIBA in other regards, however. For TMAA, the rate of the deposition is limited by the barrier for the surface mediated dissociation of the Al-N bond; for TEAA the rate is limited by the barrier for the recombinative desorption of hydrogen. Both barriers are low, in the range of ~ 18 kcal/mole. The growth rates observed are thus very fast, proceeding with appreciable reaction velocities even at 350K. These barriers are sufficiently low that it is unlikely that other organoaluminum reagents, ones necessarily generating hydrogen as a product, can be expected to yield lower growth temperatures.

These findings have helped shape the direction of current efforts to commercialize an Al CVD process. It is envisioned that this process, if implemented, will find broad utilization in the metallization of ULSI devices (with feature sizes approaching 0.25 μ m) where the conformal coverage capabilities of CVD are uniquely required. Aluminum, because of its excellent properties as a conductor and resistance to corrosion, is a highly attractive candidate material for such metallizations despite the numerous (and potentially very serious) problems which complicate current process designs. These problems—including nucleation of uniform (and/or site selective) growth, catalyzed junction erosion, morphology (especially as it relates to electromigration resistance and device failure

rates), film alloying concurrent with growth to name but a few—remain a daunting experimental challenge. Our understanding of the mechanisms of steady-state growth in these Al-CVD systems is now sufficiently advanced, however, that it is possible to consider, and hopefully establish, the nature of the more complicated surface processes that contribute to nucleation, and to consider reactive chemistries that lead to more compositionally complex materials. It is to these issues that the proposed studies are addressed.

FUTURE DIRECTIONS

Our first area of concern relates to the issue which I refer to as activated nucleation chemistries. We now know that the barriers which control the rates of aluminum film growth at steady state for several different source gasses are (with the trivial exception of transport/flux constraints) limited by the intrinsic rates of reactions occurring on the surface of the metal. For TIBA, TMAA, and TEAA, three different rate limiting steps have been identified. The reactive sticking probabilities and rates measured were found to be sensitive to temperature, surface structure, and composition. They are always highest on the elemental surface of the metal. Dissociative chemisorption on other surfaces, such as Si(111)-(7 $\times$ 7) and SiO₂, is more highly activated. The reasons underlying this are poorly understood but several lines of evidence suggest partial rationalizations. First, on an anhydrous silica surface, where ideally the only basic sites available to bind the adsorbate would be the oxygen atoms in Si-O-Si linkages, the interaction with the aluminum centers is expected to be very weak. As judged from solution phase data for the thermodynamics of complex formation between ethers and various organoaluminum compounds, this interaction for TIBA may be only of the order of the heat of vaporization of the parent compound. The bonding of the amine ligands in the alane complexes (gas phase dissociation energies of ~ 28 kcal/mole) is much stronger than similar bonds formed with oxygen centered neutral donors. It might be expected, therefore, that all three adsorbates would desorb molecularly from high quality oxide surfaces. The substrates have to be heated to very high temperatures to overcome this unfavorable partitioning into the molecular desorption channel. The identification of the species formed by the initial reactions is therefore rendered impossible; the high substrate temperatures used to promote dissociation also lead to the rapid

decomposition of the intermediates. The quality of the films obtained in this manner is also very poor.

The results obtained on silicon prove more puzzling. We have observed that film growth on these surfaces, once initiated, is accompanied by transmetallation reactions (eq. 2).

This reaction proceeds with a high rate at temperatures as low as 330K when either of the alanes is used as the precursor, a feature which presumably reflects the fairly large exothermicity of the reaction. With TIBA, the dominant silane product formed is diisobutylsilane (R_2SiH_2). These reactions require the presence of metal atoms on the surface to proceed (in this sense they are truly catalyzed). That the barriers are high on Si(111)-(7x7) and low on Si(111)/Al ($\theta_{\text{Al}} > 0.1$ monolayers) seems to mirror the reactive sticking probabilities characterizing the initial stages of growth. This suggests a mechanistic relationship may exist.

These specific examples of activated chemistries are suggestive of larger issues which are of concern to processing. Reactions of this sort are the initial chemical events which lead to the initiation of steady state growth. The structural properties established in these very early chemical events will be the ones amplified by the steady state chemistries which proceed autocatalytically.

We propose to study these processes using translational activation. In these experiments, a seeded molecular beam source of the reagents will be impinged on the various substrates, which will be held at low temperature. The translational energy of the molecule, on collision with the surface, provides the energy necessary to surmount the initial barrier to strong/dissociative adsorption. These energies can be varied, as can the angles of incidence. Using standard protocols, which have been developed and applied to great benefit in the study of other systems, a detailed picture of the adsorption process and energetics can be obtained. The correspondence between the thermal barriers and those measured here should be easy to assess. The initial characterization of the products obtained will be made through an application of vibrational (HREELS and IR) and electron spectroscopies as well as through the use of temperature programmed desorption (TPD). We will examine reactive dissociations on oxide surfaces first as we expect the chemistry for them

to be the least complicated. It will be of considerable interest to determine if the TIBA dissociation energetics actually correspond to the known barriers to β -elimination. The dissociation energies for the alanes should be lower than this; we hope to be able to examine the energetics associated with the displacement of the amine ligand coordinated to the complex by a surface donor atom. On Si(111)-(7x7) the adsorption chemistries and energetics may differ considerably. We know that, while activated, the initial reactions are effective in transferring alkyl groups and hydrogen atoms from aluminum centers to silicon. The quantitative differences that exist between oxide and elemental silicon may allow us to gauge what the intrinsic efficiencies could be for the selective filling of vias on devices using an Al CVD process. The energetics should define nominal parameters for the efficient operation of such a process. We are also very interested in observing how these ligands are transferred from aluminum to silicon. Our hope is that the vibrational spectroscopies will allow us to examine this important surface reaction directly. It also will be of value to examine silicon surfaces which bear well defined metal overlayers. For example, it is possible to prepare an ordered ($\sqrt{3} \times \sqrt{3}$) R30° overlayer of Al on Si(111) by careful evaporation of the metal followed by annealing. Surfaces of this sort will allow us to explore how low coverages of metal influence the dissociation barriers. These studies will define the gross energetics of the initial reaction chemistries on pristine surfaces other than the clean metal. We will also undertake a detailed investigation of surface modifications which promote adsorption. We have several potential schemes in mind and comment on one of these specifically. In our studies on TIBA, we noted qualitatively that surface hydroxyl groups vigorously promote adsorption. It is unclear how effective the species generated in this way are in initiating growth. We have developed in other studies, methods useful for the preparation of hydroxylated surfaces on several different materials. Reactive scattering studies conducted on these substrates should give us the kinetic information we require. The outline above provides a general overview of the experiments to be conducted in this portion of the program. The work complements well that which has been done earlier in our laboratory and should utilize our current experimental methods to good advantage. One significant aspect will remain unresolved at the completion of these studies. It is unlikely that the structure of the initial metal

deposits can be established by the techniques currently available to us. This will require the application of other methods, including scanning tunneling microscopy, in follow on experiments.

Studies of Reactive Gas Environments for CVD.

The coordination chemistries of alane discussed in the literature suggest some interesting possibilities for both enhancing and adapting the CVD processes using these sources. The first study we wish to perform relates to nucleation. One is constrained in these systems by the inherent stabilities of the alane complexes. It is not practical in a real system to consider increasing the lability of the precursor further to enhance the initiation of the deposition. The barriers for ligand substitution of various amines are likely to be low however, and this suggests a method of attack. Is it possible to combine gas flows of a precursor such as TMAA and a more bulky amine near the point of reaction and effect partial ligand substitution *in-situ* based on mass action principles? If we can, then it may prove possible to promote initiation in a benign manner (that is with no co-reactants which are incorporated into the film interface with the device). The labile materials generated in this way will undergo more facile cleavage at the substrate.

The second option follows directly from the first. The substitution of ammonia for either of the amines in TMAA or TEAA should be very facile. This product is unstable with respect to further reaction, however. It is intriguing to speculate that these reactants, combined at or near the substrate, could be effective in the deposition of AlN thin films (or precursors thereto). The combination of chemistries here (surface and gas phase) is potentially very complex. There is also little known about the potentially important surface reactions which may occur between aluminum and ammonia. The interactions of TMAA or a transient H_3NAlH_3 with aluminum or aluminum nitride also have not been studied to my knowledge. These uncertainties notwithstanding, the value of this product material in various technologies makes this project a very attractive and high priority aspect of the program.

There are other potential applications for the alane sources, most notable being their use in the growth of AlGaAs devices by CVD. This application has received only limited attention and the relevant surface chemistries and kinetics are currently unclear. There are several

advantages one can envision in using this source for AlGaAs growth. First, the lower temperatures at which one might be able to grow material relative to other aluminum sources could prove attractive with respect to minimizing interfacial reactions in complex device architectures. Second, this reagent is hydrogen rich. This should help promote the efficient removal from the surface of alkyl groups originating, for example, in the gallium source.

In our first experiments, we will use a simplified experimental design. These studies will use GaAs substrates ((111) and (100)) and examine the thermal chemistries both with and without an As flux (we will use an As_2 beam produced with a standard solid GaAs source). The parameters we will examine are both the growth habits (morphology, composition, etc.) and kinetics. The methods to be employed will include reactive scattering, Auger electron spectroscopy, electron diffraction, and X-ray photoelectron spectroscopy as applicable to particular experimental needs. The equipment needed for this work is available to the investigator. We also have considerable experience with the various materials to be utilized.

It is also interesting to consider the reactive chemistries which may occur on GaAs with other Al sources. The reactive transmetalations seen in growth on silicon, chemistries which physically gasify the substrate as new organometallic products, may also occur on compound semiconductors. I am inclined to believe that this is less likely here as the corresponding processes are much less exothermic on these substrates. They are still feasible given the overall thermodynamics involved and their importance should be explored. Doing so by reactive scattering is fairly straight forward and, using protocols similar to those developed for the silicon chemical etching studies, should yield the desired information.

We are also interested in examining the interaction of the alane reagents with oxidized GaAs. It is well known that the oxidation of GaAs yields a complex surface phase. Under mild conditions the surface layer contains Ga_2O_3 , As_2O_3 , and elemental As (more forceful conditions yield GaAsO_4). The As is segregated at the GaAs interface and can have serious negative consequences for desired device properties. Alane is a powerful reducing agent. We have observed in earlier studies that passivating oxides can be grown on many different surfaces via the thermal reaction of silane with

the native oxide of the material. Thus, for example, the native oxide overlayer on a Ni single crystal can be replaced with a thin passivating overlayer of SiO₂ when it is reacted with SiH₄ at 450K. The mechanism involved is not known but appears to be a simple reactive gas-solid ligand substitution reaction. This technique is very general but has yet to be employed in semiconductor surface passivation. There are two valuable semiconductors with well known problematic oxide surfaces, Ge and GaAs. We propose to examine such reactions on these materials. The process forming the new oxide, involving a reaction which proceeds by a ligand redistribution, should regenerate the elemental constituents necessary to reform GaAs. The species formed at the interface should therefore be very different from those generated by thermal oxidations. The potential seems sufficiently large here that directing some effort toward exploring this chemistry (with silane and the alane reagents) seems warranted. If thin non-native oxide overlayers can be grown in this manner, we subsequently will explore methods for overcoating them and testing their electronic properties.

New Directions in Studies of Steady-State Growth

We propose to add two new directions to our program in studies of steady state chemistries involved in CVD. The first is to introduce new applications of vibrational spectroscopy into the experimental design. We have extensive experience in the application of quantitative methods in surface infrared spectroscopic studies of thin film structures. Most of our work has involved static structural studies of stable organic overlayers. The examination and structural characterization of the resident species present in a steady state growth regime, for example TIBA scattering from an Al(111) surface, seem a logical and potentially high return application for these same methods. There are few (if any) other techniques with the resolution and suitability to examine the molecular structures and orientations of such complex transient species. I have confidence that our instrumentation is now sufficiently capable as to make such experiments worth undertaking. It is proposed that we make some preliminary studies as to feasibility using steady state chemistries we already understand in detail. This program, to be fully realized, will require the construction of a new, but small, UHV

chamber. The necessary spectrometer, optics, and detectors are already in our possession.

Finally, I return to the issue of new growth chemistries. It is intended that some preliminary work be directed toward the development of new CVD growth chemistries for platinum. There are several technological applications where such chemistry could be useful. They will also serve as the entry point for our longer range objective of pursuing silicide etching and growth chemistries. The investigator has an extensive background in organoplatinum chemistry and there are several sources of which we are aware which may be suitable for the growth of this metal. The growth of silicides, including PtSi, by chemical methods also has been studied extensively in our laboratory in past work. We expect significant synergisms in the merging of these two earlier interests.

KENNETH S. SCHWEIZER

Microscopic Theories of the Structure and Phase Transitions of Polymeric Materials

INTRODUCTION

Due to the long, chain-like nature of flexible polymers, statistical mechanical theories of condensed polymeric materials have traditionally been forced to invoke very crude simplifications which preclude their use as quantitative and/or predictive tools. Chemically unrealistic, coarse-grained models of polymer molecular structure are generally employed in conjunction with a fictitious lattice description. The statistical physics is then approximately solved by ignoring essentially all aspects of chain connectivity and intermolecular correlation (the "random mixing" approximation). In addition, single chain "ideality" is invoked corresponding to the assumed invariance of polymer conformation to the (amorphous) condensed phase environment. Over the last few years, Schweizer has been developing the first nonperturbative, off-lattice approach to dense polymer melts and alloys based on modern many-body integral equation methods [known as "Polymer-RISM" (Reference Interaction Site Model) theory] which allows the above limitations to be systematically removed¹⁻⁷. Thermodynamic properties, structure, and phase diagrams can be computed in a unified fashion.

By combining the integral equation approach with a novel formulation of polyatomic density functional ideas, a first principles theory of the crystallization of flexible polymers has been constructed⁸. Detailed comparisons of various theoretical predictions with both experiment^{4-6,8,9} and computer simulations^{5,7,10,11} have demonstrated that the new approaches provide an accurate treatment of the consequences of both local ("chemical") and global ("universal") single chain structure, repulsive and attractive intermolecular forces, and density and concentration fluctuations.

The general goal of this proposal is to further develop the novel theoretical approaches in order to treat more complex situations and phenomena which are of a fundamental materials science importance. Four broad directions are of initial interest. (1) Develop a fully "self-consistent" integral equation theory which goes beyond the "ideality" ansatz and thereby allows a first principles determination of the influence of chain packing on polymer conformation and vice-a-versa. The ability to describe "nonideal" behavior may be particularly important in polymer blends and copolymers due to their chemically inhomogeneous nature. (2) Develop computationally convenient methods to incorporate structural details at the level of individual chemical bonds and monomers. This direction is crucial for quantitative applications and predictive power since a host of materials phenomena (e.g. crystallization, wide angle scattering) are extremely sensitive to the local chemical architecture and short range interchain forces. (3) Develop theoretical approximation schemes to incorporate the effects of quenched ("chemical") disorder associated with statistical randomness of the polymerization process (e.g. atacticity, molecular weight polydispersity, sequence variations in copolymers). (4) Fully integrate the recent advances in polymer integral equation theory of the isotropic liquid phase with modern approaches to order-disorder phase changes, e.g. freezing of homopolymer melts, liquid-liquid phase separation (both spinodal and binodal) of polymer blends, and microphase separation of block copolymer systems.

The general theoretical method development will be carried out in concert with extensive numerical model calculations with the goal of both understanding structure-property relationships at a molecular level, and also gaining insights and intuition concerning potential novel phase behavior which may be

achievable either via synthetic modification of polymer structure or intelligent alloying of existing materials. Whenever possible, the accuracy of the new theoretical methods will be tested by comparison with both computer simulations, and scattering and phase transition measurements on systems of experimental interest. Specific projects which build on these theoretical advances are described below.

Near-Term Projects

A. Homopolymer Melts. The optical properties (linear and nonlinear) of electro-active polymeric materials are sensitive to both single chain conformation and intermolecular organization. Materials of interest generally consist of molecules of high intrinsic polarizability, the most dramatic case being conjugated polymers which exhibit extensive one-dimensional electron delocalization along the polymer backbone. In such materials, there is a strong coupling between the electronic and optical properties, the polymer conformation, and interchain packing. In previous work¹²⁻¹⁵ on dilute solutions of flexible conjugated polymers I have successfully developed theoretical methods to compute the backbone polarizability, the optical absorption and emission spectra, and the interchain induced dipole-dipole (van der Waals) interactions as a function of polymer conformation and temperature. It is proposed to combine these previous advances with the new integral equation theories in order to treat dense phases of flexible conjugated polymers. The "self-consistent" generalization of the integral equation approach (point #1 above) is especially crucial since the electron delocalization length is strongly dependent on backbone order (planarity), which in turn implies that interchain dispersion forces and packing correlations are strongly conformation-dependent. This unique feature of flexible (and hence "processable") conjugated polymers can lead to a relatively abrupt "coil-to-rod" type single chain structural transition, which strongly modifies the electronic and optical properties (e.g. color changes), and can also be intimately coupled to crystallization and other types of 3-dimensional order-disorder phase changes. The latter phenomenon will be investigated by generalizing our density functional theory of crystallization⁸ to the conjugated polymer case. Extensive model calculations will be supplemented with theoretical studies of specific materials (e.g.

alkyl-substituted polythiophenes) in order to test the theory against a variety of structural and electronic experimental observations. An understanding of the role of conjugation in polymeric materials is directly relevant to current research of Professor S.I. Stupp funded under the DOE-BES program on "Field Responsive Organic and Polymeric Materials." Single chain conformational transitions (or more generally the breakdown of the "ideality ansatz") may also occur in non-conjugated liquid-crystal forming polymers of sufficient intrinsic backbone "stiffness", and this problem will also be systematically studied.

B. Polymer Blends. The structure and phase behavior of polymer mixtures is a vast area of major scientific and emerging technological importance. Our integral equation approach has been generalized to binary blends and preliminary calculations on ideal, coarse-grained models have been recently performed.⁴⁻⁶ Novel, richly-varied fluctuation processes have been discovered which have important implications for alloy phase diagrams and small-angle neutron scattering measurements. Two new problems are proposed for initial study. (a) Mixtures of a flexible polymer with relatively small, highly polarizable dye molecules. The theory will be employed to develop an understanding of the effects of dye concentration, dielectric properties, and molecular shape on the intermolecular organization/aggregation, polymer conformation, and miscibility behavior of such blends. (b) The influence on liquid structure and phase separation of the relative aspect ratios ("stiffness") and/or quenched flexibility distribution (chemical disorder) of the two polymer species comprising a binary blend. Both these projects are directly relevant to the experimental effort of Professor S.I. Stupp cited above.

C. Copolymers. The case of copolymers is extremely rich in potential phase behavior and properties since the different chemical species are bonded together in the same chain and through synthetic manipulation can be arranged in a vast number of different periodic and/or statistically disordered ways. The Polymer-RISM integral equation approach will be generalized to treat this more complex case, thereby allowing the influence of copolymer microstructure on liquid packing and phase behavior to be systematically studied for the first time. Systems of initial interest will be (a)

diblock copolymers, (b) alternating rod-like mesogen / flexible spacer copolymers, and (c) copolymers characterized by sequence randomness. All these systems are of experimental interest to Professor Stupp, and also relate to the chemical disorder (induced via trans-esterification reactions) issues being studied experimentally by Professor J. Economy for liquid-crystalline forming polymers. Questions concerning single chain conformational transitions, intermolecular organization and radiation scattering in the isotropic state, and (micro)phase separation or crystallization will be investigated in a unified fashion for the different copolymer systems.

FUTURE DIRECTIONS

There are many other applications and extensions of work described above. (1) Blends and/or copolymers in which one component is an electro-active (e.g. conjugated) polymer and the other is a "normal" nonconjugated polymer. Such mixtures are important from a materials tractability/processability standpoint, and novel phase and/or conformational behavior may occur. (2) Construction of a density-functional theory of flexible liquid crystalline polymers. In conjunction with the Polymer-RISM integral equation theory of melt structure, a unified theory of the isotropic, nematic and crystalline phases may be developed. (3) Branched polymers. Advances in synthetic methods now allow the polymerization of high polymers with controlled branch length, density, degree of order, etc. These materials have unusual mixing properties (e.g. linear and branched polyethylenes) which could be systematically investigated with the integral equation approach. (4) Generalization of both the polymer models and theory to treat more chemically-specific aspects such as tacticity variations within a single molecule, chiral centers, and the role of strong attractive interactions such as permanent dipoles and Coulomb forces (e.g. charged ionomer materials).

As even longer range goals, it should be possible to build on the advances in the integral equation and density-functional work to construct microscopic theories of a variety of inhomogeneous systems such as polymer interfaces, polymers near surfaces, and the influence of applied electric fields. Finally, all the advances in equilibrium theory have a direct impact on understanding dynamic phenomena. Schweizer has recently developed a first principles approach to the dynamics of entangled

polymers ("mode-mode-coupling")¹⁶ which is truly microscopic in the sense that it is a description at the level of the fluctuating interchain forces. Equilibrium structure and thermodynamics enter the dynamic theory as input. Hence, for example, advances in the theory of alloy structure can be utilized to construct statistical dynamical theories of self and mutual diffusion, shear viscosity, and rheological properties of miscible polymer blends. There is also the possibility of combining the equilibrium theories with the dynamic mode-coupling approach to construct a microscopic theory of the polymeric glass transition.

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Connections With General DOE Interests

There is intense interest in industry to develop new high performance materials based on the intelligent alloying of polymers. A major computer software firm, BIOSYM Technologies, Inc. of San Diego, California, is presently developing (with industrial consortium financial support) a commercial product based on Schweizer's Polymer-RISM theory which is intended to provide insight and guidance in the rational development of new polymer alloys. Moreover, a molecular-level understanding of polymer mixing could play a major role in developing polymer "compatibilizers" which are a third component intended to induce partial mixing of two inherently immiscible polymers. This is a problem of significant environmental and energy importance since the recycling and processing of phase-separated plastics is at present a very energy-intensive and expensive process.

D. RESEARCH SUMMARIES FOR METALLURGY AND CERAMICS

D.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) Development of reliable many-body potentials for BCC and HCP metals. These potentials will be based on the Embedded Atom Method (EAM) which has already had great success in modelling FCC metals and alloys.
- b) Application of the potentials to the study of the relationship between structure, diffusion and mechanical properties of grain boundaries, and to structure and diffusion at surfaces.

HIGHLIGHTS

During the last year, we studied low, medium, and high-angle twist grain boundaries. We determined the structure of these boundaries, and the formation and migration energies of vacancies at the boundaries. Although the formation and migration energies depended highly on the boundaries' structure, their sum (which is the activation energy for self-diffusion along the boundary) was largely independent of boundary structure. The twist boundary can be described by an ordered array of screw dislocations, and vacancy motion always occurred along the dislocation lines. We began a similar analysis for tilt grain boundaries, and preliminary results also show a strong correlation between edge dislocation cores and vacancy formation/motion.

We also studied the mechanism and rate of diffusion of adatoms on the (100), (110), (111), (311) and (331) surfaces of seven FCC metals. We were able to correlate the diffusion rate with the surface structure, and also investigated the newly-discovered exchange mechanism on the (100) surface.

Finally, we tested a set of EAM models for 9 BCC metals, and two EAM models for HCP Ti. Furthermore, we have begun work on improving

the EAM by including d-d electron interactions (3-body and 4-body terms), to describe the partial covalent character of the BCC transition metals.

FUTURE DIRECTIONS

We plan to complete our studies of diffusion at tilt grain boundaries, and carry out a set of diffusion studies at edge and screw dislocations. We will also determine the local elastic constants of grain boundaries, which can differ from the bulk by over an order of magnitude. We will continue our work on improving the EAM by including the effects of d-d electron interactions. This will involve the development of new EAM-style functions, and the modification of our Molecular Dynamics and Monte Carlo computer codes.

SIGNIFICANT ACCOMPLISHMENT

Atomic Diffusion at Grain Boundaries

Scientific Achievement:

Grain boundaries are the primary diffusion path in most metals and ceramics at low to moderate temperatures, but the relationship between boundary structure and diffusion rate is not well-understood. Although it is often assumed that all grain boundaries behave similarly, we have clearly shown that diffusion depends dramatically on the boundary structure. We have carried out a detailed theoretical study of the mechanism and rate of diffusion at metallic grain boundaries, and determined their relationship to the boundaries' structure. Our results allow us to predict the mechanism and rate of diffusion for a wide class of grain boundaries (low to high-angle tilt and twist boundaries).

Significance:

The rate of diffusion in materials controls many physical processes, including mechanical failure by creep, embrittlement due to impurity segregation, and phase transformation. For typical metals and ceramics at moderate temperatures, the primary diffusion paths are grain boundaries. We have determined the diffusion mechanism, which is very difficult to study experimentally. We have shown that the rate of diffusion depends highly on the structure of the boundaries, so that diffusion rates could be controlled by controlling the boundary structure. In other words, the temperatures required for diffusion could be increased or decreased by

modifying the boundary structure. Although it is in general quite difficult to control the grain boundary structure, there are a few applications (directional cooling, micro-lithography) where it is possible, and our work will provide an understanding of how to control diffusion rates by modifying the boundary structure.

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

R. C. ALKIRE

Transport Processes in Localized Corrosion

GOALS

The purpose of this program is to relate key corrosion phenomena to molecular behavior at the solid-liquid interface. Of special interest is the breakdown and repair of protective surface films since such events depend strongly on the local chemical environment at the solid-liquid interface. Experiments therefore aim for resolution of the chemical environment, including the surface film, at the microscale. Mathematical models are used to generalize hypotheses of mechanism. Experimental techniques rely on central MRL facilities.

HIGHLIGHTS

New experimental observations are available which probe local surface chemistry in the vicinity of MnS inclusions in 304 stainless steel in 1N sulfuric acid. Auger, X-ray, depth profiling and SEM techniques were used to infer dissolution of the inclusion, incorporation of sulfur in the adjacent passive film, loss of passivity of the stainless steel host, and pit initiation.

With use of a laser technique to initiate an array of closely spaced pits, we are beginning to understand how a collection of small, relatively harmless pits, evolve into a few dangerous, deep penetrating pits. For Al corrosion in 1N NaCl, the two important effects are the effect of dissolution products on stability of the passive film, and the cathodic reaction on the passive surface surrounding the pit. We are developing a fluorescent probe for in situ measurement of dissolved aluminum in the mM range where stability of the passive film is lost.

Experimental studies demonstrate how intermetallic inclusions act as sites for pit initiation on aluminum alloys. With use of microelectrode fabrication methods, the investigation of electrochemical and chemical behavior of single inclusions is probed. Results to date indicate that local alkalinity owing to oxygen reduction at the inclusion serves to break down the passive film on the host metal.

FUTURE DIRECTIONS

The effect of adsorption of thiosulfate and chloride ions on the electronic properties of the

passive film on 304SS in neutral NaCl will be investigated in collaboration with Professor Wieckowski. Experimental observations will continue on the local surface chemistry during initiation of a corrosion pit in the vicinity of an MnS inclusion. Use of the scanning tunneling microscope will be introduced with collaboration with Professor Gewirth.

A scanning tunneling microscope base will be modified in order to create a microscopic pH monitor based on the electrochemical properties of tungsten. The probe will be used to measure in situ local pH changes in the vicinity of MnS and intermetallic inclusions.

Detailed knowledge of anodic surface films and of the solid-liquid interface will be incorporated into mathematical models of pits, crevices, and cracks.

R.S. AVERBACK

Defects, Diffusion and Non-Equilibrium Processing of Materials

GOALS

This program is directed toward developing an understanding of the fundamental aspects of non-equilibrium processing of metals, semiconducting and ceramic materials. The major areas of investigation are (i) the application of ion beam irradiation for materials modification; (ii) radiation damage in metals, intermetallic compounds and semiconductors; (iii) processing and properties of nanophase metals and ceramics.

HIGHLIGHTS

The mechanical properties of a dense nanocrystalline ceramic material have been measured for the first time. We have shown that nanocrystalline (n-)TiO₂ can be superplastically deformed, in compression, to a true strain of ≈ 0.6 at temperatures less than half the melting temperature. Moreover, these large strains can be achieved with strain rates exceeding $\approx 10^{-3}$ and without evidence of crack initiation. The work seeks to elucidate the kinetic processes controlling this deformation, although grain boundary diffusion obviously plays an important role. We have also shown that the elastic modulus and Vickers hardness of dense n-TiO₂ is comparable to or larger than that of single crystal TiO₂.

Rutherford backscattering and channeling measurements on irradiated GaAs-AlAs superlattices have shown that these III-V semiconducting compounds deviate far from traditional radiation enhanced diffusion behavior in most other materials. Several new phenomena have been revealed: (1) intermixing of GaAs-AlAs layers by energetic ion irradiation decreases as the temperature is increased from 80 to 400 K. (2) The intermixing depends strongly on the order of the layers (relative to the surface) at low temperatures but not at elevated temperatures; (3) The intermixing at low temperatures depends strongly on the electronic stopping power as well as the nuclear stopping power (damage energy). These findings are significant for a number of reasons. They show that radiation effects in III-V semiconducting compound are qualitatively different than in metals and Si and Ge. Moreover, the results show

that comparison of experimental results between different investigators must be performed far more carefully than heretofore thought.

FUTURE DIRECTIONS

Radiation enhanced diffusion and segregation at interfaces and surfaces of compound semiconductors and intermetallic compounds will be investigated using Rutherford backscattering and channeling analysis and by in situ irradiation in an electron microscope. These studies will be complemented by molecular dynamics computer simulation of cascade mixing at interfaces and surfaces. The research on nanophase ceramics will focus on methods to suppress grain growth during sintering and deformation processing and on the properties of composite nanophase ceramics.

SIGNIFICANT ACCOMPLISHMENT

Compositional Disordering at GaAs-AlAs Interfaces During Heavy Ion Irradiation

Scientific Achievement:

We have investigated compositional disordering at GaAs-AlAs-GaAs interfaces during energetic Kr⁺ irradiation over a wide range of temperatures using Rutherford backscattering and channeling analysis. Several remarkable features were observed: (i) at low temperatures, the interfacial mixing of Al and Ga depended strongly on whether the GaAs layer was above or below the AlAs layer relative to the beam direction; substantial mixing was observed at one interface but was unmeasurable at the other; (ii) at temperatures above 300 K, the intermixing was extremely small at both interfaces, i.e., mixing decreased at the higher temperatures; (iii) the intermixing was independent of both dose rate and power level; (iv) the intermixing did not scale with damage energy during irradiation with different energy Kr ion beams; (v) the GaAs layers became amorphous during irradiation at temperatures below 300 K but the AlAs layers remained crystalline over the entire range of irradiation temperatures, 80 - 523 K. These observations demonstrate that radiation effects at interfaces of III-V semiconducting compounds can be far different than corresponding effects at metal-metal, metal-elemental semiconductor or even elemental semiconductor interfaces. Particularly

striking is the lack of scaling of interfacial mixing with damage energy, suggesting that electronic stopping power must play an important role. The results imply that charged defects and strong fields control intermixing at the interfaces of semiconducting compounds.

Significance:

Compositionally graded layers of III-V semiconductor compounds play a role in advanced quantum well laser devices. Moreover, the application of ion beams for lateral patterning of these devices provides tremendous opportunities for fabricating new devices that are both smaller and more efficient. Understanding the radiation effects in III-V compounds is consequently of great importance. The present work clearly demonstrates that the "standard" radiation enhanced diffusion behavior that has been well established in pure metals and elemental semiconductors does not apply to III-V semiconductor interfaces and that radically new behavior occurs. The findings in these materials that (i) charged defects and strong interfacial fields can control interdiffusion during irradiation and that (ii) standard predictors of radiation damage and mixing, such as damage energy, are not valid, are new ideas. They demonstrate the vital need for research on radiation effects at all types of interfaces. For example, charged defects and interfacial fields may also play an important role in insulators. The studies also indicate that the selection of irradiation particle, applied electric fields and temperature might be used for patterning the material in three dimensions by self-organization in the irradiation field. It is found here that alternating layers of amorphous (GaAs) and single crystalline (AlAs) materials can be fabricated by this method. Such a structure would be impossible to obtain by other means.

Performer: Robert S. Averback, 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 work on cathodoluminescence in the transmission electron microscope has been brought to a successful conclusion with the published work on $\text{Ga}_x\text{In}_{1-x}\text{P}$. This work will not be continued.

2) Sputtered neutral mass spectroscopy, a relatively new technique, has been developed into a reliable analytic method. Instrument modifications have been completed which improved the sensitivity of the instrument by a factor of 30 allowing measurements in the ppm range to be made. We have developed improved understanding and control of the plasma operation and crater formation which has resulted in an improvement in the reliability and reproducibility of the results. The importance of sample temperature in determining the analytic results has been established. This work is being brought to a conclusion.

3) In convergent-beam electron diffraction some basic problems remain despite the widespread use of the technique for over a

decade. We have made progress in a more detailed understanding of HOLZ line formation and expect to complete this work shortly.

4) The study of surfaces by reflection electron microscopy is of growing importance as its unique ability to image and characterize surface steps becomes recognized. The aim of this program is to complement the imaging technique by a more complete development of surface diffraction -- where many basic problems remain unsolved -- and to develop instrumentation to apply these techniques to practical problems such as epitaxy.

FUTURE DIRECTIONS

This program will continue its focus on the coupling of instrumentation and physical property determination. The work will increasingly emphasize the studies of surface diffraction and the development of techniques for determining the structure and chemistry of the surface at the atomic level using surface electron scattering and imaging techniques.

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 groups acts as a resource for the MRL in developing new microanalytic methods and assisting in the application of these for many other programs.

a) Convergent-beam pattern in the "forbidden" 200 disc of silicon liquid N_2 temperature close to 60kV. b) Computer simulation of same

Atomistics of Growth and Transport at Metal and Semiconductor Surfaces

GOALS

We are examining the formation of films and overlayers on crystal surfaces, using the field ion microscope to gain an atomic view of the individual events, and their dependence upon the atomic arrangement as well as the chemical constitution of the surface.

HIGHLIGHTS

Our efforts have been focused upon diffusion on atomically smooth surfaces. To this end we have surveyed the behavior of different metal atoms -- Ir, Pd, W, and Re -- on Ir(111). As a preliminary to a detailed examination of diffusive motion we have characterized the sites at which the adatoms are held. These can be of at least two types, distinguished by their local environment and designated as fcc and hcp sites. Using a mapping technique devised in this laboratory for site determination, we have uncovered a marked chemical specificity. The refractory metal adatoms W and Re (groups VI and VII of the periodic table) prefer to occupy hcp sites; the group VIII element Pd is always at fcc sites, and self-adsorbed Ir atoms are found in both, but with a preference for hcp sites. These preferences in site occupation arise from differences in the binding energy at the two types of sites. There is another chemical specificity as well: the spatial distribution of the intensity in the image spot

from an adatom is the same for the platinum family metals, and is exactly the reverse of that for the refractories.

We have also taken advantage of the ability to determine binding sites in order to examine the condensation of atoms on Ir(111). Macroscopic studies of atom deposition on fcc metals have recently been interpreted in terms of a transient mobility, arising from slow transfer of the condensation energy to the lattice. In our experiments, we have directly examined the distribution of individual atoms over Ir(111) after condensation at temperatures at which there is no ordinary mobility. For all the atoms examined -- Ir, Pd, Re, and W -- the distribution over binding sites is the same. Regardless of differences in binding energy, at low temperatures fcc and hcp sites are occupied at random, just as expected if condensation occurs on first impact. We find no evidence for transient mobility; for the metal atoms studied, transfer of the condensation energy occurs with high efficiency.

FUTURE DIRECTIONS

Quantitative studies will be carried out to determine the energetics of binding at different sites on Ir(111) and detailed measurements will be made of atom diffusion, in order to define the individual jump processes. Diffusion will also be examined on other atomically smooth planes, with the same aim. Efforts will first be concentrated on W(110), the most densely packed plane of this crystal, but subsequent studies may be extended to other fcc metals, such as Rh(111). Preliminary work will be initiated to explore the possibility of quantitative observations of diffusion on silicon.

Field ion images of iridium (left) and tungsten adatom (right) in the very same hcp (or surface) binding site on Ir(111). The orientation of the image triangle is reversed in the two, revealing a pronounced chemical specificity in atomic behavior.

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 suitable designed transition metal organometallic precursors, (2) to study the deposition mechanisms of the films so produced, (3) to design new thin film materials, such as amorphous and micromodulated films, that are difficult or impossible to prepare using conventional methodology, and (4) to investigate the physical and mechanical properties that are characteristic of thin films prepared at low temperatures.

HIGHLIGHTS

Molybdenum disulfide films have been deposited at temperatures between 100 and 200°C from a single-source metal-organic precursor. The films, which are about 0.3 μm thick, are amorphous to X-rays. XPS and AES studies of films deposited with and without a H_2 carrier gas, show that carbon levels decrease and the Mo:S ratio approaches 1:2 as the hydrogen flow rate increases. The electrical conductivities of the films of $0.97 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature are comparable to those of polycrystalline MoS_2 films (10^{-3} to $10^1 \text{ ohm}^{-1} \text{ cm}^{-1}$).

The deposition of copper-containing thin films from volatile copper alcoxides has been achieved. Variation in deposition conditions allows the growth of either copper oxide or copper metal films. The mechanism of copper oxide deposition has been studied and shown to involve elimination of isobutylene from a tert-butoxy group to form surface hydroxyl species, which either dehydrate or hydrolyze tert-butoxy groups to give tert-butanol. Surprisingly, the formation of copper metal occurs via deoxygenation of copper(I) oxide, even though the temperatures of ca. 400°C are lower than previously thought necessary for this process.

Further studies of the mechanism of titanium carbide deposition from titanium alkyl precursors have given information about the chemical processes that take place after the initiation step. Although we previously thought that α -hydrogen elimination processes were exclusively occurring, deuterium labeling studies and isotopic analysis of the hydrocarbon byproducts clearly

show that γ -hydrogen elimination processes are predominant. Additional studies underway should allow us to map out a large portion of the CVD mechanism.

FUTURE DIRECTIONS

The deposition of solid solutions of transition metal carbonitrides will be explored using single source precursors such as transition metal dialkylamides. Laser- and plasma-assisted CVD techniques will be studied since these may be particularly suited for the deposition of these ceramic phases. Investigations of the deposition mechanism of the group 4 diborides will be undertaken with the goal of identifying the chemical intermediates present during film growth. We will continue to explore the utility of "designed" single source molecular CVD precursors to grow films of new ceramic phases.

SIGNIFICANT ACCOMPLISHMENT

The Chemistry of New Transition Metal Ceramic Compounds Synthesized by MOCVD

Scientific Achievement:

Many of the details of the chemical pathway by which titanium carbide coatings are grown at low temperatures have recently been determined for the first time. Titanium carbide films can be grown at temperatures as low as 150°C, provided that the correct starting materials are chosen, but no information about how these coatings grew was available previously. These results are the first detailed studies of how ceramic thin films are laid down from a metal-organic chemical vapor deposition precursor at low temperatures.

Significance:

Titanium carbide, TiC , finds wide use in industry as a hard coating for metal cutting tools, and as a potential low-friction coating for biomedical implants and as a corrosion and temperature-resistant coating in the aerospace industry. This interest arises from its desirable properties: high hardness, high melting point, moderate strength, and resistance to wear and corrosion. With the current discovery it may be possible to grow coatings of TiC under even milder conditions and to tailor its properties to suit specific applications.

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

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 the first single-crystal metastable semiconductor and ceramic compounds and alloys. We are presently developing both Monte Carlo and molecular dynamic models to simulate ion/surface interactions and crystal growth from energetic condensing species.

We have grown and investigated the structural, thermodynamic, optical, electronic, and vibrational properties of a homologous series of new ternary and quaternary (III-V)_{1-x}(IV₂)_x semiconducting alloys. The alloy (GaAs)_{1-x}(Si₂)_x has been shown to have potential applications in optoelectronics. (GaAs)_{1-x}(Si₂)_x/GaAs strained-layer superlattices (SLS) have been used to grow dislocation-free (GaAs)_{1-x}(Si₂)_x alloys with x up to 0.3 on GaAs(001).

We have grown the first single-crystal metastable ceramic alloys: pseudoternary NaCl-structure Ti_{1-x}Al_xN, which we have shown to have excellent thermal stability. Ti_{0.5}Al_{0.5}N, in particular, exhibits hardness and wear resistance similar to TiN but with orders of magnitude lower oxidation rate. We have mapped out the phase decomposition reaction path, which involves surface-initiated spinodal decomposition, for Ti_{0.5}Al_{0.5}N.

We have grown the first ceramic SLS, TiN/VN(001), and observed quantum-size effects in electronic transport measurements.

We have developed a new hybrid growth technique, reactive-ion MBE, to grow high-resistivity epitaxial GaN. Metastable sphalerite-structure GaN(001), which has never been grown before, was found to have a direct optical bandgap ≈ 0.2 eV smaller than the equilibrium wurtzite phase.

FUTURE DIRECTIONS

Our emphasis in the area of semiconductor growth will slowly change from that of microstructural to microchemical modification using materials such as GaN (in which N₂ does not chemisorb on Ga) and metastable GaAs_{1-x}N_x as test systems. We anticipate that an increasing fraction of our work will be centered on ceramic materials where we will, for example, investigate bulk and grain boundary diffusion barrier properties of TiN and metastable Ti_{1-x}Al_xN alloys as well as the electronic structure of, and phase transitions in, the Ti_{1-x}Al_xN system. We are also very much interested in the pseudomorphic growth of new ceramic phases and quantum confinement properties of ceramic SLS structures.

SIGNIFICANT ACCOMPLISHMENT

Growth of High-Resistivity Wurtzite and Metastable Sphalerite Structure Single-Crystal GaN by Reactive-Ion Molecular Beam Epitaxy

Scientific Achievement

Interest in the III-V wurtzite-structure compound GaN stems primarily from its large direct bandgap, ≈ 3.4 eV, and high electron ballistic drift velocity. However, GaN has proven for the past 15 years to be extremely difficult to grow due primarily to the fact that N₂ does not chemisorb on Ga. All reports of the electronic properties to date have shown the presence of high concentrations ($> 10^{18}$ cm⁻³) of shallow donors due to N vacancies. We have developed a hybrid growth technique, reactive-ion MBE, in which nitrogen is supplied to the film via a low-energy (≤ 35 eV) ion beam which consists primarily of N₂⁺ (N₂⁺/N⁺ ≈ 6) while Ga is obtained from a standard effusion cell. Typical film growth temperatures range from 700-850 °C.

GaN films grown on Al₂O₃(0112) were epitaxial wurtzite structure having the orientational relationship (2110)GaN $\parallel$ (0012)Al₂O₃ with [0110]GaN $\parallel$ [2110]Al₂O₃ and [0001]GaN $\parallel$

[0111]Al₂O₃. The first cubic structure GaN epitaxial layers were grown on MgO(001)1x1. Optical transmittance measurements showed that cubic GaN has a direct bandgap of 3.2 eV, ≈ 0.02 eV less than for the equilibrium hexagonal phase. In addition, we were able to use collisionally-induced dissociative chemisorption effects to vary the resistivity ρ of both wurtzite and sphalerite GaN by over 6 orders of magnitude with an 8-fold increase in the N₂⁺/Ga incident flux ratio. This is the first report of high resistivity epitaxial GaN.

Significance

A key feature in our research on the development of vapor-phase growth techniques for the development of new thermodynamically metastable materials has been the use of low-energy ion/surface interactions during film deposition in order to controllably alter nucleation and growth kinetics and hence film microstructure. We have recently extended this work to microchemistry on the atomic level. This opens up new capabilities in extending the range of available materials' properties for the design of devices and components which are of potential interest for energy-related applications. In addition, metastable materials provide a sensitive probe for enhancing the understanding of the relationship between atomic and electronic structure, of solution thermodynamics, and of phase transformations. We intend to extend this work to metastable optoelectronic alloys, such as GaAs_{1-x}N_x, and to ceramic systems.

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

Room temperature resistivity of wurtzite structure α -GaN grown on Al₂O₃ and zincblende β -GaN grown on MgO vs incident N₂⁺/Ga ratio.

ANDRZEJ WIECKOWSKI

Organization of the Single-Crystal, Solid-Liquid Interface: Energies, Structures and Electronic Synergism

GOAL

The economic importance of metal-based heterogeneous electrocatalysis, fuel cell technology, and corrosion of industrial materials, demands better understanding of metal surface chemistry at a solid/liquid interface. Our aim is to learn how geometry and electronic distribution control surface chemistry at such an interface and thus to enable the selective tailoring of the electronic structure to carry out desired reactions or control surface reactivity. Since surface properties of thin films can dramatically be different from the surface properties of bulk metals, our goal is to fully characterize the solid-liquid interface at single crystals containing monolayers and submonolayers of foreign admetals. The specific objective of this work is to understand the significance of the atomic-level, structural and electronic factors in the organization of the solid-liquid interface at bimetallic single-crystal electrodes containing reversibly chemisorbed anions and contrasting neutrals.

HIGHLIGHTS

In situ radiochemistry measurements of adsorption of (bi)sulfates on well-defined and polycrystalline electrodes have successfully been accomplished. The measurements were done with gold, copper, platinum, rhodium, and with deposited (sub)monolayers of copper, cadmium and silver. The research was broken down into the following components: (i) the electrochemical and ultra-high vacuum characterization of the clean electrode surface, (ii) the analysis of the initial stages of metal deposition processes (underpotential deposition), and (iii) studies of adsorption of (bi)sulfate on the clean and on the bimetallic surface obtained after the deposition. The data analysis provided atomic-level, structure/energy characteristics of the studied interface. Strong (reduction) and weak (reversible chemisorption) processes were identified and reported. First observation of its kind of the solid/liquid interface by the use of solid-state NMR has been made.

FUTURE DIRECTIONS

New, detailed correlations between the two-dimensional periodicity and order and the macroscopic thermodynamic parameters will be established at single crystal electrodes modulated by metal adatoms to provide insight into the ordered, solid/liquid interface. The work will progress with the substrate metals and (sub)monolayer metallic deposits (vide supra), and with sulfate, chloride, acetate, urea and pyridine as adsorbates. The UHV, solid-state NMR and radiochemistry data will be computer-modeled to explain interesting results from alloy electrocatalysts, and perhaps even to create a new types of catalysis.

SIGNIFICANT ACCOMPLISHMENT

Anionic Populations at Metal Electrodes in Electrocatalysis

Scientific Achievement:

It has been established in this laboratory that the rates of electrocatalytic oxidation of fuel cell molecules depend on the type of anions present in supporting electrolyte. The anions were those which are common components of solutions used in electrocatalysis and fundamental electrochemical investigations. Although the mechanistic origin of this behavior is unknown, it is undoubtedly connected with the anion interactions with the catalytic surfaces. Radiochemical, ultrahigh vacuum and NMR investigations have been conducted and reported to develop understanding of the anion surface chemistry. Our interest has been to learn how a selective modification of metal surface properties, via metal (sub)monolayer deposition, relates to anion electrosorption and its control of rates of electrocatalytic processes.

Significance:

Economic and environmental concerns, as well as the political instability in the Middle East, call for new energy sources to energize the electric and automotive power structure in the Western Hemisphere. Electrochemistry is on the front-line in the global search for alternatives to oil and socially troublesome nuclear energy. Accordingly, remarkable incentives exist to develop low cost fuel cells for use in automotive vehicles, power plants and even in space exploration. Finding new fuel cell catalysts and appropriate reaction media is vital. While the catalyst's structure and electronic properties

control the rate with which the maximum system-energy may be produced, the site blocking processes contribute to reaction slow-down and a regrettable waste of energy supply. The site blocking by anionic electrolyte components proves to be one of key factors in controlling the energy transformation efficiency. Amplifying this new observation made us study anionic populations on metal surfaces and is leading us to new understanding of solid/liquid interfaces in relation to heterogeneous electrocatalysis.

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

A. ZANGVIL

Microstructure Evolution, Interfaces and Properties in Structural Ceramic 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 studying the (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

Our pioneering study on the evolution of microstructure during hot-pressing of alkoxy-derived mullite-zirconia composites will lead to better-controlled structures and mechanical properties. It shows that the zirconia phase is developed by the nucleation, at around 850°C, of nanocrystalline metastable cubic ZrO_2 , followed by coarsening and transformation into tetragonal or monoclinic ZrO_2 particles (depending on grain size). These are found embedded in mullite grains, which, in turn, had developed from Al-Si spinel grains. In addition, elongated zircon (ZrSiO_4) grains nucleate at ~ 1200°C, then dissociate at > 1300°C into SiO_2 and rows of ZrO_2 particles. The latter are found at mullite grain junctions and control the mullite grain size.

SiC-TiC particulate composites were found to provide doubling of fracture toughness values through crack deflection and grain bridging mechanisms.

Preliminary results on nanocrystalline TiO_2 and TiO_{2-x} show that the development of nanocrystalline grains and their boundaries can be studied by conventional and high resolution

TEM of carefully prepared samples. In particular, fine clusters as well as agglomeration phenomena could be observed, and local structures (consisting of the Magnéli phases in TiO_{2-x}) could be identified and analyzed.

FUTURE DIRECTIONS

We will select potential CMC systems for studies of the mechanisms determining their most critical properties, namely, fracture toughness at ambient conditions; creep and oxidation resistance at elevated temperatures.

Nanocrystalline ceramic alloys and composites will be prepared by reactive and non-reactive magnetron sputtering. The evolution of their microstructure, with particular focus on metastable phases and interface structures, will be investigated by advanced electron microscopy, including atomic resolution studies.

Nanocrystalline TiO_{2-x} . (a) TEM image; (b) electron diffraction showing Magnéli phases; (c) high resolution lattice image.

High resolution structural image, showing limited reaction at the interface of a B_4C -BN composite.

SIGNIFICANT ACCOMPLISHMENT

Control of Microstructure and Properties Facilitated in Mullite/Zirconia-Toughened Composites

Scientific Achievement: The evolution, during sol-gel processing and subsequent hot-pressing, of the microstructure of ceramic matrix composites based on mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and partially stabilized zirconia (PSZ) has been elucidated for the first time. The most important results are as follows. (1) Reported phase evolution data from powder heat treatment experiments are not indicative of phase evolution within a hot-pressed material. Elaborate hot-pressing experiments and advanced microanalysis are required; (2) An Al-Si cubic spinel phase, crystallizing at as low as 850°C , is the precursor of the final mullite matrix; (3) Zirconia first crystallizes as nanocrystalline metastable cubic ZrO_2 , followed by coarsening and transition into mostly tetragonal ZrO_2 , embedded in mullite grains; (4) Large zircon (ZrSiO_4) grains form at $\sim 1200^\circ\text{C}$, then dissociate into ZrO_2 particles and SiO_2 . The former are found at mullite grain boundaries and control the mullite grain size.

Figure 1. Zirconia grains are nucleated within elongated zircon crystals during hot-pressing at 1200°C . The ZrO_2 grains control the grain of the final composite

Significance:

Mullite matrix composites toughened with PSZ are intended for structural applications in high temperature oxidizing environments. While sol-gel processing of the composites can lead to cleaner powders and lower processing temperatures, the control of the resulting microstructures (and properties) poses a serious

problem. Our study facilitates control of intergranular and intragranular ZrO_2 particle size and distribution, as well as control of the mullite matrix grain size, thereby enabling optimization of strength and fracture toughness of the structural composites.

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

**D.1.b PUBLICATIONS AND HONORS FOR
STRUCTURE OF MATERIALS
KC-02-01-01**

J.B. Adams

**Publications
(supported by DOE-BES at Sandia National
Laboratories)**

J.B. Adams and S.M. Foiles,
Development of an Embedded Atom Potential for
a BCC Metal: Vanadium
Phys. Rev. B41, 3316 (1990)

L.M. Holzman, J.B. Adams, S.M. Foiles and
W.N.G. Hitchon
Properties of Liquid-Vapor Interfaces Calculated
Using the Embedded Atom Method
To be published in J. Mater. Res.

J.B. Adams, W.G. Wolfer, S.M. Foiles, C.M.
Rohlfing and C.D. Van Sieten
Theoretical Studies of He in Metals
Proceedings of NATO Advanced Research
Workshop on "Fundamental Aspects of Inert
Gases in Solids" Bonas, France (1990) S.E.
Donnelly, J.H. Evans (Eds.), to be published by
Plenum Press.

J.B. Adams and W.G. Wolfer
Void Formation in Rapidly-Solidified Austenitic
Steels
Submitted to Acta Met.

**Publications
(supported by DOE-BES at Materials Research
Laboratory)**

M. Nomura, S.Y. Lee and J.B. Adams
Vacancy Diffusion Along Twist Grain Boundaries
in Copper
To be published in J. Mater. Res.

C.L. Liu, J.B. Adams, J.M. Cohen and A.F. Voter
EAM Study of Surface Self-Diffusion of Single
Adatoms of FCC Metals
Submitted to Surf. Sci.

A. Nasib and J.B. Adams
Properties of BCC Metals using the Embedded
Atom Method
Submitted to J. Mater. Res.

Honors and Awards

Membership in Sigma Xi (Scientific Research
Society)

Invited Talks

Theoretical Studies of He in Metals, NATO
Advanced Research Workshop on
"Fundamental Aspects of Inert Gases in Solids"
Bonas, France

Vacancy Supersaturation and Void Formation in
Rapidly-Quenched Steels
Fall TMS meeting.

R. C. Alkire

Publications

Kai P. Wong and Richard C. Alkire
Local Chemistry and Growth of Single Corrosion
Pits in Aluminum
J. Electrochem. Soc., 137:10, 3010-3016 (1990)

Claude Clerc and Richard Alkire
Effect of Benzotriazole on Surface Processes
During Copper Electrodeposition in Sulfuric
Acid
J. Electrochem. Soc.(accepted)

Stephen A. Perusich and Richard C. Alkire
Effect of Ultrasonic Cavitation on Passive Film
Breakdown and Repair, I. Theoretical
J. Electrochem. Soc. (accepted)

Stephen A. Perusich and Richard C. Alkire
Effect of Ultrasonic Cavitation on Passive Film
Breakdown and Repair II. Experimental
J. Electrochem. Soc. (accepted)

John N. Harb and Richard C. Alkire
Transport and Reaction during Pitting Corrosion
of Ni in 0.5M NaCl I. Stagnant Fluid
J. Electrochem. Soc.(submitted)

John N. Harb and Richard C. Alkire
Transport and Reaction during Pitting Corrosion
of Ni in 0.5M NaCl II. Flowing Fluid
J. Electrochem. Soc. (submitted)

Honors and Awards

Technical Achievement Award 1991, National Association of Corrosion Engineers

E. V. Murphree Award in Industrial and Engineering Chemistry 1991, American Chemical Society

Honorary Member 1991, The Electrochemical Society

Invited Talks

W. N. Lacey Lectures in Chemical Engineering, California Institute of Technology

University of Colorado-Boulder, National Institute of Science and Technology, Boulder

Gordon Research Conference on Corrosion

Latsis Symposium on Materials, Lausanne, Switzerland

3M Corporation, Minneapolis

R. S. Averbach

Publications

Hongming Hsieh and R.S. Averbach
Molecular Dynamics Investigation of Cluster Beam Deposition
Phys. Rev. B42, 5365 (1990).

Hongming Hsieh and R.S. Averbach
Atomic Size Effect on the Formation of Ionized Cluster Beam Epitaxy in Lennard-Jones Systems
Nucl. Instr. and Meth. B. (in press).

Hongming Hsieh and R.S. Averbach
Molecular Dynamics Simulations of the Impact of Energetic Cu Clusters on Cu and Ni Substrates
Mat. Res. Soc. Proc. (1990) in press.

R.S. Averbach, T. Diaz de la Rubia, H. Hsieh and R. Benedek
Interactions of Energetic Particles and Clusters with Solids
Nucl. Instr. and Meth. B. (in press).

R.S. Averbach, H. Hsieh, T. Diaz de la Rubia and R. Benedek
Molecular Dynamics Studies of Displacement Cascades
J. Nucl. Mater.

T. Diaz de la Rubia, R.S. Averbach, R. Benedek and I.M. Robertson
Molecular Dynamics Studies of the Primary State of Radiation Damage
Radiat. Effs. and Defects in Sol. 113, 39 (1990).

A. Barbu, A. Dunlop, D. Lesueur and R.S. Averbach
Latent Tracks Do Exist in Metallic Materials
Europhysics Letts. (in press).

R.P. Bryan, L.M. Miller, T.M. Cockerill, J.J. Coleman, J.L. Klatt and R.S. Averbach
Temperature Dependence of Compositional Disordering of GaAs-AlAs Superlattices During MeV Kr Irradiation.
Phys. Rev. B41, 3889 (1990).

Sintering and Grain Growth in Nanocrystalline Ceramics
H.J. Höfler and R.S. Averbach
Scripta. Metall et Materialia 24, 241 (1990)

H.J. Höfler, H. Hahn and R.S. Averbach
Diffusion in Nanocrystalline Materials
Defect and Diffusion Forum, Vol. 75, eds. D. Gupta, H. Jain and R.W. Siegel, (Sci-Tech Publ., Liechtenstein 1991) p. 195.

R.S. Averbach, H. Hahn, H.J. Höfler and J.C. Logas
Processing and Properties of Nanophase Amorphous Metallic Alloys: Ni-Ti
Appl. Phys. Lett. 57, 1745 (1990)

R.S. Averbach, H.J. Höfler, H. Hahn and J.C. Logas
Sintering and Grain Growth in Nanocrystalline Ceramics
Acta. Metall. et Materialia (in press).

H. Hahn, J. Logas, H.J. Höfler, P. Kurath and R.S. Averbach
Low Temperature Sintering and Deformation in Nanocrystalline TiO₂
Mat. Res. Soc. Proc. Vol.

W. Wagner, R.S. Averback, H. Hahn, W. Petry
and A. Wiedenmann
Sintering of Nanocrystalline TiO₂: A
Comparative Study Using Small Angle
Neutron Scattering and Nitrogen Absorption
J. Am. Ceram. Soc. (submitted).

H. Hahn and R.S. Averback
Deformation in Nanocrystalline TiO₂
J. Am Ceram. Soc. (submitted).

Invited Papers

Interactions of Energetic Particles and Clusters
with Solids
Int. Conf. on Ion Beam Modifications of Materials
-IBMM-90
Knoxville, TE. Sept. 1990

Molecular Dynamics Studies of Displacement
Cascades
Fourth International Conference on Fusion
Materials
Kyoto, Japan, Dec. 1989

Ion Beam Mixing at Metal Surfaces
American Physical Society Spring Meeting
Anaheim, March, 1990

Molecular Dynamics of Displacement Cascades
NATO Advanced Studies Institute
Alicante, Spain, June, 1990

Sintering and Deformation in Nanocrystalline
Ceramics
Materials Research Society, Fall Meeting
Boston, Dec. 1990

Properties of Materials with Nanometer-Sized
Microstructures
Annual Meeting of the TMS
New Orleans, Feb. 1991

Sintering and Deformation Characteristics of
Nanocrystalline Ceramics
Gordon Conference on Ceramic Materials
New Hampshire, July, 1991

J.A. Eades

Publications

J. A. Eades
Convergent-Beam Diffraction
A chapter in "Electron Diffraction Techniques",
ed. J. M. Cowley, Oxford University Press (in
press)

A Samsavar, E. S. Hirshorn, T. Miller, F. M.
Leiblsle, J. A. Eades and T.-C. Chiang
High-resolution Imaging of a Dislocation on Cu
(111)
Phys. Rev. Lett. 65, 1607-1610 (1990)

J. A. Eades
Reflection Electron Microscopy and Reflection
Electron Diffraction in the Electron Microscope
Proceedings, Sixth Latin American Symposium on
Surface Physics, Springer-Verlag (in press)

J. A. Eades, K. K. Christensen and M. L.
Andreessen
Is There a Non-channeling Orientation?
Electron Microscopy 1990, 4, 412-413 (1990)

D. K. Dewald, T. C. Lee, J. A. Eades, I. M.
Robertson and H. K. Birnbaum
An Environmental Cell Transmission Electron
Microscope
Electron Microscopy 1990, 4, 552-553 (1990)

J. B. Woodhouse and J. A. Eades
Comment on: "Stereo-Imaging Made Easy"
J. Elect. Mic. Tech. 14, 85-86 (1990)

J. A. Eades
Determination of the Unit Cell From a Single
Transmission Electron Diffraction Pattern
Proceedings *Seventh International Course on
Physics on Materials* (COSTED) in press

J. A. Eades
Microdiffraction in the Characterization of
Materials
Proceedings *Seventh International Course on
Physics of Materials* (COSTED) in press

J. A. Eades
Laue Zones: A Clarification of Nomenclature
Ultramicroscopy 32, 183 (1990)

T.C. Lee, D.K. Dewald, J.A. Eades, I.M. Robertson
and H.K. Birnbaum
An Environmental Cell Transmission Electron
Microscope
Rev. Sci. Instrum. (in press)

Honors and Awards

Past-Chairman, International Physics Group,
APS

Committee on Membership, APS

Editorial Board, Journal of Electron Microscopy
Technique

Executive Advisory Committee, International
Congress on Electron Microscopy

Director, Electron Microscopy Society of America

Invited Talks

Departmental Seminar, Nuclear Engineering,
UIUC, February 27, 1990

School on Electron Microscopy, Cadiz, Spain,
March 26-April 4, 1990

Departmental Seminar, Barcelona, Spain, April
6, 1990

Annual Meeting of the EM Society of Venezuela,
Cumana, July 16-18, 1990

Sixth Latin-American Symposium on Surface
Physics, Cusco, Peru, September 7, 1990

Second Ibero-American Workshop on Surfaces &
Interfaces, Yukay, Peru, September 10-14, 1990

G. Ehrlich

Publications

S. C. Wang and G. Ehrlich
Imaging and Diffusion of Individual Iridium
Adatoms on Ir(111)
Surf. Sci. **224** (1989) L997-L1003

S. C. Wang and G. Ehrlich
Structure, Stability, and Surface Diffusion of
Clusters: Ir_x on Ir(111)
Surf. Sci. **239** (1990) 301-332

S. C. Wang and G. Ehrlich
Observations of Cluster Structures on fcc(111)
in *The Structure of Surfaces III*, Springer Series in
Surface Sciences, In Press

M. F. Lovisa and G. Ehrlich
Quantitative Determinations of the Temperature
Dependence of Diffusion Phenomena in the
FIM
Surf. Sci., In Press

S. C. Wang and G. Ehrlich
Determination of Atomic Binding Sites on the
fcc(111) Plane
Surf. Sci., In Press

S. C. Wang and G. Ehrlich
Atom Condensation on an Atomically Smooth
Surface: Ir, Re, W, and Pd on Ir(111)
J. Chem. Phys., In Press

Invited Talks

Atomic Motion on Metal Surfaces
John E. Dorn Memorial Lecture, Northwestern
University, April 1990

Direct Observation of Surface Diffusion
Scanning Microscopy 1990, Bethesda Maryland,
May 1990

Direct Observation of Surface Diffusion and
Clustering
37th International Field Emission Symposium,
Albuquerque, N.M., July 1990

Atomic Interactions on Crystals: A Direct View
LASST-ACSIS 5th Annual Joint Workshop on
Interface Phenomena, Bar Harbor, Maine,
August 1990

G.S. Girolami

Publications

G. S. Girolami and J. E. Gozum
Low Temperature MOCVD Routes to Thin Films
from Transition Metal Precursors
Mat. Res. Soc. Symp. Proc. **168**, 319 (1990)

A. R. Hermes and G. S. Girolami
Phosphine Complexes of Trivalent Early
Transition Metals. X-ray Crystal Structure of
the d^1-d^1 Dimer $[TiCl_3(dippe)]_2$ and
Synthesis of the Alkyl $CrMeCl_2(dippe)(thf)$
Inorg. Chem. **29**, 313 (1990)

D. M. Rogers, S. R. Wilson and G. S. Girolami
Bis(cyclooctatetraenyl)zirconium: X-ray Crystal
Structure and Solution and Solid State NMR
Spectra
Organometallics, in press

J. E. Gozum and G. S. Girolami
Zirconium and Hafnium Polyhydrides.
Preparation and Characterization of
 $M_2H_3(BH_4)_5(PMe_3)_2$, $MH(BH_4)_3(dmpe)$, and
 $MH_2(BH_4)_2(dmpe)_2$
J. Am. Chem. Soc., in press

P. M. Morse, S. R. Wilson and G. S. Girolami
A Compound with a Hf-Hf Bond. The First
Structurally Characterized Hafnium(III)
Complex: $Hf_2Cl_6[(i-Pr)_2PCH_2CH_2P(i-Pr)_2]_2$
Inorg. Chem. **29**, 3200 (1990)

O. Bilsel, J. Rodriguez, D. Holten, G. S. Girolami,
S. N. Milam and K. S. Suslick
Observation of a New Low-Energy Fluorescent
 $^1(\pi, \pi^*)$ Excited State in Strongly-Coupled
Porphyrin Dimers
J. Am. Chem. Soc. **112**, 4075 (1990)

R. J. Morris and G. S. Girolami
On the π -Donor Ability of Early Transition
Metals: Evidence that Trialkylphosphines
Can Engage in π -Back-Bonding and X-ray
Structure of the Titanium(II) Phenoxide
 $Ti(OPh)_2(dmpe)_2$
Inorg. Chem. **29**, 4167 (1990)

R. J. Morris and G. S. Girolami
High-Valent Organomanganese Chemistry. Part
I: Synthesis and Characterization of Mn^{III}
and Mn^{IV} Alkyls
Organometallics, in press

R. J. Morris and G. S. Girolami
High-Valent Organomanganese Chemistry. Part
II: Synthesis and Characterization of Mn^{III}
Aryls
Organometallics, in press

K. Kim, W. S. Lee, H.-J. Kim, S.-H. Cho, G. S.
Girolami, P. A. Gorlin and K. S. Suslick
Synthesis and Structure of the First Transition
Metal Bis(porphyrinato) Complex.
Characterization of $Zr(TPP)_2$ and $Zr(OEP)_2$
Inorg. Chem., submitted.

Awards and Honors

Henry and Camille Dreyfus Teacher-Scholar
Award

A. P. Sloan Foundation Fellow

University Scholar, UIUC

Fellow, Center for Advanced Study, UIUC

Chemistry Department Teaching Award

Invited Talks

M & T Chemicals, Somerville, New Jersey, 1990

Harvard University, Cambridge, Massachusetts,
1990

Massachusetts Institute of Technology,
Cambridge, Massachusetts, 1990

State University of New York, Buffalo, New
York, 1990

Northwestern University, Evanston, Illinois,
1990

22nd Central Regional ACS Meeting, Midland,
Michigan, 1990

Solid State Chemistry Gordon Conference,
Plymouth, New Hampshire, 1990

Quantum Chemicals, Rolling Meadows, Illinois,
1990

200th National ACS Meeting, Washington, D.C.,
1990

University of New Mexico, Albuquerque, New
Mexico, 1990

Los Alamos National Laboratories, Los Alamos,
New Mexico, 1990

McGill University, Toronto, Canada, 1990

PhD Graduates

Robert J. Morris, Ph.D. 1990; accepted post-doctoral position at the University of California at Berkeley

Paige M. Morse, Ph.D. 1990; accepted staff position at Shell Development Company, Houston, Texas

J.E. Greene

Publications

L. Hultman, J.-E. Sundgren, and J.E. Greene
Formation of Polyhedral N₂ Bubbles During
Reactive Sputter Deposition of Epitaxial Tin
(100) Films
J. Appl. Phys. 66, 536 (1989)

U. Jansson, J.-O. Carlsson, L.C. Markert and J.E. Greene
Phase-Selective CVD of Boron Carbide by
Nucleation Control on Patterned Substrates
J. Vac. Sci. Technol. A7, 3172 (1989)

J.E. Greene, S.A. Barnett, J.-E. Sundgren, and A. Rockett
Low-Energy Ion/Surface Interactions During Film
Growth from the Vapor Phase: Effects on
Nucleation and Growth Kinetics, Defect
Structure, and Elemental Incorporation
Probabilities
In *Plasma-Surface Interactions and Processing of
Materials*, ed. by O. Auciello, A. Grass-Marti,
and D.L. Flamm, NATO Advanced Study
Institute, Series E: Applied Sciences Vol. 176,
Kluwer Academic Publishers, Boston (1990)

J.E. Greene and J.-E. Sundgren
The Role of Low-Energy Ion/Surface Interactions
During Crystal Growth from the Vapor Phase:
Effects on Microchemistry and Microstructure
In *Characterization of Plasma-Enhanced CVD
Processes*, ed. by D.E. Ibbotson, G. Lucovsky,
and D. Hess, Materials Research Society Vol.
165, Pittsburgh (1990), p. 127

D. McIntyre, J.E. Greene, G. Hakansson, J.-E.
Sundgren, and W.-D. Munz
Oxidation of Metastable Single-Phase
Polycrystalline Ti_{0.5}Al_{0.5}N Films: Kinetics
and Mechanisms
J. Appl. Phys. 67, 1542 (1990)

R.C. Powell, G.A. Tomasch, Y.-W. Kim, J.A.
Thornton, and J.E. Greene
Growth of High Resistivity Wurtzite and
Zincblende Structure Single-Crystal GaN by
Reactive-Ion, Molecular Beam Epitaxy
In *Wide Bandgap Semiconductors*, ed. by J.T.
Glass, N. Fujimori, and R. Messier, Materials
Research Society Vol. 162, Pittsburgh (1990),
p. 525

J.E. Greene
Nucleation, Growth, and Microstructural
Evolution in Films Grown by Physical Vapor
Deposition
In *Deposition Technologies for Films and
Coatings*, ed. by R.F. Bunshah, Noyes
Publications, Park Ridge, NJ, in press

J.A. Thornton and J.E. Greene
Sputter Deposition Processes
In *Deposition Technologies for Films and
Coatings*, ed. by R.F. Bunshah, Noyes
Publications, Park Ridge, NJ, in press

J.A. Thornton and J.E. Greene
Plasmas Used in Deposition Processes
In *Deposition Technologies for Films and
Coatings*, ed. by R.F. Bunshah, Noyes
Publications, Park Ridge, NJ, in press

L. Hultman, W.-D. Munz, J. Musil, S. Kadlec, I.
Petrov, and J.E. Greene
Low-Energy (≈ 100 eV) Ion Irradiation During the
Growth of TiN Deposited by Reactive
Magnetron Sputtering: Effects of Ion Flux on
Film Microstructure
J. Vac. Sci. Technol., in press

Honors and Awards

Immediate Past-President and Member of the
Board of Directors of the American Vacuum
Society (AVS)

Editor of CRC Critical Reviews in Solid State
and Materials Science

Chairman of the Thin Film Division of the
International Union of Vacuum Science,
Techniques, and Applications (IUVSTA)

Plenary lecturer at the 8th International
Conference on Thin Films, San Diego, CA April
1990

Invited speaker at the Gordon Conference on the
Chemistry of Electronic Materials

Invited Talks

Low-Energy (50-500 eV) Accelerated-Ion Doping
Gordon Conference on the Chemistry of Electronic
Materials
Ventura, CA, February 1990

Accelerated-Ion Doping During Si MBE:
Chemistry on the Atomic Level
GDR Physical Society Meeting
Dresden, GDR, March, 1990

Low-Energy Ion/Surface Interactions During
During Vapor Phase Film Growth: Controlling
Microchemistry and Microstructure at the
Atomic Level

8th International Conference on Thin Films
San Diego, CA, April, 1990

Growth of High Resistivity Wurtzite and
Zincblende Structure Single-Crystal GaN by
Reactive-Ion Molecular-Beam Epitaxy,
Physical Electronics Workshop
Urbana, IL, April 1990.

PhD Graduates

Paul Fons, now a NSF Post-doctoral Fellow in the
Applied Science Dept., Tsukuba University,
Tsukuba, Japan

A. Wieckowski

Publications

C. K. Rhee, M. Wasberg, G. Horanyi, and A.
Wieckowski,
Strong Anion/Surface Interaction: Perchlorate
Reduction on Rh(100) Electrode Studied by
Voltammetry
J. Electroanal. Chem., **291**, 281 (1990)

E. K. Krauskopf and A. Wieckowski
Radiochemical Methods to Measure Molecular
Adsorption at Solid Electrodes.
In *Frontiers of Electrochemistry*, P. N. Ross and J.
Lipkowski (eds.), VCH Publishers, in press

L. M. Rice-Jackson, G. Horanyi, and A.
Wieckowski

Radiotracer Study of Adsorption of HSO_4^- and
 SO_4^{2-} Ions on a Smooth Copper Electrode in
Acid and Neutral Media
Electrochim. Acta, in press

P. Zelenay, G. Horanyi, C. K. Rhee, and A.
Wieckowski

Voltammetric and Radioactive Labeling Studies
of Single Crystal and Polycrystalline
Rhodium Electrodes in Sulfate-Containing
Electrolytes
J. Electroanal. Chem., in press

G. Horanyi and A. Wieckowski
Radiotracer Study of Adsorption of HSO_4^- Ions
Induced by Cd^{2+} Adatoms at a Smooth
Polycrystalline Platinum Electrode
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P. J. Slezak, K. W. H. Chan, H. T. Hoang and A.
Wieckowski

A ^{13}C NMR Study of the Adsorbed Products of
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Piotr Zelenay, Lesa M. Rice-Jackson, J.
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Neutral Media
Surf. Sci., submitted

Honors

1990 Honorable Lectureship of the Government of
Taiwan.

Invited Talks

Materials Development Center, Taiwan,
Chungshan Institute of Science and
Technology, January 3, 1990

Nuclear Energy Research, Lung-tan, Taiwan,
January 4, 1990

Gordon Research Conference on Electrochemistry,
Ventura, CA, January 15-19, 1990 (Invited
plenary lecture)

Symposium on Surface Science, La Plagne/Savoie,
France, March 11-17, 1990

University of Milan, Italy, March 20, 1990

199th ACS National Meeting, Boston, MA, April
22-27, 1990

Laval University (Canada), May 4, 1990

177th Meeting of the Electrochemical Society,
Montreal, Canada, May 6-11, 1990

Direct Methanol/Air Fuel Cell Workshop,
(DOE), Washington, DC, May 14-16, 1990

W. R. Grace, Columbia, MD, Research Division,
May 25, 1990

Brookhaven National Laboratory (Solid-State
Physics Seminar), November 2, 1990

PhD Graduates

Lesla M. Rice-Jackson
Research Staff Member, Shell Development
Company, Houston, TX 77251-1380

A. Zangvil

Publications

R. Ruh, K.S. Mazdiasni and A. Zangvil
Mullite-SiC Whisker-Reinforced Ceramic
Composites: Characterization and Properties
In *Fiber Reinforced Ceramics*, edited by K.S.
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Direct HVEM Observations of Transitions in
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in the Presence of a Controlled
Oxygen Atmosphere
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A. Zangvil, C.C. Lin and R. Ruh
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Mullite-Based Composites with ZrO_2 and
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J. Am. Ceram. Soc., to be published

C.C. Lin, A. Zangvil and R. Ruh
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C.C. Lin and A. Zangvil
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Derived Mullite - MgO - Partially-Stabilized-
Zirconia System
J. Am. Ceram. Soc., to be published

Invited Talks

Mechanical and Microstructural
Characterization of Mullite - ZrO_2 - SiC
Whisker Composites
Am. Ceram. Soc. 92nd Annual Meeting, Dallas,
TX, April 1990

Mechanical and Microstructural
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Whisker Composites
Am. Ceram. Soc. Pacific Coast Meeting, Seattle,
WA, October 1990

Microscopic Mechanisms and Kinetics of
Oxidation of SiC Whiskers in Mullite-Based
Matrices
Am. Ceram. Soc. 93rd Annual Meeting,
Cincinnati, OH, April 1991

MS and PhD Graduates

M. Thomas Cross, M.S.; Accepted a position as
Ceramic Process Engineer with Advanced
Nuclear Fuel Corp., Richland, WA.

Center for Microanalysis of Materials

Publications

Alexander E. Greene, Jr.
Sensitive High Vacuum Monitoring for Philips
Electron Microscopes Which Employ Ion Getter
Pumping
Electron Microscopy 1990 (San Francisco Press
1990) 1, 188

M. C. Yoo, K. Kim, J. M. Rigsbee, M. E. Mochel
Fabrication of Catalytic Nickel Clusters Using
Ionized Cluster Beam Technique
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R. N. Wright, C. D. Van Siclen, M. E. Mochel, S.
G. Usmar
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N. Holonyak, Jr., K. C. Hsieh and R. D.
Burnham

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J. S. Major, Jr., J. M. Dallasasse, L. J. Guido, J. E.
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A. Richard and N. Holonyak, Jr.

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

C.J. ALTSTETTER

**Mechanisms of Environmentally Induced
Embrittlement**

GOALS

The goal of this research program is to discover fundamental reasons why hydrogen modifies the mechanical behavior of metals. Hydrogen embrittlement has been identified as a dangerous phenomenon in alloys based on iron, nickel, zirconium, titanium and other elements which are used in energy-related applications, and the conditions for which hydrogen-induced cracking can be manifested have been extensively studied. The kinetics of hydrogen entry, movement and trapping in metals have been documented and correlated with the kinetics of crack propagation. The missing information in our efforts to understand and control hydrogen embrittlement is the reason why metals containing hydrogen are embrittled. We would like to be able to answer questions such as "How much hydrogen is required to cause embrittlement?," "Why are some alloys more susceptible than others?," "How and why does hydrogen modify dislocation generation and motion?," and "Does hydrogen decrease the bond strength at slip planes and interfaces?."

This program consists of two complementary projects; namely, the study of the effect of hydrogen concentration and temperature on (a) yielding and slip line configuration in alloys (austenitic stainless steels, presently) and (b) the kinetics of dislocation motion in the same materials.

HIGHLIGHTS

Both of these projects are in the phase of setting up equipment and developing techniques. Submicron thickness specimens are being cathodically charged at elevated temperatures in order to establish uniform concentrations of hydrogen. In the first project specimens are being tensile tested in order to observe their yielding and flow behavior and then investigated by SEM and TEM to observe the slip line distributions and dislocation configurations. In the second project

specimens are loaded statically and the strain vs time behavior is being recorded.

FUTURE DIRECTIONS

More sophisticated TEM experiments will be conducted using the gaseous hydrogen, straining stage facility. In addition, once we have surveyed the behavior of austenitic stainless steels we will apply our techniques to other alloys such as ferritic steels and nickel-based alloys which are subject to stress corrosion cracking and hydrogen embrittlement. At the same time, we will use different environments for our tests in order to elaborate the effects of entry or exit of hydrogen during plastic deformation. These tests will be required in order to relate our knowledge of fundamental dislocation behavior to the enormous published literature on the phenomenology of hydrogen embrittlement and stress corrosion cracking using different test methods and environments.

The Mechanical Properties of Grain Boundaries and Interfaces

GOALS

This program is directed towards understanding the structural and chemical properties of grain boundaries and interfaces with an emphasis on those aspects which control their response to external stresses. Interactions of dislocations with these interfaces are being studied with the techniques of *in situ* TEM, and microchemical effects are being studied with high resolution STEM and AES. Attention is being focussed on the effects of hydrogen, boron and sulfur.

The effects of hydrogen on the behavior of dislocations and on fracture are a continuing interest of this program with much of the work being carried out in the environmental cell TEM. Measurements of the thermodynamics of dislocation motion are being carried out as are finite element calculation of the concept of strain field shielding by mobile hydrogen atmospheres.

Dislocation structures at propagating crack tips in GaAs, MgO, Fe and a number of fcc metals have been studied using *in situ* TEM methods in an attempt to understand the mechanisms of the ductile - brittle transition in metals and non-metallic systems and to relate fracture in semi-brittle materials with local plasticity.

HIGHLIGHTS

We have demonstrated that the rules governing slip transmission into adjacent grains in the ordered $L1_2$ Ni_3Al system are the same as in disordered fcc crystals. The most important factor appears to be the selection of slip systems which leave residual grain boundary dislocations having the smallest Burgers vectors and hence have the lowest residual elastic energy. In Ni_3Al these residual dislocations appear to have little mobility in the grain boundary and hence lead to a buildup of the local stress. These slip transmission behaviors are the same with and without segregated B in hypostoichiometric Ni_3Al . In the absence of segregated B, stresses are relieved by crack initiation and propagation, while the addition of B appears to increase the grain boundary cohesion energy.

The theory of dislocation shielding due to H atmospheres has been developed using calculations of H distributions corresponding to

energy minimization of the system. Interaction stresses between shielded dislocations and obstacles (other dislocations, point defects, etc.) were calculated by summing the forces between the dislocations, obstacles and the respective shielding atmospheres. It was observed that the H rearranged its configuration to decrease the interaction energies and the obstacle stresses.

Direct determination of the effects of H and C on the thermodynamics of dislocation motion in Ni were carried out to experimentally test the concepts of the dislocation shielding theory. Using stress relaxation methods, it was observed that H atmospheres changed the "shape of the activation barriers which impeded dislocation motion at low strain rates. This had the effect of decreasing the "activation volume" and the "activation enthalpy" for dislocation motion which resulted in a significant increase in the dislocation velocity as a result of the addition of H. As expected, the addition of C resulted in increases in the activation volume and enthalpy and significant decreases in dislocation velocities.

Structural and chemical aspects of bonding metals to ceramics and polymers are being studied using the Ti/ Al_2O_3 , Cr/ Al_2O_3 , Ti/polyimide and Al/polyimide systems; chosen for their importance in the semiconductor packaging industry and for the variety of interesting scientific behaviors exhibited. Cross-sectional and planar TEM techniques were used for structural studies and AES, SIMS, and XPS were used for microchemical studies of the chemistry at the interfaces.

FUTURE DIRECTIONS

The program will continue to examine the role of interfaces in the deformation and fracture processes and the effect of interface chemistry and hydrogen on these processes. The principal techniques will be *in situ* normal TEM for structural studies and AES, SIMS, and XPS for the microchemical studies. The systems discussed above will continue to be studied in the next contract period with the emphasis being placed on the role of grain boundaries in deformation and the nature of the interfaces in the metal/ceramic and metal polyimide systems. We will continue our studies of hydrogen effects with emphasis being placed on H interactions with grain boundaries and interfaces.

SIGNIFICANT ACCOMPLISHMENT

Factors Affecting The Adhesion of Metals to Polyimides

Scientific Achievement

Several important phenomena which determine the adhesion of metals to polyimide (PMDA-ODA) have been revealed by studies of the chemistry and structure of metal/polyimide interfaces. Bonding of the metal to the polymer results from direct bonds formed between the metal atoms (Al, Ti, Cr) and the O in the carbonyl groups of the polyimide. Little bonding results from interactions of the metal with the C or the N in the functional groups; hence the strength of the metal/polymer bond depends directly on the density of the carbonyl groups at the polymer surface. Common surface treatments, such as low energy ion bombardment used to clean the surface, preferentially decrease the density of the surface accessible carbonyl groups and consequently decrease the strength of the bonding. Such surface treatment is often done to clean the surface and does have the beneficial effect of "roughening" the surface thus increasing the bonding surface available. Anneals in oxygen gas at temperatures of the order of 300 C after ion bombardment has the effect of allowing restructuring of the surface and a restoration of the surface chemistry; i.e. a reformation of the surface carbonyl groups.

Another factor which affects the bonding of several metal/polyimide interfaces is the formation of hydrides in the metal phase during anneals in high hydrogen fugacity gaseous atmospheres. In systems such as the Ti/polyimide or Ti/Al₂O₃, the use of hydrogen containing gaseous atmospheres allows the accumulation of hydrogen near the metal/polymer or metal/ceramic interface due to the high tensile stresses which develop in these regions. This hydrogen accumulation can cause the formation of hydrides which cause a further volume change as high as 23% and the resulting stresses can cause fracture to occur at the interface. It is observed that the fracture actually takes place through the polymer adjacent to the actual interface.

Significance:

Knowledge of and control of the interfaces between metals and polyimides is one of the most

important classes of technological problems facing the semiconductor industry at this time. Packaging procedures for integrated circuits are needed which allow the manufacture of the complex devices and ensure the integrity of the device during use. As integrated circuits become smaller, and the current densities increase, new metallic interconnects are required and the interfaces with the substrates become ever more critical. Polyimide layers are being used as dielectric material and to provide a stress relief mechanism between the substrate and the interconnects. A number of aspects of current practice lead to decreased bonding between the metal and the polyimide.

Based on our results we would suggest anneals at about 300 C in an oxygen atmosphere after ion bombardment of the surface of the polyimide. This would allow reforming the carbonyl groups to which the metal atoms bond and should lead to much stronger interfacial bonds.

Based on our results we would suggest that if hydride forming metals are used in the semiconductor package, the annealing gas not be the commonly used "forming gas" but that a non-hydrogen containing atmosphere be used. This would prevent the formation of a hydride and avoid the very large volume changes associated with this hydride.

Performer: H.K. Birnbaum, University of Illinois at Urbana-Champaign.

Surfaces and Grain Boundaries in Intermetallic Compounds

GOALS

This research program has two goals; understanding the role grain boundaries play in the deformation and fracture of intermetallics, and understanding the kinetics and thermodynamics of oxide formation on intermetallics. We are also studying how materials properties can be tailored by the segregation of impurities and microalloying species to grain boundaries. Environmental effects on alloy performance have also been investigated for cases where grain boundary effects are known (hydrogen, and sometimes oxygen, induce embrittlement and intergranular fracture). This basic information is needed to assist in the design and development of ductile high temperature alloys.

HIGHLIGHTS

It has been suggested that the improved ductility in Ni_3Al is, in part, a consequence of the existence of a structurally and chemically disordered region at the grain boundary. The chemistry at characterized grain boundaries has been determined by STEM/EDX with a 1 nm electron probe. The grain boundaries were characterized using electron diffraction techniques. To date $\Sigma 3$, 13, and 19a boundaries in well annealed Ni_3Al and $\text{Ni}_{76}\text{Al}_{24}$ alloys with and without B. No indication of significant segregation of Ni at the grain boundaries was observed, contrary to reported observations on non-equilibrium material. This result was independent of the Σ value of the grain boundary. Based on these results, if grain boundaries in ductile hypo-stoichiometric Ni_3Al have a nickel-rich phase, the enrichment and spatial extent is insufficient to be detected by EDS using a 1 nm diameter electron probe.

The dislocation structure vicinal to grain boundaries has been observed in bulk deformed ductile Ni_3Al samples. the nature of the dislocations observed entering and leaving the grain boundary are different. Incoming dislocations are primarily APB coupled dislocations whereas extended faults bounded by

partial dislocations emerge from the grain boundaries. these faults can be significant in length (several micrometers). Their thermal stability indicates that the bounding partial dislocations are strongly pinned. Thermal annealing studies have shown that the partials are unpinned at relatively low temperatures at about 300 C.

These results are indicative of a build-up of dislocation density at the grain boundaries as a result of plastic deformation. The role of these dislocation structures in the fracture of the ordered intermetallics is being studied.

We have also shown that our picture of the development of duplex surface oxides is also appropriate for oxide formation at internal grain boundaries in Ni_3Al . Fast grain boundary in-diffusion of oxygen has been observed and this diffusion and oxide chemistry is being related to embrittlement. In surface oxide growth, oxygen isotope diffusion analysis has identified three mechanisms by which oxide growth proceeds: a) short circuit in-diffusion of oxygen together with Ni out-diffusion, b) Predominantly by short-circuit metal out-diffusion through a porous alumina, and c) Ni outdiffusion and oxygen lattice diffusion through protective alumina. While Cr macroalloying alleviates embrittlement, it inhibits the transition to process (c) at high temperatures, thereby degrading the alloy performance.

FUTURE DIRECTIONS

The chemistry of grain boundaries in intermetallics and the role chemistry plays in determining the deformation and fracture response of materials will continue to be studied. The dislocation structures vicinal to the boundaries and the obstacles pinning the partial dislocations will be further investigated. The study will also be extended to include BCC and HCP systems to test the generality of the slip transfer criteria that we have developed for FCC systems. When our efforts in understanding grain boundary oxidation are completed, attention will be focussed upon using the methodology developed (imaging SIMS and AES) to determine cosegregation of beneficial microalloying agents and embrittling elements (S,H) and the relationship to grain boundary structure and orientation.

Ni AES map of grain boundaries at the oxide-metal interface in Ni_3Al . There appears to be NiO with an outer surrounding layer of Al_2O_3 growing down inward the grain boundaries.

SIGNIFICANT ACCOMPLISHMENT

Oxygen Diffusion Along Alloy Grain Boundaries

Scientific Achievement:

We have obtained direct evidence, through the use of isotopic diffusion markers, for the different oxide growth mechanisms of Ni_3Al alloys. Transitions between these regimes for different temperatures and macroalloying composition have been identified. To understand the formation of the duplex oxide growth, we have been able to relate both the oxide chemistry and the diffusion processes. Ni_3Al oxidizes by the growth of nickel oxide via outward diffusion of nickel, together with inward oxygen diffusion through a mixed inner oxide layer (I), a porous alumina (II) or a protective alumina (III). Macroalloying with chromium reduces the extent of mechanism (I) at low temperature, but delays the transition from mechanism (II) to (III) at high temperatures. Imaging analysis has revealed for the first time that these duplex structures are also found along grain boundaries that are fast inward oxygen diffusion pathways.

Significance:

Alloys suitable for high temperature structural applications must have high mechanical strength and oxidation resistance. Ni_3Al contains no strategic materials and has high oxidation resistance, but must be alloyed with chromium to overcome oxygen embrittlement when under stress. We are relating the embrittlement of Ni_3Al in oxygen to the duplex grain boundary chemistry caused by fast inward diffusion along the boundaries. Despite the ductility improvement afforded by chromium macroalloying, the inhibition of the protective

oxide growth mechanism renders the alloy unsuitable for use at high temperature due to excessive oxidation. By understanding the mechanisms for oxide growth and how the oxide chemistry and diffusion affects fracture, we are providing information with which other macroalloying species may be chosen to affect both oxidation protection and ductility in this and other alloys.

Performer: C.M. Loxton, University of Illinois at Urbana-Champaign

High Temperature Mechanical Behavior of Ceramics

GOALS

Advanced heat engines require higher operating temperatures for greater efficiencies. Ceramic materials offer great potential for use in these engines since the development of more fracture resistant materials. 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 dependant processes as well as the interaction between them must be quantified to develop durability assessment methodologies for these materials. The development of damage evolution models to estimate long term behavior from short term tests is a critical step towards the development of material systems for low heat rejection engines.

HIGHLIGHTS

The mechanical behavior of polycrystalline alumina has been studied under static and cyclic tensile loading at 1200C using smooth cylindrical specimens. A series of tests with different cyclic waveforms has been conducted. Results show that cyclic loading with a short duration of maximum stress provides a beneficial effect on the lifetime of ceramic materials when measured in terms of time to failure and compared to static loading at the same maximum stress. This phenomena has not been observed in metals or ceramics tested at room temperature. Similar observations have been made by other investigators in silicon nitride and silicon carbide reinforced alumina matrix composites. Crack growth studies have shown increased retardation as the testing frequency is increased. These effects are attributed to the viscous boundary phase that forms at high temperatures. Static fatigue occurs by the nucleation of cavities and the growth of microcracks on the grain boundaries. A viscous phase on the boundary carries part of the load and reduces the local driving force on the crack. At low frequencies the boundary flows and is unable to support any of the load giving rise to faster crack growth.

FUTURE DIRECTIONS

Modeling mechanical behavior of ceramics at high temperatures and stresses remains the focus of this work. This requires a better understanding of the role of viscous boundary phases on the mechanical behavior of monolithic and composite ceramic materials. Critical mechanical tests are performed to elucidate the mechanisms. This is followed by microscopic work to understand and quantify the controlling mechanisms.

SIGNIFICANT ACCOMPLISHMENT

Durability of Ceramic Materials

Scientific Achievement:

Cyclic loading has been shown to extend the lifetime of ceramic materials under some types of loading. Current studies indicate that static fatigue is the most damaging and the primary factor that must be considered in time delayed strength degradation. Viscous phases that enhance the fabrication of ceramic components can also improve their durability. These results are the first systematic study of the interaction between static and cyclic fatigue of ceramics at high temperatures and will serve as a basis for the development of durability assessment methodologies.

Significance:

Advanced heat engines require higher operating temperatures to achieve greater operating efficiencies to meet more stringent economic and regulatory requirements. Ceramic materials offer great potential for these applications. Full scale testing of engines is expensive and time consuming. New engines can no longer be designed by trial and error. Analytical methods for determining the performance and expected durability of the components are essential for American manufactures to remain competitive in the world marketplace with timely reliable products. Damage models are a critical part of this technology.

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

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 experimental in nature, relying on mechanical testing and microstructural analysis to study crack properties.

HIGHLIGHTS

The highlights of the program in the past year include the development of a technique for employing double edge notch and center crack panels to study crack growth. These specimen geometries have not been successfully employed previously here or elsewhere. Rather, previous work has relied on compact tension or single edge notch panels where a large component of the crack driving force is due to bending. This means that surface effects are overemphasized in the crack growth data. The present methodology does not suffer from this drawback and reliable subcritical crack growth data are obtained.

The use of the double edge notch and center crack tension panel specimens was possible only once bending strains were minimized through the development of a precise specimen alignment technique.

The results of several successful tests are shown in the figure. Crack growth rate data are plotted as a function of the stress intensity parameter range and show typical stage II growth followed by fast fracture at the critical stress intensity. The value of the critical stress intensity, about $4.3 \text{ MPa}\sqrt{\text{m}}$, is consistent with measurements of that parameter in other studies. The subcritical crack growth data, however, is unique to our studies. These specimen geometries have been employed to study the effects of cyclic and static fatigue, and can be employed for examining creep crack growth as well at elevated temperatures. Preliminary microstructural analysis (SEM and TEM) has been carried out.

FUTURE DIRECTIONS

The program is now fully focused on the understanding of the evolution and early growth of cracks and flaws in structural ceramics. The approach developed here has the significant advantage that crack dynamics and crack tip microstructure can be directly analyzed to establish the micromechanisms of crack initiation and growth. In the next year, we will employ the technique to study elevated temperature crack growth effects, and advance our understanding of the microstructural basis for subcritical crack growth by performing TEM studies of the crack tip region in interrupted tests. Also, we will apply our techniques to the examination of subcritical crack growth in other structural ceramics, notably silicon nitride and advanced ceramic composites with matrix toughening agents.

In the subsequent years, we will continue to examine fatigue and creep crack growth in advanced structural ceramics, and relate the observations to the evolution of damage microstructure and means for improvement. Also, we will start to examine the influence of environment on crack advance at elevated temperatures by testing in controlled atmospheres.

SIGNIFICANT ACCOMPLISHMENT

A Method for Measuring Subcritical Crack Growth in Structural Ceramics

Technical Achievement

Subcritical crack growth rates in structural ceramics have been measured by means of center crack tension panel specimens. This technique eliminates the difficulties encountered with

several other specimen geometries where bending contributes significantly to the crack driving force. Bending enhances the contribution of surface and near surface flaws due to higher near surface stresses. The center crack tension panel specimen eliminates the contribution of bending, and provides a means for measuring subcritical crack advance rates typical of bulk material. The technique requires precise specimen alignment, which is accomplished by affixing the ceramic panel to metal alloy end fixtures by means of an alignment jig. The end fixtures are held by pins in universal joint grips for mechanical loading. Crack growth rates are monitored by optical measurements.

Significance:

A major issue in the development of structural ceramics for engineering application is their durability under varying loads and duty cycles. It is now clear that ceramics of interest are prone to fatigue-type failure where small flaws are able to grow to critical size under thermal or mechanical cycling. Growth may also occur under constant (static) loading conditions. Several attempts have been made to characterize the extension of subcritical flaws, primarily by means of mechanical loading techniques which rely on a large degree of bending. Due to the stress gradients, these techniques elevate surface stresses and accentuate the role of surface and near surface flaws in the failure process. The present technique does not involve significant bending stresses and, therefore, yields a better measure of flaw growth characteristics in bulk material. The center crack tension panel specimen has additional significant advantages over many other specimen geometries. These include the ability to fabricate representative specimens from relatively small amounts of material, the ability to study the micromechanisms of crack advance due the well defined region of crack tip influence, and the ability to study advanced ceramics with enhanced toughness.

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

**D.2.b PUBLICATIONS AND HONORS FOR
MECHANICAL PROPERTIES
KC-02-01-02**

C.J. Altstetter

Publications

D.G. Ulmer and C.J. Altstetter
Mechanism for Hydrogen Embrittlement of
Austenitic Stainless Steels
Hydrogen Effects on Material Behavior, N.
Moody and A. Thompson, editors, TMS,
Warrendale, PA, 1990, p.421

D. Wortherm, I. Robertson, F. Leckie, D. Socie and
C. Altstetter
Inhomogeneous Deformation in Inconel 718 During
Monotonic and Cyclic Loadings
Met. Trans. A (in press)

D. Ulmer and C. Altstetter
In-Situ Determination of Hydrogen Diffusivity
Proc. XIVth Conf. Appl. Cryst., Z. Bojarski,
editor, Katowice, (in press)

D. Ulmer and C. Altstetter
X-Ray Studies of Hydrogen Embrittlement in
Austenitic Stainless Steels
Proc. XIVth Conf. Appl. Cryst., Z. Bojarski,
editor, Katowice, (in press)

D. Ulmer and C. Altstetter
Hydrogen-Induced Strain Localization and
Failure of Austenitic Stainless Steels at High
Hydrogen Concentrations
Acta Metallurgica and Materiala (in press)

Invited Talks

Studies of Hydrogen Embrittlement of Austenitic
Stainless Steels
Polish Academy of Sciences, Warsaw, August 1.

X-ray Studies of Hydrogen Embrittlement in
Austenitic Stainless Steels
XIVth Conf. on Applied Crystallography,
Cieszyn, Poland, August 8.

Processing and Properties of Nanophase
Intermetallic Compounds
Federation of Advanced Materials Industries,
Chicago, September 11.

Hydrogen Embrittlement of Face-Centered Cubic Alloys
Los Alamos Scientific Laboratory, October 26.

H.K. Birnbaum

Publications

R. Peddada, K. Sengupta, I.M. Robertson and H.K. Birnbaum
Structure and Chemistry of the Ti/Sapphire Interface
Acta Met./Scripta Met. Conference on Metal Ceramic Interfaces (Pergamon Press, Oxford), ed. by M. Ruhle, A.G. Evans, M.F. Ashby, and J.P. Hirth, (1990), pp. 115-120

H.K. Birnbaum
Mechanisms of Hydrogen Related Fracture of Metals
Proceeding of the Conf. on Environmental Effects on Fracture; (N.A.C.E., Houston), ed. by M.B. Ives; (1990), pp. 21-29

S.H. Doong, T.C. Lee, I.M. Robertson and H.K. Birnbaum
An In Situ TEM Study of the Fracture Mechanisms of Al/SiC_p Composites
Fundamental Relationships Between Microstructure and Mechanical Properties of Metal-Matrix Composites, (The Minerals, Metals, and Materials Soc.), ed. P.K. Liaw and M.N. Gungor, (1990), pp. 301-311

H.Z. Xiao, I.M. Robertson and H.K. Birnbaum
A TEM Study of Ternary Hydrides Formed in the Ti₃Al Intermetallic
Proceedings of the XIIth Int. Cong. for Electron Microscopy, (1990), p. 978

T.C. Lee, I.M. Robertson and H.K. Birnbaum
An In Situ TEM Deformation Study of the Slip Transfer Mechanisms in Metals
Metall. Trans. A, **21A**, 2437-2447 (1990)

T.C. Lee, I.M. Robertson and H.K. Birnbaum
A TEM In Situ Deformation Study of the Interaction of Lattice Dislocations With Grain Boundaries in Metals
Phil Mag. A, **62**, 131-153 (1990)

D.K. Dewald, T.C. Lee, I.M. Robertson and H.K. Birnbaum
Dislocation Structures Ahead of Advancing Cracks
Metall. Trans. A, **21A**, 2411-2417 (1990)

P. Rozenak, I.M. Robertson, and H.K. Birnbaum
HVEM Studies of the Effects of Hydrogen on the Deformation and Fracture of AISI Type 316 Austenitic Stainless Steel
Acta Metall. **38**, 2031-2041 (1990)

H.K. Birnbaum
Mechanisms of Hydrogen Related Fracture of Metals
Hydrogen Effects on Material Behavior, (T.M.S., NY), ed. by N. Moody and A. Thompson, (1990), pp. 639-660

P. Rozenak, I.M. Robertson, and H.K. Birnbaum
HVEM Studies of the Effects of Hydrogen on the Deformation and Fracture of AISI Type 316 Austenitic Stainless Steel
Hydrogen Effects on Material Behavior, (T.M.S., NY), ed. by N. Moody and A. Thompson, (1990), pp 386-397

G.M. Bond, I.M. Robertson and H.K. Birnbaum
Deformation and Fracture at Grain Boundaries in Ni₃Al
High Temperature Aluminides and Intermetallics, (T.M.S., NY), ed. by S.H. Wang, C.T. Liu, D.T. Pope, and J.O. Steigler, (1990), pp 301-326

H.K. Birnbaum
Hydrogen Effects on the Mechanical Response of Metals
Proceedings of the DOE San Diego Mtg. on Hydrogen in Solids, ed. by S. Meyers, Jnl. of Nuclear Materials, in press

S.R. Peddada, I.M. Robertson, and H.K. Birnbaum
A Microstructural Investigation Into the Effect of the Ambient Atmosphere on Chromium/Polyimide Interfaces
1990 MRS Symposium on Advanced Metallizations in Microelectronics, in press

Kabul Sengupta and H.K. Birnbaum
Study of Ti/Polyimide Interface in Reducing Environments
Proc. of the Second Symp. on Metallized Plastics: Fund. and Applied Aspects, (Electrochemical Society), in press

E.A. Clark and H.K. Birnbaum
Electrical Resistance Studies of Hydrogen
Diffusion in Niobium-An Old Problem
Revisited
Proceedings of Conf. on Metal Hydrides, Banff,
1990; *J. of Less Common Metals*, in press

T.C. Lee, D.K. Dewald, J.A. Eades, I.M.
Robertson, H.K. Birnbaum
An Environmental Cell Transmission Electron
Microscope
Review of Scientific Instruments, in press

I.M. Robertson, T.C. Lee, and H.K. Birnbaum
On The Use Of The TEM To Investigate The
Mechanisms Of Grain Boundary
Embrittlement
J. Ultramicroscopy, submitted for publication

T.C. Lee, I.M. Robertson, and H.K. Birnbaum
Interaction of Dislocations With Grain
Boundaries In Ni₃Al
Acta Metallurgica, et Materiala, submitted for
publication

Invited Talks

Hydrogen in Metals
DOE Panel on Hydrogen in Solids, Jan., San Diego

Environmental Cell Deformation and Fracture
XII Int. Congress on Electron Microscopy, Seattle,
Aug. 12-18

In Situ TEM Study of the Slip Activation Across
Grain Boundaries
XII Int. Congress on Electron Microscopy, Seattle,
Aug. 12-18

Hydrides in Ti Aluminides
Int. Conf. on Metal Hydrides, Banff, Can., Sept.
1990

A Retrospective Study of Hydrogen
Embrittlement
First Herb Johnson Memorial Lecture, Cornell
University, Dec. 1990

Ph.D. Graduates

D.K. Dewald, Ph.D. December 1990, presently at
Michigan Technical University
E. Sirois, Ph.D. December 1990, presently a
Research Associate at the Univ. of Illinois

C.M. Loxton and I.M. Robertson

Publications

S. Sircar, K. Chattopadhyay, C. Ribaudo, J.
Mazumder, C.M. Loxton and A.M. Venezia
Microstructure and Oxidation Properties of
Niobium Alloys
In *Laser Materials Processing III*, Eds. J.
Mazumder and K.N. Mukherjee (The
Minerals, Metals and Materials Society,
1989) 37-53

S.H. Doong, T.C. Lee, I.M. Robertson and
H.K. Birnbaum
An *In-situ* TEM Study of the Fracture Mechanisms
of Al/SiCp Composites
In *Fundamental Relationships between
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Metal-Matrix Composites* Eds P.K. Liaw and
M. N. Gungor, (The Minerals, Metals and
Materials Society, 1990) 301

A.M. Venezia, C.M. Loxton and J.A. Horton
Temperature and Pressure Effects on the
Oxidation of Ni₃Al Alloyed with Chromium
and Zirconium
Surface Science, 225, 195-205, (1990)

A.M. Venezia, J.E. Baker and C.M. Loxton
Oxygen Diffusion During the Oxidation of Ni₃Al
Alloys
In *Secondary Ion Mass Spectrometry, SIMS VII*,
Eds. A. Benninghoven, C.A. Evans, K.D.
McKeegan, H.A. Storms and H.W. Werner, (J.
Wiley and Sons) 719-723

T.C. Lee, I.M. Robertson and H.K. Birnbaum
A TEM in situ deformation study of the
interaction of lattice dislocations with grain
boundaries
Phil. Mag., 62, 131-153, 1990

P. Rozenak, I.M. Robertson and H.K. Birnbaum
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Deformation and Fracture of AISI Type 316
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Acta Met. Mat. 38, 2031 - 2040, 1990

T.C. Lee, I.M. Robertson and H.K. Birnbaum
An *in situ* TEM Deformation Study of the Slip
Transfer Mechanisms in Metals
Met. Trans A, 21A, 2437, 1990

D.K. Dewald, T.C. Lee, I.M. Robertson and H. K. Birnbaum

Dislocation Structures Ahead of Advancing Cracks

Met. Trans A., 21A, 2411, 1990

S.W. MacLaren, J.E. Baker, L.J. Guido, N. Holonyak, Jr., M. Anderle and C.M. Loxton
Ion Beam Mixing and Sample Effects on SIMS and SNMS Depth Resolution When Sputtering SiO₂/Si and Compound Semiconductor Interfaces

In *Secondary Ion Mass Spectrometry, SIMS VII*,
Eds. A. Benninghoven, C.A. Evans, K.D. McKeegan, H.A. Storms and H.W. Werner, (J. Wiley and Sons, 1990), 679-683

I.M. Robertson, G.M. Bond, Raja Subramanian and H.K. Birnbaum

Deformation and Fracture of Ni₃Al: An *in-situ* TEM Study

NASP Workshop Proceedings, Scottsdale, Arizona 1990

Shiing-Hwa Doong, Darrell F. Socie and Ian M. Robertson

Dislocation Substructures and Non-Proportional Hardening

J. of Eng. Mat. and Technology, in press

D.W. Wortherm, I.M. Robertson, F.A. Leckie, D.F. Socie and C.J. Altstetter

Inhomogeneous Deformation in Inconel 718 During Monotonic and Cyclic Loadings

Met. Trans., in press

T.C. Lee, D.K. Dewald, J.A. Eades, I.M. Robertson and H.K. Birnbaum

An Environmental Cell Transmission Electron Microscope

Review Scientific Instruments, submitted

R.T. Haasch, A.M. Venezia and C.M. Loxton
The Relationship Between Transport Processes and Chemistry in the Oxidation of Ni₃Al Alloys

Acta Met. et Mat., submitted

S.W. MacLaren, J.E. Baker, N.L. Finnegan and C.M. Loxton

Topography Development During Sputtering of GaAs and InP; Evidence for the role of Surface Diffusion in Ripple and Sputter Cone Formation

J. Vac. Sci. Technol., submitted

D.F. Socie

Publications

D.A. Wortherm, I.M. Robertson, F.A. Leckie, D.F. Socie and C.J. Altstetter

Inhomogeneous Deformation in Inconel 718 during Monotonic and Cyclic Loading
Metallurgical Transactions, 1990

S.H. Doong and D.F. Socie
Constitutive Modeling of Metals Under Nonproportional Cyclic Loading
J. Eng. Mat. & Tech., 1990 (in press)

S.H. Doong, D.F. Socie and I.A. Robertson
Dislocation Substructures and Nonproportional Loading
J. Eng. Mat. & Tech., 1990 (in press)

S.H. Doong and D.F. Socie
Deformation Mechanisms of Metals Under Complex Nonproportional Loading
European Group on Fracture, 1990 (in press)

T. Hoshide and D. F. Socie
Influence of Microstructural Factors on Cracking Behavior in Biaxial Fatigue
American Society for Testing and Materials, In press

J. Lin, T. Mayer and D.F. Socie
Cyclic Fatigue of Alumina
American Society for Testing and Materials, submitted

J. Lin and D.F. Socie
Static and Cyclic Fatigue of Alumina at High Temperatures
J. Am. Cer. Soc., submitted

Invited Talks

American Society for Testing and Materials
Annual Fatigue Lecture.

MS Graduates

Thomas Mayer, MS May 1990
Thesis Title: Cyclic Fatigue of Alumina
Employer: Ford Motor Company

J.F. Stubbins

Publications

J. F. Stubbins, A. M. Ougouag, and J. G. Williams
The Effects of Mechanical Stress Gradients on
Irradiation Induced Embrittlement of Pressure
Vessel Steels

ASTM STP, 1046, vol. II, 305-322 (1990)

K-Y. Hour and J. F. Stubbins
Crack Growth Behavior and Failure Mechanisms
in Three Heat Resistant Materials at
Elevated Temperature
Acta Metallurgica 38, 1463-1474 (1990)

K-Y. Hour and J. F. Stubbins
Fatigue Crack Growth Behavior of Alloy 800H at
Elevated Temperature
ASME Journal of Engineering Materials and
Technology, (in press)

J. F. Stubbins, A. M. Ougouag, and J. G. Williams
The Effect of Stress Driven Segregation on Crack
Growth Rates Under Static and Cyclic Loads
Proceedings of the 4th Int. Symp. on
Environmental Degradation of Materials in
Nuclear Power Systems-Water Reactors,
National Association of Corrosion Engineers,
(in press)

K. Nagarathnam and J. F. Stubbins
Elevated Temperature Oxidation Behavior of
Heat Resistant Alloys
Oxidation of Metals (submitted)

K-Y. Hour and J. F. Stubbins
Crack Growth Response in Three Heat Resistant
Materials at Elevated Temperature
Proceedings of the 22nd National Symposium on
Fracture Mechanics, Atlanta, GA, June 26-28,
1990, publication in an ASTM Special
Technical Publication

Honors

IBM Innovations Award, December 1990

Invited Talk

Surface Modification of Alloys with Ion Beams
Materials Engineering Seminar, University of
Illinois, April 27, 1990

Irradiation Performance of Copper and Copper
Alloys for Divertor Applications
Fusion Studies Laboratory, University of Illinois,
November 26, 1990

MS and PhD Graduates

S. Raghuraman, M.S., Continuing PhD on
MRL/DOE-BES Program

Brian Jelke, M.S., Employed at Commonwealth
Edison Co.; Chicago, IL

K-Y Hour, Ph.D., Continuing Post Doc at UIUC,
fractional time on MRL/DOE-BES Program

David Leet, Ph.D., Employed at Techtroniks;
Portland, OR

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

HAYDN CHEN

Structure and Dynamics of Ordering
Transformations in Metal Alloys and Silicide
Thin Films

GOALS

The objective of this research is to obtain a fundamental understanding of the kinetics and mechanisms of thermally induced ordering transformations in condensed matter. Current interest lies in the kinetic studies of decomposition and dissolution processes in several technologically important systems including Ni-based superalloys and Al-Li light metals. In addition, the transformation kinetics of metal-silicides from thin metal films deposited on hydrogenated amorphous silicon layers are also being investigated. These silicides are being studied with the goal of improving the integrity of thin film structure and searching for low-temperature processing methods.

HIGHLIGHTS

For the first time, electroless plating of palladium thin films on hydrogenated amorphous Si has been accomplished using a palladium-amine bath. The morphology and microstructure of the Pd aggregates were characterized by STEM, EDX, SEM and AES. Marked differences in morphology and distribution of the Pd aggregates on activated a-Si:H and c-Si substrates were observed. The as-deposited films with higher coverage were obtained from the $\text{NH}_3/\text{NH}_4\text{Cl}$ bath; they were typically more uniform and crack-free. But films obtained from the citrate bath suffered from incorporated hydrogen, resulting in bare spots, microcracks and local a-Si film peeling. New, improved methods for electroless deposition of Pd on a-Si:H is being pursued. Our work in Ni-based and Al-Li alloys emphasizes new information concerning the decomposition and reversion kinetics obtained from a simultaneous measurements of time-resolved small angle and wide angle x-ray scattering experiments utilizing synchrotron radiation both at NSLS in Brookhaven National Laboratory, USA, and at

the Photon Factory in Tsukuba, Japan. Our results in Al-Li show that at low enough aging temperatures, presumably below the ordering instability temperature, ordering process precedes decomposition. In contrast, at higher aging temperatures, ordering seems to play little or no roles in the kinetic evolution of the δ' precipitates. This study represents the first attempt to systematically investigate the transformation paths involving the decomposition from a supersaturated solid solution into a mixture of two phases, one of which is ordered. Therefore, both ordering and decomposition are taking place concomitantly which results in various mechanisms and kinetics behavior depending upon the alloy composition and aging conditions considered.

FUTURE DIRECTIONS

The silicide research will emphasize kinetic evolution of Pd_2Si thin films from electrolessly plated Pd on a-Si:H using the *in-situ* x-ray diffraction techniques developed in our laboratory. Besides, the dependence of silicide growth rate on the deposition condition and on the film thickness of the a-Si:H will be studied together with a thorough characterization of the resultant silicide films in terms of their chemistry, morphology, texture and microstructure.

Continuing research using time-resolved scattering techniques with synchrotron x-rays is expected. More detailed and quantitative study in Al-Li alloys with various compositions is to be carried out at various aging temperatures in order to substantiate the conclusions reached by us based upon the present results.

New initiatives are planned concerning the influence of elastic strain fields on the coarsening behavior and morphology change in Ni-Al-Si ternary system. We will also have plan to study the primary and secondary grain growth in Al thin films deposited by e-beam evaporation method and in a confined (i.e., with a coating of C thin layer) condition. The purpose of this work is to study the effect of stress on the grain growth behavior.

SIGNIFICANT ACCOMPLISHMENT

New Phenomenon in the Decomposition Behavior of Al-Li Alloys

occur, thereby providing data for further investigations.

Performer: H. Chen, University of Illinois at Urbana-Champaign.

Scientific Achievement:

It has been shown for the first time that the ordering process precedes the decomposition of δ' precipitates below the ordering instability temperature in Al-Li binary alloys. The extent to which the concomitant processes of ordering (100 peak) and decomposition take place depends on alloy composition and aging temperature. Observations were made using high flux synchrotron x-rays at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory, which allowed simultaneous measurements of small angle scattering and wide-angle superlattice reflection intensities. A composite figure is shown below that includes the temperature profile as well as the integrated intensities showing the faster rate of ordering as compared with that of δ' decomposition (SAXS) at 196°C for an Al-12at.%Li alloy.

Significance:

Many technologically important alloys such as Ni-based superalloys, Al-Li light metals, etc., rely on the ordered precipitates to improve their mechanical strength and corrosion resistance. Ways to improve the properties through alloying and thermal-mechanical processing have constantly been pursued. Recent theoretical studies point out some new transformation processes and paths that such alloys may take to reach their equilibrium structures during aging. Our findings provide the first experimental evidence that some of the processes do indeed

WALTER G. KLEMPERER

Materials Chemistry of Oxide Ceramics; Field Responsive Organic Inclusion Complexes

GOALS

This program is concerned with controlling ceramic processing on a molecular level and examining relationships between the 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 structure is retained in the ultimate product. Two areas have been targeted for investigation: sol-gel processing of oxide ceramics and hydrothermal processing of new organic/inorganic composites, clathrasils.

HIGHLIGHTS

Sol-gel polymerization of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ in CH_3CN under neutral conditions yields very high surface area ($S_{\text{BET}} > 900 \text{ m}^2/\text{g}$) xerogels. This property is seen to result from the structure of the gels on the molecular level. According to N_2 adsorption studies, model studies, and TEM studies, the large size and rigidity of the cubic $[\text{Si}_8\text{O}_{12}]$ core structure leads to polymers whose rigidity inhibits extensive crosslinking of the type observed in $\text{Si}(\text{OCH}_3)_4$ -derived xerogels.

As a first step toward understanding molecular growth pathways in the sol-gel processing of metal oxides, an ^{17}O NMR technique has been developed for identifying early transition metal polyoxoalkoxides in solution. $[\text{Ti}_8\text{O}_6](\text{OC}_2\text{H}_5)_{20}$, $[\text{Ti}_7\text{O}_4](\text{OC}_2\text{H}_5)_{20}$, and $[\text{Ti}_{10}\text{O}_8](\text{OC}_2\text{H}_5)_{24}$ have been isolated from hydrolyzed $\text{Ti}(\text{OC}_2\text{H}_5)_4$ solutions and structurally characterized using single crystal x-ray diffraction techniques. Oxygen-17 NMR spectroscopy was then used to show that only the first two of these three species are actually present in hydrolyzed $\text{Ti}(\text{OC}_2\text{H}_5)_4$ solutions at significant concentrations.

Single crystals of the dodecasil-3C clathrasils $17\text{SiO}_2 \cdot \text{M}$ (M = cyclohexane, cyclopentane, piperidine, pyrrolidine, cyclopentylamine, and cyclobutylamine) were grown using hydrothermal techniques. Each material displayed two phase transitions, one between 59 and 180°C and the other between -110

and -1°C . These phase transition temperatures could be systematically varied by varying the size of the guest molecule M .

FUTURE DIRECTIONS

A study of titania sol-gel polymerization will be undertaken in which the properties of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ - and $[\text{Ti}_7\text{O}_4](\text{OC}_2\text{H}_5)_{20}$ -derived thin films will be compared. These studies will then be extended to zirconia and ternary titanium oxide systems.

In the clathrasil area, two-zone hydrothermal seeded growth techniques will be examined as a potential route to large (cm-sized) single crystals suitable for optical applications.

SIGNIFICANT ACCOMPLISHMENT

A New Technique for Characterizing Metal Oxide Clusters Formed During Sol-Gel Processing

Scientific Achievement

The structures of three titanium oxide clusters formed in organic solvents have been characterized using a new ^{17}O NMR spectroscopic technique. Reaction of $\text{Ti}(\text{OR})_4$ with water enriched in the oxygen-17 isotope yields oxoalkoxides $[\text{Ti}_x\text{O}_y](\text{OR})_2$ that are selectively enriched at their oxide oxygen, but not their alkoxide oxygen, sites. As a result, they display simple, characteristic ^{17}O NMR spectra:

Significance:

Sol-gel processing of metal oxide ceramics offers an attractive alternative to traditional processing methods since the hydrolysis/condensation chemistry involved proceeds in solution in a stepwise fashion that in theory can be controlled on a molecular level:

In practice, efforts to control sol-gel processing on a molecular level have been frustrated by an inability to determine the formulas and structures of the intermediate clusters $[M_aO_b](OR)_c$ involved. The newly developed ^{17}O NMR technique allows characterization of the metal oxide clusters formed in solution for the first time. The understanding of cluster growth processes to be gained using this technique will be essential for rational development of new sol-gel processing techniques.

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 concerned with the chemical synthesis, crystal growth, ceramic processing, microstructure development, characterization and property measurements on new and improved ceramic materials for energy related applications. The purpose is to generate a basic understanding of the interrelationships that exist between processing and properties for polycrystalline materials. A goal is to model polycrystalline properties on single crystal values, and determine factors which limit materials performance. Of particular interest are structure-property relations in ferroelectric materials and superconductors. Recent developments include the fabrication of electrical ceramics by the molecular building block approach to chemical synthesis. To this end, polymeric condensation reactions have been investigated in sol-gel processing for the low temperature densification and crystallization of field-responsive materials. The objective is to integrate functional devices on semiconductors. The research has been successful and devices have been demonstrated.

HIGHLIGHTS

We were the first to integrate high dielectric content ($K > 2000$) ferroelectric relaxor materials onto silicon at reduced temperatures. Materials in the $Pb[Mg_{1/3}Nb_{2/3}]_{1-x}Ti_xO_3$ (PMNT) system and the $Pb(Zn_{1/3}Nb_{2/3}]_{1-x}Ti_xO_3$ (PZNT) system were studied in detail. We were the first to synthesize heterometallic alkoxide-based precursors (e.g., $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$) which aided greatly in the molecular pathway to ceramic synthesis. Crystals were grown at room temperatures and the solid state structure determined by x-ray diffraction. The evolution of oxide structure was followed by spectroscopic methods (e.g., NMR, FTIR). From an understanding of hydrolysis and condensation reactions, and thermal treatments, PMNT and PZNT could be formed into the perovskite phase at low temperatures. Ferroelectric random access memory (FRAM) elements and dynamic random access memories (DRAM) have been demonstrated. This has come about due to the molecular building block approach to ceramic

synthesis, with close collaboration with Professor W. G. Klemperer.

FUTURE DIRECTIONS

Future directions will include research on molecular pathways to ceramic synthesis, with emphasis on structures in solution during polymeric condensation reactions. Crystals of oxo-alkoxides will be grown, and their structures determined. Ultrastructures will be investigated in detail, and the role of nanostructure, surface area and free volume will be investigated as the thermodynamic driving forces for low temperature densification and crystallization. We plan to investigate and enhance the rearrangement and visco-elastic processes for densification of high quality microstructures. In addition, the role of substrates and interfaces on preferred orientation and texturing will be investigated for the realization of pseudo-single crystal properties. Additional field responsive materials will continue to be investigated. Molecular nanocomposites based upon organic inclusion complexes within oxide framework structures have unusual symmetries and optical response characteristics. We plan to investigate these opportunities in the future.

Frequency dependence of dielectric constant and $\tan \delta$ for PMNT thin layers

SIGNIFICANT ACCOMPLISHMENT

Molecular Pathways in Ceramic Synthesis

Scientific Achievements:

We have recently demonstrated the synthesis of energy conversion and detection materials by metallo-organic routes. For example $\text{Pb}_2\text{Zn}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_3\text{H}_7\text{O}_2)_4$ was used for the fabrication of piezoelectric $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$; $\text{LiNb}(\text{OCH}_2\text{CH}_3)_6$ for electro-optic LiNbO_3 ; and $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cu}(\mu\text{-OCH}_4\text{H}_9)_2\text{Cu}(\text{O}_2\text{C}_5\text{H}_7)$ for superconducting $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$. In all cases, single crystals were grown from concentrated solutions, and their solid-state structures determined unambiguously by x-ray diffraction. The materials have not been synthesized previously and are expected to have major impacts on the future fabrication of advanced electrical ceramic devices. The synthesis of heterometallic alkoxide precursors is particularly difficult but technically rewarding. The method allows for the formation of metal-oxygen-metal bonds ($\text{M}_1\text{-O-M}_2$) at low temperatures, and the establishment of network structures for ceramic synthesis. In addition, the synthesis route spatially distributes the constituent cations in an homogeneous manner, fixes the stoichiometry and controls the purity. These are all beneficial aspects for the fabrication of high quality ceramics.

Significance:

The molecular building block approach to ceramic synthesis is a potential upset technology in ceramic processing. It avoids the handling of conventional powders, and the attendant problems associated with the coordination of fine powders for macro-defect free structures. Polymeric condensation of metalloorganic precursors allows for the formation of network structures at temperatures close to room temperature through controlled hydrolysis reactions. The method is particularly suited to the fabrication of thin-layer devices and coatings which densify at reduced temperatures. It is a low temperature method of ceramic processing, and increasingly amenable to semiconductor technology. This will allow for the future integration of functional devices with semiconductors. Immediate advantages are noted in electronic packaging, where capacitors can now be integrated onto integrated circuits, rather than attached with resistive and inductive losses. The materials synthesized in this research

program respond and transduce in a predictable manner with respect to external forces and fields. The logic function and ferroelectric memory should give rise to adaptive and smart material systems. A key factor in realizing this future technology is the ability to integrate functional devices with semiconductors for control and feedback purposes. The molecular building block approach to ceramic synthesis is one such method which is compatible with the low temperature processing of semiconducting devices. This should give rise to important developments in that are smart material systems.

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

Crystal structure of $\text{Pb}_2\text{Zn}_2\text{C}_2\text{H}_3\text{O}_{24}(\text{C}_3\text{H}_5\text{O}_2)_4$

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

An improved empirical atomic interaction potential allows more accurate simulation of the energy barriers and rates of diffusion on the technologically important $\text{Si}(001) 2 \times 1$ surface. Anomalous behaviors of the conventional interatomic potentials are eliminated while the quality of simulation of bulk material is retained. The results of molecular statics calculations based on this potential provide important input parameters for the Monte Carlo model under development by this project.

An improved model for strain relaxation in heterostructures has been devised. The most significant point is that the driving force for strain relief is small and increasing very slowly just above the critical thickness. Hence, strain relief should frequently be kinetically or entropically limited for layers near the equilibrium onset of strain relief. Further, it was shown by explicit calculation of a number of dislocation network configurations that substantial errors should be introduced into the network during its formation. Thus, it is likely that strain relief will be substantially incomplete at the end of growth for many heterojunctions.

A detailed microscopy study of the crystallography and defect structure of CuInSe_2 single crystals and polycrystalline thin films has yielded both basic information useful for further analysis of these materials and details of practical importance for design of solar cells. A convergent beam diffraction ZAPMAP for CuInSe_2 has been assembled and indexed. Selected area diffraction pattern results suggest a method for characterization of the density of antisite defects. Several $a\langle 110 \rangle$ -type superdislocations, dissociated into $a/2\langle 110 \rangle$ dislocations have been observed. Ordered networks of misfit dislocations at grain

boundaries in polycrystalline CuInSe₂ have been observed, indicating that a well-defined, narrow grain boundary between the crystallites exists, free of second phases.

Demonstration of high-efficiency CuInSe₂/CdS thin film solar cells is one of the most exciting recent developments in the field of renewable energy sources. The results of this work indicate that major defects do not inhibit the operation of solar cells. Furthermore, the devices need not be limited by second phases even if deposited significantly off of the ideal composition. It is therefore clear that many of the potential "show stoppers" for application of the CuInSe₂ to solar cells and scale up of existing deposition technologies to large areas will not prove to be significant.

FUTURE DIRECTIONS

The formalism developed to model strain relief in heterostructures will be extended to mesa structures where the effective film area is very small. Calculations will quantize the magnitude and fluctuations in residual strain expected in thin films. This will permit a clear assessment of the potential value of strained layer structures in practical devices. Synergistic development of Monte Carlo and molecular dynamics simulations of epitaxial growth will continue. This will permit modelling of continuously finer scale phenomena associated with crystal growth. Concurrent experimental efforts on surface and bulk structure and chemistry of thin films will continue.

SIGNIFICANT ACCOMPLISHMENT

Incomplete Strain Relief in Heterostructures Predicted

Scientific Achievement:

Calculations show that it is not only possible but likely that strain relief will be substantially incomplete at the end of growth for many heterojunctions. The model has shown how kinetic limitation of strain relief is due, in part, to a very gradual accumulation of the driving force for dislocation formation. Significant strain relief should occur only well beyond the critical thickness predicted by a conventional energy balance. The maximum

driving force available for strain relief was shown to be related to film thickness as illustrated in the following figure.

Further, it was shown by explicit calculation of a number of dislocation network configurations that substantial errors should be introduced into the network during its formation which will be retained in the final dislocation network. A functional form for the density of threading dislocations in growing, strained thin films has also been derived.

Significance:

The model developed contributes significantly to assessing the potential value of compound semiconductors in strained layers for advanced device applications. One of the primary approaches proposed for increasing the capabilities of state of the art microelectronic devices is by the use of heterojunctions. A large experimental effort is currently underway worldwide to produce such materials. However, serious problems in controlling both the threading dislocation density and the residual strain have been encountered. The model developed here permits quantitative calculation of the magnitude and variation which can be expected in residual strain and threading dislocation density across a large wafer.

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

Processing Monodisperse Ceramic Powders

GOALS

The goal of this program is to gain a fundamental understanding of the chemical and physical processes limiting the fabrication of advanced materials. In particular, the three thrusts of this program are aimed at developing; i) quantitative models for the precipitation of uniform ceramic precursor particles, ii) methods of processing green bodies with low flaw densities that result in controlled microstructures on firing, and, iii) an in depth understanding of the growth mechanisms of large crystals of optically and electronically active clathrasils.

HIGHLIGHTS

A lack of technologies for preparing agglomerate free ceramic precursor powders is a fundamental stumbling block to the fabrication of many advanced ceramics. Our research has focussed on identifying physical and chemical themes that underlie the formation of uniform precipitates. We find that colloidal stability plays a key role in controlling precipitate morphology. Details of the particle interaction potentials gained from studies of shear induced aggregation demonstrate the sensitivity of precipitate morphology to electrostatic and solvation repulsive forces. Alkoxide derived silica and titania particles and colloidal gold have been used as models. The importance of this work lies in its demonstrating that when schemes for preparing uniform particles are sought, rather than focussing on the length of the nucleation period, attention should be turned to the colloidal stability of the growing particles.

In our studies of methods of fabricating low flaw density green bodies, we have focussed on changes in rheological properties associated with particle flocculation. We are using a model system of uniform silica particles where the interaction potential can be varied from repulsive to attractive in a reversible manner. We find that as the attraction is increased, the suspensions gel. Analysis of the flow properties near the gel temperature suggest that this process is similar to sol/gel or percolation transitions seen in organic polymerization reactions and is intimately associated with the glass transition seen at volume fractions near close packing.

FUTURE DIRECTIONS

Key to precipitation of inorganic solids are the thermodynamic properties and interaction potentials of large molecules or small particles. We are initiating studies of the interaction potentials of large polyoxyanions which will act as models of small metal oxide particles.

The influence of attractive potentials on suspension rheology and the implications of a percolation transition occurring in flocculating suspensions will be investigated. Conditions will be sought leading to flowable suspensions with volume fractions in excess of 0.6.

Titania sphere precipitated from titanium alkoxides under conditions where the particles are stabilized by increasing particle surface charge density. Average particle size is 0.7 μm .

SIGNIFICANT ACCOMPLISHMENT

Advances in Precipitation of Ceramic Powders

Scientific Achievement:

Control of agglomeration is a key step in the formation of uniform submicron particles. The importance of electrostatic and short range

Typical precipitate morphology in absence of charge stabilization $1 \mu\text{m} = 1.5 \text{ cm}$.

solvation repulsive interaction potentials in achieving colloidal stability has been established in studies of silica and titania particles formed from alkoxides. By controlling the interaction potential, an agglomerate free precipitate can be synthesized and the final particle size varied from tens of nanometers to over a micron in diameter. The research has shown that even if particles are stable to Brownian aggregation, shear forces such as occur in a well mixed reactor can often destabilize the suspension with the result being a precipitate composed of large agglomerated masses. This work identifies control parameters of great importance in the scale-up of precipitation reactions and is expected to impact on advanced ceramic fabrication technologies.

Significance:

Development of technologies for producing agglomerate free, submicron, ceramic precursor powders is seen as a major stumbling block in the fabrication of advanced ceramics. While many recipes are available for preparing small (mg) quantities of uniform particles, scale-up of these reactions has proven difficult. This is now

largely recognized as a problem in understanding the mechanisms which result in uniform precipitates. Identification of colloidal stability and the role of short range solvation forces as being of key importance opens new possibilities for development of reactor conditions and control schemes such that large quantities of high quality powders can be prepared in an economic manner.

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

D.3.b PUBLICATIONS AND HONORS FOR
PHYSICAL PROPERTIES
KC-02-01-03

H. Chen

Publications

- G. E. White and Haydn Chen
An *In Situ* Observation of the Growth Kinetics
and Stress Relaxation of Pd₂Si Thin Film on
Si (111)
J. Appl. Phys., 67(8), 3689-3692 (1990)
- B.J. Shaiu, H.T. Li, H.Y. Lee and H. Chen
Decomposition and Dissolution Kinetics of δ'
Precipitation in Al-Li Binary Alloys
Met. Trans. 21A, 1133-1141 (1990)
- Haydn Chen, J. Anderson, K. Oshima, H.
Okajima and J. Harada
On the Atomic Short Range Order Structure in
Au-Fe Alloys
Phys. Rev. B42(4), 2342-2346 (1990)
- G. E. White and Haydn Chen
In Situ Study of Film Stresses in Metal Silicides
Using Absorption Edge Contour (AEC)
Mapping
J. Appl. Phys., 68(7), 3317-3321 (1990)
- C. Marsh and Haydn Chen
An *In Situ* X-ray Diffraction Study of Precipita-
tion from a Supersaturated Solid Solution:
The γ' Precipitate in a Ni-12.5at.% Al Alloy
Acta Met., 38(11), 2287-2298 (1990)
- Haydn Chen and J.E. Epperson
Multidisciplinary Study of Phase Separation in a
Supersaturated Ni-Si Alloy
Proc. Morris E. Fine Symposium, TMS Publication
(in press)
- H.Y. Lee, Haydn Chen, G.B. Stephenson and B.
Park
Time-Resolved Scattering Study of The Early-
Stage Decomposition and Ordering Processes
in an Al-12at.% Li Alloy
J. Appl. Cryst. (in press)

Haydn Chen, H.Y. Lee, M.S. Yu, G.B. Stephenson
and B. Park
Early-Stage Transformation Kinetics of δ'
Precipitation in Al-Li Alloys
MRS Proceeding on the Kinetics of Phase
Transformations (1990)

Haydn Chen, M.S. Yu, H. Okuda, M. Tanaka and
K. Osamura
Time-Resolved Small-Angle X-ray Scattering
Study of Reversion Kinetics of Precipitates in
an Al-12at.%Li Alloys Utilizing Synchrotron
Radiation
MRS Proceeding on the Kinetics of Phase
Transformations (1990)

M.L. Chou, N. Manning, and Haydn Chen
Electroless Deposition and Characterization of
Pd Thin Films on Hydrogenated Amorphous
Silicon
MRS Proceeding on Evolution of Thin Films and
Microstructures (1990)

J.E. Epperson, V.S. Rainey, C.G. Windsor, K.A.
Hawick, and H. Chen
A Small Angle Neutron Scattering Investigation
of the Kinetics of Phase Separation in an Fe-
27.5at%Cr-5.6at%Ni Alloy
MRS Proceeding on Kinetics of Phase
Transformations (1990)

J.P. Anderson, Haydn Chen and J.E. Epperson
The Short Range Order Structure of an As-
Quenched Ni-12.5 at. % Si Alloy - A
Synchrotron X-ray Diffuse Scattering Study
Acta Metall. (1990) submitted

H.Y. Lee, S.S. Hsu and Haydn Chen
Time-Resolved Small-Angle X-ray Scattering
Study of the Coarsening Kinetics of δ'
Precipitation in Al Alloys Containing 8 and 9
at.% Li
Scripta Met. (1991) submitted

Honors and Awards

Award by the Japanese Light Metal Education
Foundation, Inc., 1990-1993.

Chairman of the Phase Transformations
Committee of ASM International, 1990

Member of the Program Advisory Board, USA
Pulsed Neutron Sources at IPNS and
LANSCE, 1988-present.

Elected member of the APSUO (Advanced Photon Source Users Organization) Steering Committee, 1989-present.

Elected Executive Officer of the Small Angle Scattering Special Interest Group of the American Crystallographic Association, 1988-present.

Member of Sigma Xi

Invited Talks

X-ray Study of Phase Transformation Dynamics in Al-Li Alloys
Department of Physics, Univ. of Illinois, Urbana, IL March 30, 1990.

Combined Use of Small-Angle Scattering, Wide-Angle Diffraction, and Electron Microscopy for the Studies of Decomposition Kinetics in Metallic Alloys
Symposium on Recent Advances in Small-Angle Scattering,
ACA Annual Meeting New Orleans, April 8-13, 1990.

Kinetics of Decomposition and Ordering Processes in an Al-12at.%Li Alloy
Institute of Applied Physics, University of Tsukuba, Japan, June 20, 1990;

Kinetics of Decomposition and Ordering Processes in an Al-12at.%Li Alloy
Department of Metallurgy, University of Tokyo, Japan, June 22, 1990.

Kinetics of Decomposition and Ordering Processes in an Al-12at.%Li Alloy
Workshop on the Dynamics of Phase Separation with Ordering

Kinetics of Decomposition and Ordering Processes in an Al-12at.%Li Alloy
KEK, Tsukuba, Japan, June 27-29, 1990.

Time-Resolved X-ray Scattering Studies of the Ordering and Decomposition Processes in Al-Li Alloys
School of Materials Engineering, Purdue University, Indiana, Oct. 22, 1990.

W.G. Klemperer

Publications

W.G. Klemperer and S.D. Ramamurthi
A Flory-Stockmayer Analysis of Silica Sol-Gel Polymerization
J. Noncryst. Sol. **121**, 16, 1990

H. K. Chae, W. G. Klemperer, D.A. Payne, C.T.A. Suchicital, D.R. Wake, and S. R. Wilson
Clathrasils: New Materials for Nonlinear Optics
in *New Materials for Nonlinear Optics*, edited by Galen Stucky, in press

P. Cagle, W.G. Klemperer, and C. Simmons
Molecular Architecture and Its Role in Silica Sol-Gel Polymerization
Mat. Res. Soc. Symp. Proc., in press

P.J. Kulesza, L.R. Faulkner, J. Chen and W.G. Klemperer
Solid State Electrochemistry: Voltammetric Monitoring of Redox Transitions in Single Crystals of Silicotungstic Acid
J. Am. Chem. Soc., in press

H.K. Chae, W.G. Klemperer, D.A. Payne and C.T.A. Suchicital
Molecular Engineering of Phase Transition Temperatures in Dodecasil-3C Clathrasils
Proceeding of the 7th International Symposium on the Applications of Ferroelectrics, in press

W.G. Klemperer and F.S. Rosenberg
Solution Structures of Early Transition Metal Polyoxoalkoxides by ^{17}O NMR Spectroscopy
J. Am. Chem. Soc. (submitted)

Invited Talks

Michigan State University

Ohio State University

M.R.S. Symposium on Better Ceramics Through Chemistry, San Francisco

Fourth International Conference on the Chemistry of the Platinum Group Metals, University of Cambridge

Westinghouse, Savannah River

University of South Carolina

A.C.S. Symposium on Inorganometallic Chemistry, Washington, D.C.

A.C.S. Ralph K. Iler Memorial Symposium on the Colloidal Chemistry of Silica, Washington, D.C.

A.C.S. Symposium on the Applications of Analytical Techniques to the Characterization of Materials, Washington, D.C.

ARCO Chemical Company

Second International A.C.S. Topical Workshop on Advances in Silicon-Based Polymer Science, Makaha, Hawaii

Ph.D. Graduates

Frank S. Rosenberg, Postdoc, University of Illinois

Hee K. Chae, Postdoc, University of Illinois

D.A. Payne

Publications:

L. F. Francis, Y-J. Oh and D. A. Payne
Sol-Gel Processing and Properties of Lead Magnesium Niobate Powders and Thin Layers
J. of Mat. Science, **25:12**, 5007-5013 (1990)

S. B. Desu and D. A. Payne
Interfacial Segregation in Perovskites: I, Theory
J. Am. Ceram. Soc., **73** (11) 3391-3397 (1990)

S. B. Desu and D. A. Payne
Interfacial Segregation in Perovskites: II, Experimental Evidence
J. Am. Ceram. Soc., **73** (11) 3398-3406 (1990)

S. B. Desu and D. A. Payne
Interfacial Segregation in Perovskites: III, Microstructural and Electrical Properties
J. Am. Ceram. Soc., **73** (11) 3407-3415 (1990)

S. B. Desu and D. A. Payne
Interfacial Segregation in Perovskites: IV, Internal Boundary Layer Devices
J. Am. Ceram. Soc., **73** (11) 3416-3421 (1990)

C. T. A. Suchicital and D. A. Payne
Flux Growth of Single Crystal Lead Titanate
J. Crystal Growth, **104**, 211-217 (1990)

N. K. Kim and D. A. Payne
Amorphous Lead Iron Tungstate Prepared by Twin-Roller Quenching
J. Mat. Res., **5** (10): 2045-2048 (1990)

K. D. Budd and D. A. Payne
Optical Properties and Densification of Sol-Gel Derived PbTiO₃ Thin-layers
Sol-Gel Optics, SPIE Proc. **1328** 450-455 (1990)

D. J. Eichorst and D. A. Payne
Sol-Gel Processing of Lithium Niobate Thin-Layers for Optical Applications
Sol-Gel Optics, SPIE Proc. **1328** 456-465 (1990)

D. S. Hagberg, D. J. Eichorst and D. A. Payne
Electrical and Optical Properties of Alkoxide-Derived Lithium Niobate Thin Layers
Sol-Gel Optics, SPIE Proc. **1328** 466-473 (1990)

R. W. Schwartz, C. D. E. Lakeman and D. A. Payne
The Effects of Hydrolysis Conditions, and Acid and Base Additions, on the Gel-to-Ceramic Conversion in Sol-Gel Derived PbTiO₃
Better Ceramics Through Chemistry IV, eds. C. J. Brinker, B. J. J. Zelinski, D. F. Clark and D. R. Ulrich, *Mat. Res. Soc. Symp.* **180** 335-340 (1990)

L. F. Francis and D. A. Payne
Processing, Perovskite Phase Development, and Dielectric Properties for Sol-Gel Derived Pb[Mg_{1/3}Nb_{2/3}]_{0.9}Ti_{0.1}O₃ Thin Layers
Ferroelectric Thin Films, eds. A. I. Kingon and E. R. Myers, *Mat. Res. Soc. Symp.* **200** 173-178 (1990)

D. J. Eichorst and D. A. Payne
Evolution of Molecular Structure in Alkoxide-Derived Lithium Niobate
Better Ceramics Through Chemistry IV, eds. C. J. Brinker, B. J. J. Zelinski, D. F. Clark and D. R. Ulrich, *Mat. Res. Soc. Symp.* **180**, 669-674 (1990)

C. T. A. Suchicital and D. A. Payne
Thermal Analysis and X-ray Diffraction Studies of the High Temperature Phase Transformation in PbTiO₃ Single Crystals
Ceramic Transactions, **8**, 169-174 (1990)

Z. K. Xu, P. D. Han, L. Chang, A. Asthana and D. A. Payne.

Electron Microscopy Studies of High T_c Phase Development in Melt-Quenched Bi-Ca-Sr-Cu Oxides.

J. Mater. Res., 5 (1); 39-45 (1990)

P. D. Han, A. Asthana, Z. Xu and D. A. Payne
Growth Twins in $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_8$

Superconductor Single Crystals

J. Mat. Res., 5 (5): 909-912 (1990)

P. D. Han and D. A. Payne

Crystal Growth of High T_c Superconductors in the System Bi-Ca-Sr-Cu-O

J. Crystal Growth, 104, 201-210 (1990)

P. D. Han and D. A. Payne

Influence of Flux Composition on the Superconducting Properties of Single Crystal $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$

Mat. Letts., 9 (9); 157-160 (1990)

A. Asthana, P. D. Han, Z. K. Xu, L. Chang, D. A. Payne and P. J. Gilbert

Evolution of the High T_c Phase in Rapidly Solidified Bi-Ca-Sr-Cu Oxides

High Temperature Superconductors: Fundamental Properties and Novel Materials Processing, eds. J. Narayan, C. W. Chu, L. F. Schneemeyer and D. K. Christen, Mat. Res. Soc., Vol. 169, (1990)

D. J. Eichorst, K. E. Howard, D. A. Payne and S. R. Wilson

The Crystal Structure of $\text{LiNb}(\text{OCH}_2\text{CH}_3)_6$: A Precursor for Lithium Niobate Ceramics

Inorg. Chem., 29 [8]; 1458-1459 (1990)

L. F. Francis, D. A. Payne and S. R. Wilson

Crystal Structure of a New Lead Zinc Acetate Alkoxide, $\text{Pb}_2\text{Zn}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_3\text{H}_7\text{O}_2)_4$

Chemistry of Materials, 2 (6); 645-647 (1990)

S. D. Ramamurthi and D. A. Payne

Structural Investigations of Prehydrolyzed Precursors Used in the Sol-Gel Processing of PbTiO_3

J. Am. Ceram. Soc., 73 (8); 2547-2551 (1990)

D. J. Eichorst, D. A. Payne, and A. N. A. Wragg
The Effects of Solution Chemistry on the Sol-Gel Processing of Lithium Niobate

Ceramic Thick and Thin Films, ed. B. Hiremath, Am. Ceram. Soc., 375-384 (1990)

D. Ramamurthi and D. A. Payne

NMR Spectroscopic Investigations of PbTiO_3 Sol-Gel Processing

Better Ceramics Through Chemistry IV, eds. C. J. Brinker, B. J. J. Zelinski, D. F. Clark and D.

R. Ulrich, Mat. Res. Soc. Symp. 180, 79-84 (1990)

S. D. Ramamurthi and D. A. Payne

Nanometer Sized ZrO_2 Particles Prepared by Sol-Emulsion-Gel Methods

J. Am. Ceram. Soc. 73 (9); 2760-2763 (1990)

P. D. Han, J. A. McMillan, A. Asthana, Z. Xu, L. Chang and D. A. Payne.

Analysis of Large-Area Twin-Structures in Single Crystal $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_8$

Physical Review B, accepted Dec. 1990

A. Asthana, P. D. Han, Z. Xu, L. Chang, D. A. Payne and P. J. Gilbert

Enhancement of the High T_c Phase in Bi-Ca-Sr-Cu-O by Ceramic Processing Methods

Physica C, submitted Dec. 1990

Honors

International Advisory Board, Journal, Materials Science Communications

Invited Talks

Murata Manufacturing Co., Japan, 1/5/90

Seoul National University, Seoul, Korea, 3/16/90

Materials Research Society, San Francisco, CA, 4/19/90

American Ceramic Society, Dallas, TX, 4/24/90

VII ISAF Symposium, Urbana, IL, 6/7/90

SPIE Sol Gel Optics, San Diego, CA, 7/13/90

Chemistry of Electronic Ceramic Materials, Jackson Hole, WY, 8/17/90

Dow Corning, Midland, MI, 10/16/90

American Ceramic Society, Seattle, WA, 10/25/90

American Ceramic Society, Orlando, FL, 11/13/90

British Ceramic Society, London, UK, 12/19/90

PhD Graduates

Lorraine Falter Francis, Assistant Professor,
University of Minnesota,
Department of Chemical Engineering and
Materials Science

Zhengkui Xu, Postdoc, University of Illinois at
Urbana-Champaign
Department of Materials Science and Engineering

A.A. Rockett

Publications

A. Rockett
The Influence of Surface Structure on Growth of Si
(001) 2x1 from the Vapor Phase
Surf. Sci. **227**, 208 (1990)

B.-H. Tseng, A. Rockett, T.C. Lommasson, L.C.
Yang, C.A. Wert, and John A. Thornton
Chemical and Structural Characterization of
Physical-Vapor Deposited CuInSe₂ for Solar
Cell Applications
J. Appl. Phys. **67**, 2637 (1990)

C.J. Kiely, A. Rockett, J.-I. Chyi, and H. Morkoç
The Initial Stages of Growth of InSb on
GaAs(100) by MBE - A Highly Lattice
Mismatched Heterointerface
Mat. Res. Soc. Symp. Proc. Fall, 1989, vol. **159**, p.
63 (Materials Research Society, Pittsburgh,
1990)

S. Strite, M.S. Ünlü, K. Adomi, G.-B. Gao, A.
Agarwal, A. Rockett, H. Morkoç, D. Li, Y.
Nakamura, and N. Otsuka
GaAs/Ge/GaAs Heterostructures by Molecular
Beam Epitaxy
J. Vac. Sci. Technol. B **8**, 1131 (1990)

C.J. Kiely, R.C. Pond, G. Kenshole, and A.
Rockett
A TEM Study of the Crystallography and Defect
Structures of Single Crystal and
Polycrystalline Copper Indium Diselenide
Phil. Mag. A, in press

A. Rockett and C.J. Kiely
Factors Affecting the Formation, Uniformity, and
Density of Misfit and Threading Dislocation
Arrays During Heteroepitaxial Growth
J. Vac. Sci. Technol. A, in press

Honors

Chairman of the Illinois Chapter of the
American Vacuum Society (1990, 1991)

Invited Talks

"CuInSe₂ Growth by the Hybrid Sputtering and
Evaporation Process," Salford University
Colloquium Series, Salford, UK, January, 1990.

"Simulations of Si (001) 2x1 Growth from the
Vapor Phase," Winter Epitaxy Workshop,
Obertraun, Austria, Feb. 5-9, 1990.

"Ion-assisted Doping and Growth of Epitaxial
Thin Films," Beam-Solid Interactions Gordon
Research Conference, Holderness, NH, July, 1990.

"Epitaxial and Heteroepitaxial Growth of
Semiconductors by Molecular Beam Epitaxy,"
IBM Colloquium Series, Yorktown Heights, NY,
September, 1990.

C.F. Zukoski

Publications

L. Marshall and C.F. Zukoski
Experimental Studies on the Rheology of Hard
Sphere Suspensions Near the Glass
Transition
J. Physical Chemistry **94**, 1164-1171 (1990)

L. P. Voegtli and C.F. Zukoski
Origins of Polymer Colloid Surface Charge
In *Scientific Methods for the Study of Polymer
Colloids and their Applications*, F. Cancau
and R. H. Ottewill, eds., pages 269-290,
Kluwer Academic Publishers, London, 1990

C.F. Zukoski, G.H. Bogush, M.K. Chow and J.L.
Look
Precipitation of Uniform Particles: The
Importance of Aggregation
MRS Symposium on Better Ceramics Through
Chemistry IV, April 1990

J.L. Look, G.H. Bogush and C.F. Zukoski
Colloidal Interactions in the Precipitation of
Uniform Particles

Accepted, Faraday Discussions on Colloidal
Dispersions, September, 1990

L.P. Voegtli and C.F. Zukoski
Adsorption of Ionic Species to the Surface
Polystyrene Latexes

Accepted, J. Colloid Interface Sci., June 1990

L.P. Voegtli and C.F. Zukoski
A Perturbation Treatment of the Order/Disorder
Phase Transition in Colloidal Suspensions

Accepted, J. Colloid Interface Sci., June 1990

G.H. Bogush and C.F. Zukoski
Studies of the Kinetics of Precipitation of
Uniform Silica Particles through the
Hydrolysis of Condensation of Silicon
Alkoxides

Accepted, J. Colloid Interface Sci., August 1990

G.H. Bogush, and C.F. Zukoski
Uniform Silica Particle Precipitation: An
Aggregative Growth Model

Accepted, J. Colloid Interface, Sci., April 1990

Invited Talks

Structure and Flow in Electrorheological
Suspensions

Department of Chemical Engineering
University of Washington, Seattle

Rheological Properties of Ordered and
Disordered Suspensions
Eaglehard Corporation, Woodbridge, NJ

Flow of Suspensions Near Close Packing
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign

Aggregation and Particle Growth: Floc Structure
and Crystalline Orientation
Materials Research Society, San Francisco

Flow of Dense Suspensions
Department of Chemical Engineering
California Institute of Technology, Pasadena

Uniform Particle Formation from Alkoxides:
Mechanisms of Growth
American Chemical Society National Meeting,
Washington

Ph.D. Graduates

L.P. Voegtli
Phase Transition Behavior of Colloidal
Suspensions

G.H. Bogush
The Precipitation of Uniform Silica Particles
Through the Controlled Hydrolysis of Silicon
Alkoxides

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

I.M. ROBERTSON

Radiation Effects in Materials

GOALS

This program is aimed at understanding the structural changes induced in materials subjected to heavy-ion irradiation. In particular, the program is aimed at investigating the probability that a vacancy loop will be created when a metal is irradiated with heavy ions, and the yield dependence on ambient temperature and energy density. In semiconductor systems the aim is to understand the crystalline-to-amorphous transition that occurs on ion implantation in simple and compound semiconductors.

HIGHLIGHTS

The crystalline-to-amorphous mechanism has been investigated in GaAs, GaP and in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. We have demonstrated that the crystalline-to amorphous state can be achieved by the direct impact of a single energetic ion. The probability of this occurring is sensitive to the material and the irradiation/observation temperature. In GaAs, the amorphous zones created by the direct impact mechanism are unstable at room temperature, crystallizing at $T_{\text{anneal}} \geq 250\text{K}$. In the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system direct impact amorphization occurs only when $x \leq 0.20$. For systems containing higher Al levels, amorphization is delayed by at least an order of magnitude in ion dose over that in GaAs. This higher dose for amorphization in the AlGaAs system is independent of the ion dose rate; at least to dose rates of $10^{12} \text{ ions cm}^{-2} \text{ sec}^{-1}$. This difference can be explained by either a higher crystallization rate in the AlGaAs system compared to GaAs or a different amorphization mechanism; i.e., a point defect buildup mechanism rather than a direct impact mechanism dominates in AlGaAs.

In metals the efficiency with which displacement cascades produce vacancy loops has been investigated as a function of melting temperature. The alloys selected, Cu-Ni and Ag-Pd, allow the melting temperature to be systematically varied. From room temperature

irradiation of these alloys we have found that the probability of an isolated displacement cascade collapsing to form a loop decreases with increasing melting temperature. This is in agreement with the model developed from molecular dynamic computer simulation of cascades. However, the relationship between loop formation and melting temperature is not simple.

FUTURE DIRECTIONS

In the next fiscal period we will focus our attention on determining the degree of antisite disorder associated with the amorphous zones. This may explain the different crystallization rates observed in GaAs. The work on ion implantation of layered systems will be extended to examination of multilayered heterostructures. The aim of this will be to determine the degree of layer intermixing caused by the ion implantation and subsequent annealing treatments. Work will continue on the loop formation mechanisms in the Cu-Ni and Ag-Pd alloys.

SIGNIFICANT ACCOMPLISHMENT

Amorphization of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs by Ion Implantation

Scientific Achievement:

It has been shown that AlGaAs requires a higher ion dose to achieve a completely buried amorphous layer than GaAs. The critical dose for amorphization is dependent on the Al concentration. Comparing $\text{Al}_{0.85}\text{Ga}_{0.15}\text{As}$ with GaAs, formation of an amorphous layer is delayed by at least one order of magnitude in ion dose in the AlGaAs compared to the GaAs system. This higher amorphization dose in AlGaAs is insensitive to the ion dose rate at least to dose rates $\leq 2 \times 10^{12} \text{ ions cm}^{-2} \text{ sec}^{-1}$. This difference may indicate that either the lifetime of individual amorphous zones is shorter in AlGaAs than in GaAs (<1 sec compared to days) or the mechanism for amorphization in these two systems is fundamentally different. It has also been shown that the amorphous to crystalline transition can be enhanced by irradiating with a sub-threshold electron beam, which might imply that the defect responsible for this transition is a dangling bond type defect.

D.4.b PUBLICATIONS AND HONORS FOR
KC-02-01-04

I.M. Robertson

Publications

T. Diaz de la Rubia, R.S.Averback, R.Benedek
and I.M.Robertson
Molecular Dynamics Studies of the Primary State
of Radiation Damage
Radiat. Effects and Defects in Solids, 113, 39, 1990

J.S.Vetrano, I.M.Robertson and M.A.Kirk
Experimental evidence Favoring Local Melting
Within Heavy-ion Generated Displacement
cascades in Copper
Scripta Metall. et Mat. 24, 257, 1990

I.M.Robertson, J.S. Vetrano, M.A.Kirk and
M.L.Jenkins.
On the Formation of Vacancy Type Dislocation
Loops From Displacement Cascades in
Nickel.
In press, *Phil Mag.* 1990

J.S.Vetrano, I.M.Robertson, R.S.Averback and
M.A.Kirk
Cascade Collapse in Cu and Ni
*15th Symposium of Effects of Radiation on
Materials*, Nashville 1990, accepted

Tho X. Bui, I.M.Robertson and M.A.Kirk
Effect of Internal Hydrogen on the Vacancy loop
Formation Probability in Al
*15th Symposium of Effects of Radiation on
Materials*, Nashville 1990, accepted

I. Jencic, M.W. Bench, I.M. Robertson and
M.A.Kirk
A Comparison of the Amorphization Induced in
 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs by Heavy-ion
Irradiation
J.Appl.Phys., Accepted

I. Jencic, M.W. Bench, I.M. Robertson, M.A.Kirk
and J. Peternelj
A Comparison of the Rates of Amorphization in
the $\text{Al Ga}_{1-x}\text{As/GaAs}$ System
IBBM Conf., Knoxville 1990, Accepted

M.W.Bench, I.M. Robertson and M.A.Kirk
TEM Investigation of the Damage Produced in
Individual Displacement Cascades in GaAs
and GaP
IBBM Conf., Knoxville 1990. Accepted

Room temperature crystallization of an amorphous
zone produced in GaAs by direct impact of an
energetic heavy-ion.

Significance:

The use of ion implantation to induce
compositional disordering in heterostructure
systems has lead to the development of devices
with novel optical and electronic properties. To
understand and be able to model this effect
detailed information on the crystalline-to-
amorphous transition and the reverse transition
are needed. The information provided by this
program should lead to new descriptions and
models of the compositional disordering induced
by ion implantation in these heterostructure
systems.

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

D.5 SIGNIFICANT ACCOMPLISHMENTS FOR KC-02-01

Superplastic Behavior in Nanocrystalline TiO₂

Scientific Achievements:

Simple models based on diffusional creep predict that ceramics and other brittle materials can be deformed at low temperatures with a high strain rate and high strain rate sensitivity, i.e., superplastically, if the grain size of the material is extremely small. We developed methods to synthesize dense ceramic materials with grain sizes of 10 - 15 nm using nanophase processing and demonstrated that superplastic behavior (in compression) can be achieved at temperatures less than about half of the melting temperature. In Fig. 1 it is shown that nanophase (n-) TiO₂ can be deformed to a true strain of ≈ 0.6 at 800°C under an applied stress of 60 MPa and with no indications of cracking. An important part of this research has been the development of techniques for synthesizing the nanophase ceramics that can be fully densified while retaining their ultra-small grain size. These and our other measurements on mechanical properties are the first on dense nanophase ceramics. Stress-strain rate measurements show that the strain rate sensitivity is 0.3 and that strain rates of 0.01 are possible at half the melting temperature. Preliminary analysis of the grain size dependence and stress exponent suggests that in such ultra-fine grained materials as these nanophase ceramics, diffusional creep may be limited by the efficiency of sources and sinks of point defects in the grain boundaries rather than the mobility of defects, as assumed in the Coble and Nabarro-Herring models of creep.

Significance:

The potential applications for ceramic materials that can be plastically deformed to their final shape, i.e., near net shaping, are enormous. This work demonstrates, for the first time, that nanophase ceramics can be superplastically deformed in such a way. We have also shown that unique microstructure of nanophase materials provides a means to investigate deformation mechanisms. An important part of this work has been the development of synthesis procedures for producing dense nanophase ceramics in sufficiently large volumes for materials testing. In addition, these procedures now make it possible to synthesize composite nanophase ceramics thus providing many opportunities to tailor ceramic materials on a nanoscale level for improved fracture toughness (for example by adding ZrO₂ particles for transformation toughening) or grain growth suppression (using second phase inclusions).

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

SIGNIFICANT ACCOMPLISHMENTS

Embrittlement of Intermetallics; Significance of Alloy Additions

Scientific Achievement:

Many intermetallic compounds have very attractive mechanical properties for high temperature applications. The use of these materials is often limited by their low temperature ductility and their ability to be fabricated into useful shapes. In recent years it was shown, largely at Oak Ridge National Laboratory, that many of these problems can be alleviated by careful control of microalloying. In the important case of Ni_3Al , the addition of B greatly increased the low temperature ductility and reduced the tendency for intergranular fracture; although the basic understanding of the reasons for this improvement were not in hand. We have been able to establish the basis for this ductility improvement with the use of *in situ* TEM deformation studies.

Two very different basic mechanisms for the increased ductility have been proposed; an increase in the cohesive strength (bonding) across the grain boundaries, and an increase in the ability of dislocations to traverse the grain boundaries from one grain to the next. Direct observations of the response of Ni_3Al , with and without Boron, to stresses have shown that the grains exhibit extensive plastic flow in both cases. The interactions of dislocations with the grain boundaries are the same in both types of alloys, with the result being that the dislocations pile-up against the boundaries forming local stress concentrations. The principal difference is that when B is segregated to grain boundaries, the grain boundary is strengthened sufficiently to allow the stress concentration to be relieved by initiation of dislocation generation in the adjacent grain. In the absence of the Boron, the response of the grain boundary to the stress concentration is to initiate a crack which then propagates along the grain boundary leading to premature intergranular fracture.

Significance:

Understanding the basis for low temperature ductility in intermetallic alloys is necessary for intelligent alloy design. A solution to the embrittlement of these alloys is required if they are to be used successfully in energy systems which take advantage of their excellent high

temperature properties, as cracking during fabrication and cooling cycles must be avoided. Establishment of the mechanism of the strengthening effect of Boron on grain boundaries in Ni_3Al suggests that this effect is a very general one. Boron, as well as other elements, which prefer to be at grain boundaries rather than at free surfaces are the types of alloy additions which are likely to be successful in improving ductility, for the reasons we have shown. Hence, the selection of microalloy additions can be based on a rational approach which employs segregation studies as a screening method.

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

E. RESEARCH SUMMARIES FOR SOLID STATE PHYSICS

E.1.A. EXPERIMENTAL RESEARCH KC-02-02-02

A. C. ANDERSON

Low Temperature Studies of Defects in Solids

GOALS

The principal goal of Professor Anderson's research is to obtain experimental data on a variety of defect structures in order to a) provide a basic understanding of the defects and b) predict the thermal and electrical properties of materials when defects and disorder are present.

HIGHLIGHTS

Thermal and electrical conductivities, specific heats, thermal expansions, and dielectric and ultrasonic dispersions have been measured on a variety of metals, polymers, ceramics and composite materials to better understand the role of defects in phenomena such as superconductivity and to understand the interactions of electrons and phonons with defects.

Electrical and thermal transport have been measured in sintered samples of high-temperature superconductors. Application of a large magnetic field reduces the thermal conductivity, an effect Anderson has attributed to phonon scattering by magnetic fluxoids. The effect is an order of magnitude weaker in high-temperature superconductors than in conventional superconductors such as Nb.

The phonon-dislocation interaction has been studied in Ge. The interaction is static as expected for a crystal having a large interatomic force constant. The interaction agrees in frequency dependence and in magnitude with calculations over the past thirty years by Klemens and others. Although the static interaction is discussed in textbooks and is widely assumed to exist, Anderson's is the first definitive measurement of this weak interaction.

FUTURE DIRECTIONS

Studies will be made of the thermal properties of twin boundaries in martensitic

materials and of domain boundaries in ferroelectrics. Measurements will be concluded of thermal transport in isotopically pure diamond.

SIGNIFICANT ACCOMPLISHMENT

Low Temperature Studies of Defects in Solids

Scientific Achievement:

1) The phonon-dislocation interaction.

For over thirty years there has been broad confusion in the literature regarding the influence of dislocations on thermal transport in crystals. Most of this controversy has been answered by Anderson's work. If the interactions between atoms of the solid are weak, as in ionic solids, the dislocation may flutter and scatter phonons dynamically and strongly. If the atomic forces are strong as in germanium, the dislocation is sessile and scatters phonons only weakly. The frequency dependencies and magnitudes of both processes have been measured in Anderson's laboratory and shown to be in good agreement with existing theory. The work just completed was on the static phonon scattering mechanism in germanium, a difficult measurement since the scattering is so weak.

2) Phonon scattering from magnetic fluxoids in superconductors.

Anderson has shown that the scattering of phonons by magnetic fluxoids in a high-temperature superconductor is an order of magnitude weaker than for a conventional superconductor such as niobium. The reason for this difference is not known. This observation provides another test for the theory of high-temperature superconductivity currently being sought by others.

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

TAI-CHANG CHIANG

Properties of 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 of materials 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 for sample preparation, synchrotron-radiation photoemission for band structure and core level studies, scanning tunneling microscopy for real-space inspection of the surface, and electron diffraction and Auger spectroscopy for sample characterization.

HIGHLIGHTS

GaSb is an important semiconductor material for electronic applications. The (1×3) reconstruction of the GaSb(100) surface grown by molecular beam epitaxy has been examined with both synchrotron-radiation photoemission and scanning tunneling microscopy for a determination of the atomic structure and the nature of the reconstruction which involves the reduction of surface dangling bonds. This (1×3) configuration is obtained by Sb-stabilization during growth and is the most stable phase. Results of photoemission from the core levels indicate that the surface consists of $2/3$ atomic layer of Sb and $1/3$ atomic layer of Ga on an Sb-terminated bulk structure. Scanning tunneling microscopy results are consistent with this finding; the $2/3$ atomic layer of Sb on the surface is seen to consist of rows

of Sb dimers separated by lines of Ga atoms. As in the case of GaAs(100), the surface exhibits intrinsic partial disorder. The bulk electronic band structure has also been determined, and the results are in excellent agreement with theory.

FUTURE DIRECTION

Professor Chiang will improve and refine his experimental techniques and develop new approaches for a more precise control and characterization of material properties. He is developing X-ray probes for surface and interface studies and methods for chemical species identification down to near the atomic level. He will also study a wide variety of material systems for a general understanding of the effects and phenomena pertaining to artificial structures and crystal growth. The aim is to be able to predict, control, and tailor material properties. Currently, several systems are under investigation, including the prototypical Ag-Si, Ag-Ge, and alkali-metal-Si interface systems and the adsorption and growth of di-silane on Si surfaces.

SIGNIFICANT ACCOMPLISHMENT

Determination of the GaSb(100) Surface Structure

Scientific Achievement:

By using both synchrotron-radiation photoemission and scanning tunneling microscopy, the atomic structure of GaSb(100)- (1×3) grown in situ by molecular beam epitaxy has been determined. This (1×3) configuration is obtained by Sb-stabilization during growth and is the most stable phase. Results of photoemission from the core levels indicate that the surface consists of $2/3$ atomic layer of Sb and $1/3$ atomic layer of Ga on an Sb-terminated bulk structure. Scanning tunneling microscopy results are consistent with this finding; the $2/3$ atomic layer of Sb on the surface is seen to consist of rows

- - Top Layer of Ga
- - Top Layer of Sb
- - 2nd Layer of Sb

separated by lines of Ga atoms. As in the case of GaAs(100), the surface exhibits intrinsic partial disorder. The bulk electronic band structure has also been determined, and the results are in excellent agreement with theory.

Significance

One of the most fundamental issues in surface studies is the determination of surface atomic structure and the nature of reconstruction. The surface reconstruction is often related to a reduction of chemically active dangling bonds on the surface to minimize the free energy. The dangling bonds play a large role in the atomic processes during adsorption and growth. With the use of scanning tunneling microscopy, the surface topographic features can be examined with atomic resolution. Synchrotron-radiation photoemission provides further information concerning the surface site population and electronic effects. These results combine to provide a detailed understanding of the surface atomic structure and properties.

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

R.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 energies and electronic properties of crystals, surfaces and interfaces.

HIGHLIGHTS

1. We have completed work to predict ways that thin layers can be used to control the band offsets at interfaces in semiconductor quantum wells and superlattices. Theory predicts that significant changes are possible and very recent experimental work at the U. of Minnesota simulated by our predictions indicated experimental changes have been made using GaAs in Ge [A. Munoz, N. Chetty and R.M. Martin].
2. We have developed a new theoretical method to determine an energy density from density functional calculations. By integrating over surface regions we have determined surface energies which were not possible to obtain by previous theoretical methods. Our primary applications have been to interfaces and surfaces of GaAs, where we find (-1-1-1) arsenic terminated surfaces to be lower energy than any other surfaces of GaAs [N. Chetty and R.M. Martin].
3. Our group has made a major advance in the theory of pseudopotentials by including many-body correlation effects with the core electrons. This is important because it has recently become possible to treat the valence electrons by accurate many-body methods. Therefore, the proper inclusion of effects of the cores is now the chief limitation for accuracy of predictions for properties such as electronic band gaps. The new pseudopotentials are derived by a many-body Greens function treatment of the atom, which includes core relaxation and correlations. Once derived, they are as easy to use as previous potentials and are more transferable. We have tested the potentials on many atoms and the Na₂ molecule and have shown there are significant

improvements over previous single-particle methods, especially for transition metals and post-transition elements like Ga and Ge.

FUTURE DIRECTIONS

The directions Professor Martin plans to pursue in the near future are theoretical predictions for surfaces of metals, defects in semiconductors and correlated electron systems, such as magnetic and superconducting oxides. The methods used will be many-body techniques that go beyond previous theoretical capabilities. One approach uses Quantum Monte Carlo methods, developed in collaboration with Prof. D.M. Ceperley. We have shown these methods can give essentially exact results for crystalline silicon and we will apply the same methods to calculate surface energies of Al, where there are long-standing unresolved differences between . We will investigate the possibility to predict structures of defects in semiconductors, which can also resolve problems of great interest for decades. The second approach uses Greens function methods to calculate excited electronic states not possible in Quantum Monte Carlo. In the near future we will apply our new pseudopotentials to improved predictions for band gaps in GaAs and related semiconductors. Our longer term goal is to be able to calculate quantitatively the electronic gaps and magnetic properties for materials such as the transition metal oxides, which are examples of Mott Insulators.

SIGNIFICANT ACCOMPLISHMENT

Theory of Solids, Surfaces and Heterostructures

Scientific Achievement:

A new method has been developed for calculation of energies of surfaces and it has been applied to determination of energies for several surfaces of GaAs which could not be found by previous methods. The most important new result is that the arsenic terminated (111) surfaces are found to be the most stable of all surfaces of GaAs that have been considered in previous calculations.

Significance:

Electronic structure calculations can now be done sufficiently well that energies can be predicted accurately with no parameters. This

has been done using the density functional method; however, all methods developed so far have been limited to the prediction of one single total energy from each calculation. Surface energies are then found as differences between large energies of cells with and without surfaces. Furthermore, for symmetry reasons with these methods it is impossible to find energies of low symmetry surfaces like the (111) and (-1-1-1) surfaces of III-V and II-VI semiconductors. A new approach by Martin determines an energy density as a function of position; integrals of this density over regions give several energies from one calculation. It has been applied to GaAs where in one calculation the bulk crystal energy and the formation energy for two surfaces are directly found. It has been established for the first time that the As terminated (-1-1-1) surfaces are very low in energy, the most stable of all surfaces considered so far in theoretical work.

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

H. MORKOÇ

Semiconductor Heterostructures

GOALS

This research program explores the unique interfaces between semiconductor heterostructures including semiconductor-semiconductor, insulator-semiconductor, and metal semiconductor interfaces for advanced electronics and optoelectronics applications.

HIGHLIGHTS

It is well-known that high density of defect states is created when a freshly grown compound semiconductor sample is exposed to air. These defect states usually pin the surface Fermi energy deep in the energy gap. This effect makes modulation of the surface electric potential and, therefore, the realization of metal-insulator-semiconductor field effect transistors (MISFETs) impossible. Morkoç believes that surface Fermi energy pinning can be avoided by *in-situ* deposition of gate dielectric in ultra high vacuum (UHV). In this project, he intends to investigate various methods in obtaining a low defect density insulator/compound-semiconductor interface and gate quality dielectrics. The effect of a thin elemental semiconductor layer grown on compound semiconductor before the deposition of gate dielectric will also be studied.

Various compound semiconductors can be grown in our newly completed gas-source MBE (GSMBE) chamber and transferred to the newly completed UHVCVD chamber for the deposition of semiconductors and gate dielectrics utilizing an electron cyclotron resonance (ECR) source. With this approach the uncontrollable self oxidation of the sample is eliminated. The UHVCVD chamber provides the necessary cleanliness and the ECR source supplies a low-energy highly-ionized chemical beam for the deposition of high quality gate dielectrics with low interface state density suitable for MISFET applications. Thin elemental semiconductor cap layers grown on compound semiconductor have been shown to passivate the surface toward the deposition of gate dielectric. These cap layers can either be grown in the UHVCVD or Si/Ge MBE chamber which is also vacuum connected to the rest of the system.

In a parallel approach, wide bandgap semiconductors in place of dielectrics will be investigated for their properties as barriers in

metal-insulator-semiconductor and/or semiconductor-insulator-semiconductor structures. The solid source MBE system in the EpiCenter is equipped with an ECR gun to create N, N₂ radicals for growth of GaN films for this purpose.

FUTURE DIRECTIONS

The newly installed GSMBE and UHVCVD systems provide the ultimate in flexibility in obtaining exciting combinations of semiconductor interfaces which are not only interesting to study from the scientific point of view but also device point of view. This program will focus on heteroepitaxy and novel interfaces based on both elemental and III-V compound semiconductors.

SIGNIFICANT ACCOMPLISHMENT

Semiconductor Heterostructures

Significant Accomplishments

While setting up gas source MBE and UHVCVD systems for *in-situ* deposition of gate quality dielectrics, Morkoç has pursued a slightly different route to gain an understanding of the MOS structures based on compound semiconductors. One of these routes involved the investigation of the effect of a thin elemental semiconductor on the surface Fermi energy of compound semiconductors. Morkoç has shown that surface Fermi level pinning is not an intrinsic property of compound semiconductors grown in UHV. A much reduced surface electric field was found in the GaAs surface when capped with a 20 Å Ge layer compared to an uncapped GaAs surface. This shows that the surface Fermi level of GaAs is unpinned and can be moved within the bandgap. Similar results were obtained with a Si capped GaAs surface. A metal-oxide-semiconductor junction was fabricated with SiO₂ as the dielectric. High frequency capacitance-voltage curve shows that the surface electric field of the capped GaAs can be modulated by an applied bias. The SiO₂ used in the MOS diode was deposited ex-situ (will be *in-situ* now that the UHVCVD system is completed) in a remote-plasma CVD chamber using silane, oxygen, and helium. High quality SiO₂ is routinely obtained. For a 1000 Å thick oxide, break-down fields larger than 3 MV/cm and leakage currents on the order of 6 nA/cm² at 30 V bias have been obtained. The interface state density of the GaAs sample capped with Si is measured to be

$6 \times 10^{11} / \text{eV} / \text{cm}^2$ around mid-gap by high frequency C-V measurements. This seemingly high interface state density, which cannot be annealed by heat treatment, is caused by the uncontrollable oxidation of the surface upon exposure to air during the sample transfer from the growth chamber to the deposition chamber. This can be avoided by the use of our new set-up which involves the vacuum connected MBE and UHV-CVD systems for *in-situ* deposition of gate dielectrics.

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

C. P. FLYNN

Growth and Properties of Novel MBE Structures

GOALS

Professor Flynn explores the mechanisms of epitaxial growth by molecular beam epitaxy in order to create new materials, structured on an atomic length scale, for novel scientific and technical purposes. He is seeking a global understanding of growth mechanisms with a view to establishing a predictive framework that reveals what stable and metastable structures are accessible to synthesis by molecular beam methods. Ongoing research largely concerns ionic and metallic crystals but incorporates also the flood of work on semiconductors from other laboratories.

HIGHLIGHTS

Important new results have been obtained in the areas of oxide growth, the growth of crystals that possess a tuned tilt with respect to the substrate lattice, and in fundamental studies of the way growth is nucleated on metal surfaces. Building on last year's success in synthesis of MgO crystals Flynn has been able to grow CaO and SrO, both at low growth temperatures, in accordance with Flynn and Yang's predictions (last year). The work has been extended to Y_2O_3 ; current effort focuses on sapphire, Al_2O_3 , which is an important substrate component, among other merits.

A major step has been taken to generalize the discovery last year that crystals may be grown with a preselected tilt with respect to the substrate orientation. The initial research, confined to hcp rare earths, has been extended to other hcp crystals. Most important is the discovery and control of the analogous processes in fcc crystals, with huge tuned tilts up to 10° in high quality single crystals. (110) is the pseudomorphic plane for fcc. The mechanism which creates the predictable tilt has been verified by studies of the prism-slip crystals Ti and Zr, which do not tilt, and basal-slip crystals including Mg and the rare earths, which do exhibit this important new behavior. These results thus point unambiguously to the role of dislocation glide in the basal plane.

In initial investigations of nucleation control Flynn has been able to grow high quality Ti crystals in six different orientations for use in

anisotropy studies. No such feat of control has been even approached in previous work. The results reveal unexpected information about the mechanisms that operate during the initial nucleation of the epilayers that can be created on different surface orientations under ledge growth conditions. One case depends on symmetry alone while four others relate to the matching of substrate and epilayer surface lattice meshes. In the most important new observation we have verified that nucleation actually occurs at ledges, and that the ledges determine the epilayer orientation.

In collaboration with Ruhle at Stuttgart and Heuer at Case Western we have begun high resolution TEM studies of MBE grown interfaces. These reveal excellent interfaces with long terraces with misfit accommodated by dislocations that stand-off from the interface for Nb on Al_2O_3 but lie in the interface for MgO on Al_2O_3 . Further work progresses.

FUTURE DIRECTIONS

In addition to the present focus on growth of novel metal and ceramic systems, future work will emphasize metal-ceramic interfaces and multilayer structures synthesized from alternating metal and ceramic components. These are of some interest as models of interfacial bonding and cracking, and as electronic components in novel superconducting assemblies. Applications of synthesized structures to new opportunities in the understanding of materials behavior under irradiation are proposed elsewhere.

R.O. SIMMONS

Properties of Crystalline and Liquid Condensed Gases

GOALS

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

HIGHLIGHTS

Temperature dependences of the isochoric pressure have been precisely measured in hcp ^4He for a series of samples over the wide range of molar volumes 17 to 20.9 cm^3 . The results have been analyzed in terms of thermal vacancy and phonon pressure, in order to deduce both activation energies for thermal vacancy formation and free volumes of vacancy formation.

Measurements have continued of the deep inelastic scattering of neutrons by condensed ^4He , in order to determine the longitudinal momentum distribution of different samples. hcp solids have been studied over the wide range of molar volumes 15.1 to 20.9 cm^3 . Further, a $20.9 \text{ cm}^3/\text{mole}$ isochoric series of samples was measured at successively higher temperatures and pressures corresponding to hcp, bcc, and liquid phases, respectively. It is found that the single-particle kinetic energy $\langle E_k \rangle$ in this quantum system is dominated by the molar volume, and that the influence of temperature and even of phase is relatively small (<4%), as predicted by path-integral Monte Carlo simulations of Ceperley.

For solid and liquid Ar values of $\langle E_k \rangle$ have been directly measured, by deep inelastic neutron scattering, over the temperature range 18 to 110 K. Comparisons are being made with expected values i) derived from quasi-harmonic phonon densities of states from measurements, and ii)

expectations from dynamical theories such as variational path-integral calculations.

FUTURE DIRECTIONS

Now that the feasibility of neutron inelastic scattering measurement of translational motion of molecular impurities in noble gas crystals has been demonstrated, a quantitative examination of temperature and volume dependences of $\langle E_k \rangle$ in the prototype system Ar-H₂ will be completed. In the quantum system ³He-⁴He we will complete studies in liquid and bcc phases, for which isotopic differences in $\langle E_k \rangle$ are expected to be large.

The prospect that x-ray inelastic scattering can be developed as a quantitative tool at the APS, under construction at Argonne, leads to an interest in such development, especially since work in this project has now come up against several limitations of neutron inelastic scattering, including limited energy resolution, the need for relatively large sample sizes, and in the case of ³He, formidable neutron absorption. Meanwhile, during inelastic beamline development, for this project a series of synchrotron x-ray studies of crystalline condensed gases is planned at the Brookhaven NSLS. These include diffraction studies of defects in high-density He crystals and of phase transformations in solid hydrogen and other molecular crystals.

SIGNIFICANT ACCOMPLISHMENT

Properties of Thermal Vacancies in HCP Helium-4

Scientific Achievement:

For the first time, isochoric measurements have been made of the temperature dependence of thermal pressure in a series of hcp ⁴He specimens characterized by x-ray diffraction. The precisely measured pressures were analyzed, at each molar volume in the wide range 17.0 to 20.9 cm³/mole, as a sum of a thermal vacancy pressure and a phonon pressure. The phonon pressures are thermodynamically related to published high-precision isochoric heat capacity measurements. The figure shows an example of the results, for a crystal melting at 1.78 K with a zero-point pressure of 2994 kPa. The line is an analytical expression for the vacancy pressure. The derived vacancy activation energy is $f = 12.9$ K and the

free volume of formation v_f is 55% of an atomic volume. Comparisons with results at other molar volumes yield the density variation both of f and of v_f . f is found to be considerably smaller than either the diffusion activation energy given in the literature from analysis of ³He impurity NMR measurements or from positive ion conductivity studies. The differences between the values of the respective activation energies, near a factor of two, can be interpreted as defect migration energies. These large differences are contrary to common expectations that vacancy migration in this Bose quantum system is dominated by tunneling phenomena. The differences are similar, however, to results found earlier in this project for the light isotope ³He.

Significance:

Physical properties of many materials are influenced by the defects they contain. Properties of point defects in monatomic crystals are typically obtained in a manner, however, which is subject to unknown systematic errors. Such uncertainties arise because it is difficult to check, in an independent way, the procedure by which defect properties are derived. One way to do this is by significant variations in the external conditions, for example, by changes in the density of the system sufficient to produce a range of melting points. Because of their great compressibility, the solid heliums provide unique systems for producing results over large density ranges and different crystal structures. For them, one can even obtain higher-order terms in the defect free energy which are inaccessible in usual solids, such as the density dependence of the formation volume. For heliums, as well, interatomic forces are well known, which makes possible realistic calculation of crystal properties. This latest result on thermal vacancy

properties in hcp ^4He significantly extends knowledge about point defects in the heliums, which earlier in this project has been obtained for bcc and hcp phases of ^3He .

Performer: R. O. Simmons, University of Illinois at Urbana-Champaign

CHARLES 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 study of supported catalysts of Group VIII metals (Ru, Rh, Pd, Os, Ir, Pt) and high temperature superconductors. Specific topics under study 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: Measurement of normal state and superconducting state NMR properties and comparison with those of conventional (Bardeen, Cooper, Schrieffer) superconductors, with a goal of helping to explain the mechanism of superconductivity (why the transition temperatures are so high).

HIGHLIGHTS

(1) Surfaces:

(a) Study of C-C and C-H scission of CCH_2 species on Pt and Ir, by observation at elevated temperatures of ^{13}C resonance and $^1\text{H} - ^{13}\text{C}$ spin echo double resonance. The ^{13}C NMR lines of molecules containing H (CCH_2 or CCH) are shifted in frequency from those without H (C_2) permitting us to monitor the relative amounts of each species. We find that on Pt the C-H bonds begin to break at lower T's than the C-C bond.

(b) Study of the reaction $\text{CCH}_2 + \text{H} \rightarrow \text{CCH}_3$ on Pt/ Al_2O_3 has shown unequivocally that the support plays a role as a source of H.

(c) Using a new method of measuring diffusion, as well as the method of motional narrowing, we have shown that the diffusion rate of CO on small Pd particles (dispersion 46%) is much slower than that on larger particles (dispersion 22% or 12%), in contrast to Pt of the same dispersion for which the diffusion rate is independent of dispersion.

(d) The effect of the alkali promoters Na, K, Rb, Cs adsorbed on Pt has been observed on the resonance properties of ^{13}C molecules.

(2) High T_c Materials:

(a) Measurements of the ^{63}Cu , ^{17}O , and ^{89}Y spin-lattice relaxation times in the 93K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been performed

in the normal and superconducting state. The ratio of the rates, W_{1c} to W_{1a} , when the applied magnetic field is oriented parallel to the c or a axes respectively, is independent of temperature in the normal state, but changes dramatically in the superconducting state. This result is surprising in terms of current theories, and is believed to give an important clue as to the nature of the superconducting state

(b) Slichter's group has shown that measurements of the transverse relaxation time of ^{63}Cu nuclei provides a new test of theories of the electron system of the CuO_2 planes.

FUTURE DIRECTIONS

Slichter will continue studies of both metal surfaces (catalysts) and high T_c materials: Surfaces. The studies are largely focussed on studying reaction rates (C-C scission, diffusion, promoters), and modelling them through reaction equations. High T_c Superconductors. Continuation of efforts to understand the normal and superconducting properties, with emphasis on anisotropy of relaxation rates in the superconducting state, of $\text{YBa}_2\text{Cu}_3\text{O}_7$. These studies will be extended to other materials.

SIGNIFICANT ACCOMPLISHMENT

NMR Studies of the Mechanism of High T_c Superconductivity

Scientific Achievement:

Slichter has employed ^{63}Cu , ^{65}Cu , ^{17}O , and ^{89}Y nuclear magnetic resonance (NMR) of the 93K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ to obtain detailed information about the electrical and magnetic properties of various atomic constituents of the material. By this means he has recently discovered a surprising and unexpected phenomenon in the superconducting state which appears to contradict important theoretical conclusions arrived at from earlier studies of this material.

The nature of the surprise is as follows: Measurements in the normal state of the nuclear spin-lattice relaxation rate of the Cu nuclei in the CuO_2 planes of the material show that it possesses a large crystalline anisotropy. That is to say, the relaxation rate when the applied field lies parallel to the CuO_2 planes is different

from its value when the applied field is perpendicular to the plane. The anisotropy is independent of the temperature T . Comparison of the relaxation rate among the different atomic species (Cu, O, Y) has led to a detailed explanation of the nature of the magnetic properties of the material as being a so-called antiferromagnetic Fermi liquid.

Slichter has discovered that the anisotropy of the relaxation rate changes dramatically when the sample is cooled into the superconducting state. This result is a great surprise in terms of the picture of this material which has evolved from earlier NMR studies of the normal state, indicating that important physics is still missing from the theory and thus needs to be discovered.

Significance:

The discovery of a class of materials which are superconductors at much higher temperatures than previously observed has opened the possibility of many new technical uses of superconductivity. But no one knows why these materials have such high transition temperatures, and therefore no one can design materials with an eye to increasing the transition temperatures. One class of theories is based on variations of the classic Bardeen, Cooper, Schrieffer (BCS) Theory. Other theories appear to be unrelated. By measuring temperature dependence of the Knight shifts at the two Cu sites (plane and chain) Slichter's group has shown that both can be described within a particular subset of the BCS Theory (the spin-singlet models). The new results appear to contradict the earlier conclusions, suggesting that one must either utilize a more complex form of the BCS Theory, or possibly even abandon it entirely for these materials.

Performer: C. P. Slichter, University of Illinois at Urbana-Champaign

J. P. WOLFE

Carrier Transport in Quantum Wells -- Picosecond Imaging

GOALS

This project is concerned with the motion of photoexcited carriers in semiconductor quantum wells (QW) by combining picosecond pulse-probe techniques with spatial imaging. Professor Wolfe has developed a new technique for studying the in-plane motion of carriers deposited in a QW by pulsed laser excitation. Overall goals are to characterize the physical processes of energy relaxation and energy transport of nonequilibrium carriers.

HIGHLIGHTS

The lifetime of photoexcited carriers in GaAs quantum wells is only about 1 nanosecond; therefore, extremely high time and spatial resolution are required to observe the carrier propagation before electron-hole recombination occurs. Picosecond imaging is achieved by using two synchronously pumped dye lasers in a pulse-probe arrangement; one laser (pump) creates a high density of nonequilibrium carriers, and the second laser (probe) is tuned to the wavelength of the exciton absorption in order to observe the change in optical absorption. The laser beams are focused to about 3-micrometers and may be spatially scanned with respect to each other. Time-resolved profiles of the nonequilibrium carrier distribution are analyzed to give the effective diffusion constant. Wolfe's previous results uncovered interesting dependences of the diffusivity on the excitation power and crystal temperature, ascribed to phonon-wind and hot-spot effects.

This year Wolfe has extended the experimental capabilities by using a tunable pump beam, which allows changing the excess kinetic energy given to the photoexcited electron-hole pairs. A number of interesting effects have been observed: 1) The diffusivity of the nonequilibrium carriers increases with excess energy but is nonzero for resonant pumping (zero excess energy), 2) the diffusivity increases rather rapidly with temperature between 10 and 40 K, 3) the reduction in exciton absorption due to nonequilibrium carriers appears to be due to lifetime broadening of the line, in contrast to previously published interpretations involving

phase-space filling, 4) a variety of red and blue shifts of the exciton line are observed, depending on the wavelength of the pump laser.

FUTURE DIRECTIONS

Wolfe will exploit these new experimental tools to gain an understanding of the energy relaxation and transport processes of carriers in semiconductor quantum wells. Theoretical modeling of the data will include the scattering and thermalization of nonequilibrium carriers. Photoluminescence techniques will be added to complement the present information.

SIGNIFICANT ACCOMPLISHMENT

Characterization of the Optical Bleaching of Exciton Absorption Lines

Scientific Accomplishment:

By combining spectroscopic and imaging techniques, Wolfe has been able to directly observe the diffusion of photoexcited carriers in a semiconductor quantum well. The diffusivity depends on the power and wavelength of the excitation pulse, as well as the crystal temperature. The carriers are observed by a non-linear optical effect: the "bleaching" of the exciton absorption line in the presence of a high density of carriers. In the past, the exact source of this bleaching effect has not been isolated. Time resolved spectroscopy while the peak of the exciton line decreases, has revealed that, the integrated absorption spectrum remains constant. This striking result indicates that the "bleaching" is associated with lifetime broadening due to scattering rather than a phase-space filling.

Significance :

Non-linear optical responses of the sharp excitonic lines in semiconductors could be employed for high speed optical switching applications. An understanding of the physical processes underlying the spectroscopic bleaching and carrier diffusion can contribute to this application. At a basic level, the relaxation and transport of carriers confined to a quasi-2-dimensional layer has wide interest.

Performer: J.P. Wolfe, University of Illinois at Urbana-Champaign

GOALS

Professor Zabel's research is aimed at the investigation of structures and phase transitions of surfaces and epitaxial films. At the present time he investigates by high resolution x-ray 1) scattering the structure and annealing behavior of GaAs on Si(100) and the interfacial structure of pseudomorphic Si layers in GaAs; 2) the structure and epitaxy of thin Nb layers on sapphire (1120) and the structural changes occurring upon hydrogen uptake; 3) the roughening transition of alkali-halide crystal surfaces. In all cases, state-of-the-art x-ray scattering methods are applied, including x-ray total reflectivity measurements and x-ray surface scattering techniques.

GaAs on Si represents an important advanced material in semiconductor technology. However, the epitaxial growth is not without problems. Zabel attempts to relate the growth mechanism to the structural properties, in order to provide information on the mismatch, tetragonal distortion, interface and surface roughness, and the low temperature annealing behavior. Similarly, thin pseudomorphic Si layers sandwiched in GaAs promise an abundance of exciting electronic and optical properties. Here again, one tries to understand the pseudomorphic structure and the interfacial relationship.

Nb on sapphire is one of the most successful epitaxial metal layers ever grown. In spite of this success the epitaxial relation to the substrate is still poorly understood. Hydrogen uptake into the film allows to modify the epitaxial relation to the substrate, i.e. to change the commensurate/incommensurate relation to the substrate reciprocal lattice, which will, in turn, shed light on the epitaxial problem.

The equilibrium shape of surfaces is of fundamental interest. While metals often exhibit a roughening transition at high temperature, ionic crystals in contact with their vapor show a smoothing transition, i.e. higher index crystal planes become stable above a smoothing transition temperature. In his x-ray specular reflectivity measurements Zabel tries to identify this temperature T_S and to determine the roughness parameters as a function of the temperature and the time.

HIGHLIGHTS

Graduate student Norene Lucas is conducting the experiments on the pseudomorphic Si layer in GaAs and has identified for the first time that the interface for this highly mismatched system is sharp up to a layer thickness of 7 Å and becomes rough beyond this thickness. This is the first structural indication for a "critical film thickness" of Si on GaAs.

Another student, Paul Reimer, is investigating the Nb/sapphire system and has revealed evidence for two distinct orderings during the epitaxial growth. He studied 1000-3000 Å Nb films grown in several different orientations. Only the [110] oriented (the bcc close packed plane) Nb films showed a second, narrow Bragg spot parallel to the film plane, indicating an enhanced in-plane structural correlation. The exceptionally well-ordered portion of the sample grew larger on loading with hydrogen, possibly due to strain redistribution and alteration of the epitaxial relation to the substrate.

Graduate student YouSong Gu is studying the equilibrium shape of NaCl and has found that there is a phase transition at a temperature of about 650°C for both (110) and (111) surfaces. Below this temperature, both surfaces are unstable and get coarse with time, while at temperatures above 650°C, the surfaces are stable and relatively smooth.

FUTURE DIRECTIONS

The above described experiments will be completed by the end of 1991.

Program on Point Defects in Semiconductors

GOALS

The goal of this research is to determine for the first time the symmetry and magnitude of the lattice distortion of EL2 centers in GaAs and DX centers in AlGaAs.

The physics of metastable defects has been the central and the most important issue in the research on physics of point defects in semiconductors for the last 10 years. The most widely known and technologically important metastable defects are the AsGa antisite related EL2 defect in semi-insulating GaAs and DX centers in n-AlGaAs. While the metastable properties of these defects have been explained by phenomenological configuration coordinate diagrams, the symmetry and the lattice distortion involved in the transition from the ground into the metastable excited state of these defects is unknown. Although the ultrasonic technique has been previously used to characterize irradiation-induced defects in semiconductors, no systematic attempt has ever been made to apply it to the well-studied growth or doping-induced defects. The ultrasonic technique, when combined with electrical, optical and the EPR techniques of the Weber group in Berkeley should be capable of determining the microscopic structure of such metastable defects in semiconductors.

HIGHLIGHTS

In a survey of the ultrasonic response of both shear wave polarizations from 2 to 300K in a specimen containing EL2 centers, only small changes with optical illumination were found. However, the sensitivity of the technique to elastic constant changes (3×10^{-7}) and temperature changes (3×10^{-6}) was sufficient, and necessary, to indicate the existence of a relaxation in C_{44} above room temperature. If a peak is found with further measurements at high but not at low temperatures, it will be strong evidence that the configuration and dynamics of the defect is controlled by atomic rather than electronic displacements.

FUTURE DIRECTIONS

It is expected that the techniques used for the study of the EL2 center will be extended to other important defects in semiconductors such as the DX center and hydrogen impurity defects in Si.

SIGNIFICANT ACCOMPLISHMENT

The Diaelastic Effect in Iron

Scientific Achievement:

The diaelastic susceptibility of iron containing self-interstitials has been measured and found to be large, negative and nearly isotropic. This provides strong evidence that the interstitial is in a split configuration.

Significance:

In the early 1970's, concern about dimensional stability arising from expected swelling effects led to consideration of an expensive active control system for the design of the first breeder reactor. With the discovery in this laboratory of a large negative diaelastic susceptibility in copper, it was realized by design engineers that irradiation creep could be expected to keep up with the swelling if the diaelastic susceptibility was assumed to be as large in iron as in copper. This assumption allowed the design to be changed to a simpler passive system, saving an estimated 150 million dollars on the first breeder reactor alone. However, this assumption is brought into question by recent theoretical calculations by Schober at Jülich, who predicts small values for iron. The present results restore the status of this question by showing that the diaelastic susceptibilities of iron are an order of magnitude larger than predicted by theory and are in fact comparable to those found for copper, as assumed earlier.

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

**E.1.b. PUBLICATIONS AND HONORS FOR
SOLID STATE PHYSICS
KC-02-02-02**

A.C. Anderson

Publications

D. M. Zhu, A. C. Anderson, T. A. Friedmann and
D. M. Ginsberg
Thermal Conductivity of Polycrystalline
YBa₂Cu₃O_{7-δ} in a Magnetic Field
Phys. Rev. B **41**, 6605-6609 (1990)

D. M. Zhu and W. Guan
Transport Critical Currents of a Superconducting
HoBa₂Cu₃O_{7-x} Film
Physica C **169**, 201-204 (1990)

D. M. Zhu and A. C. Anderson
Scattering of Phonons by Sessile Dislocations in
Deformed Germanium
J. Low Temp. Phys. (Accepted)

A. C. Anderson
Thermal Transport Below 10K
Thermal Conductivity 21 ed. C. J. Cremers
(Plenum, New York City) (in press)

D. M. Zhu, Y. M. Xia and W. Y. Guan
Critical Currents in HoBa₂Cu₃O_{7-δ} Films on
ZrO₂ Substrate
(To be published)

Invited Talks

Glasses, Biomolecules and Evolution,
Santa Fe, NM, May 17-23 Santa Fe Workshop

Frustrating Glass,
Penn. State Univ., State College, PA

T. C. Chiang

Publications

A. Samsavar, T. Miller, and T.-C. Chiang
Photoemission Determination of the Final-band
Dispersion in Ag(111)
J. Phys. Condens. Matter **2**, 1141 (1990)

D. H. Rich, A. Samsavar, T. Miller, and T.-C.
Chiang
Adsorbate-to-Si(100) Bonding Coordination
Numbers and Structural Determinations From
Synchrotron Photoemission Studies
Phys. Scr. **41**, 83 (1990)

T. Miller, A. Samsavar, M. Mueller, G. Franklin,
and T.-C. Chiang
Electronic States of Metallic Superlattices and
Quantum Wells
Phys. Scr. T **31**, 35 (1990)

D. H. Rich, T. Miller, and T.-C. Chiang
Electronic and Chemical Properties of In and Sb
Adsorbed on Ge(001) Studied by Synchrotron
Photoemission
Phys. Rev. B **41**, 3004 (1990)

M. A. Mueller, T. Miller, and T.-C. Chiang
Determination of the Bulk Band Structure of Ag
in Ag/Cu(111) Quantum-Well Systems
Phys. Rev. B **41**, 5214 (1990)

A. Samsavar, E. S. Hirschorn, T. Miller, F. M.
Leiblsle, J. A. Eades, and T.-C. Chiang
High-Resolution Imaging of a Dislocation on
Cu(111)
Phys. Rev. Lett. **64**, 1607 (1990)

G. E. Franklin, D. H. Rich, A. Samsavar, E. S.
Hirschorn, F. M. Leiblsle, T. Miller, and T.-C.
Chiang
Photoemission and Scanning Tunneling
Microscopy Study of GaSb(100)
Phys. Rev. B **41**, 12619 (1990)

A. Samsavar, T. Miller, and T.-C. Chiang
Correlation Between Surface Core Levels and
Surface States in Si(111)-(7x7) Probed by Ag
Adsorption
Phys. Rev. B **42**, 9245 (1990).

PhD Graduates

D. H. Rich, Postdoctoral Fellow, Jet Propulsion
Laboratory

A. Samsavar, Postdoctoral Fellow, IBM, T. J.
Watson Research Center

R. M. Martin

Publications

A. Munoz, N. Chetty, and R. M. Martin
Modification of Heterojunction Band Offsets by
Thin Layers at Interfaces: Role of the
Interface Dipole

Phys. Rev. B **41**, 2976-2981 (1990)

E. Shirley, R. M. Martin, G. B. Bachelet, and D.
M. Ceperley

Role of Exchange and Correlation Used in
Generating Pseudopotentials

Phys. Rev. B **42**, 5057-5066 (1990)

N. Chetty and R. M. Martin

Energy Density Calculations Applied to GaAs
Polar Surfaces

To be published in Springer-Verlag Series:
International Conf. on Studies of Surfaces
(ICSOS -3, July, 1990)

F. Vukaljevic, E. Shirley, and R. M. Martin,
Single-body Methods in 3d Transition Metal
Atoms

Phys. Rev. B. Accepted

N. Chetty and R. M. Martin

Determination of Integrals at Surfaces Using the
Bulk Crystal Symmetry

Phys. Rev. B. (submitted)

Invited Talks

The nature of carbon: electronic calculations in
solid and liquid phases

Workshop on Total Energy Methods, Paris,
France, Jan. 4-6, 1990

Tutorial on the Car-Parrinello Method

APS meeting, Anaheim, CA, March 11 1990

Attempts to derive the Hamiltonian for the CuO
superconductors

Gordon Conference, Ventura, CA, March 19-24,
1990

Iterative Methods in Electronic Structure
Calculations

1990 Many-Body Encounter, Clemson, SC, May 4-
6, 1990

The nature of carbon: electronic calculations in
solid and liquid phases

Colloquium at Insituto de Fisica, Ensenada,
Mexico, June 21, 1990

Liquid Carbon, Seminar at Lawrence Livermore
Lab, June 28, 1990

Electronic Structure of the Copper Oxides

DARPA MRC Workshop on Superconductivity,
La Jolla, CA, July 18-19, 1990

Derivation of Models for Electrons in the Copper
Oxide Superconductors

European Physical Society Conf. of
Computational Physics, Amsterdam, Sept.,
1990

Ph.D. Graduates

Nithayanathan Chetty, Post-Doctoral Research
Associate, Technical University of Denmark,
Lyngby, Denmark.

H. Morkoç

Publications

S. Strite, M.S. Ünlü, K. Adomi, G.B. Gao, A.
Agarwal, A. Rockett, H. Morkoç, D. Li, Y.
Nakamura and N. Otsuka

GaAs/Ge/GaAs Heterostructures by Molecular
Beam Epitaxy

J. Vac. Sci. Technol., B8, 1131, 1990

D. Huang, J.I. Chyi and H. Morkoç

Carrier Effects on the Excitonic Absorption in
GaAs Quantum-well Structures: Phase-space
Filling

Phys. Rev. B, **42**, 5147, 1990.

G. Ji, T. Henderson, C.K. Peng, D. Huang and H.
Morkoç

Analysis of Energy States in Modulation Doped
Multiquantum Well Heterostructures
Solid State Electron., **33**, 247, 1990

M.B. Patil and H. Morkoç

Self-consistent Calculation of Electron Density in
a Two-channel Modulation Doped Structure
Solid State Electron., **33**, 99, 1990

S. Noor Mohammad, M.B. Patil, J. Chen, M.S. Ünlü and H. Morkoç
Analytical Model for I-V Characteristics of JFETs with Heavily Doped Channels
Solid State Electron., **33**, 53, 1990

H.J. Ou, J.M. Cowley, J.I. Chyi, A. Salvador and H. Morkoç
Microanalysis on the (200) Diffraction Intensity to Determine the Al Concentration for AlGaAs-GaAs Multiple-quantum-well Structures
J. Appl. Phys. **67**, 698, 1990

K. Adomi, S. Strite and H. Morkoç
Antiphase-domain-free GaAs Grown on Pseudomorphic Si(100) Surfaces by Molecular Beam Epitaxy
Appl. Phys. Lett., **56**, 469, 1990

C.J. Kiely, A. Rockett, J.I. Chyi and H. Morkoç
The Initial Stages of MBE Growth of InSb on GaAs (100) - A High Misfit Heterointerface
MRS Sym. Proc. **159**, 63, 1990

S. Iyer, H. Morkoç, N. Otsuka and H. Zabel
Molecular Beam Epitaxy of GaAs on Si
Comments on Cond. Mat. Phys., **15**, 1, 1990

S.F. Fang, K. Adomi, S. Iyer, H. Morkoç, H. Zabel, C. Choi and N. Otsuka
GaAs and Other Compound Semiconductors on Si
J. Appl. Phys. Reviews, **68**, 31-58, 1990

K. Adomi, S. Strite, H. Morkoç, Y. Nakamura, and N. Otsuka
Characterization of GaAs Grown on Si Epitaxial Layers on GaAs Substrates
J. Appl. Phys., in press

S. Noor Mohammad and H. Morkoç
Analytical Treatment of MODFET Heterojunction Quantum Well in GaAs/AlGaAs System
Solid State Electron., in press

S. Noor Mohammad, M.S. Ünlü and H. Morkoç
Optically Controlled Current Voltage Characteristics of Ion-implanted MESFETs
Solid State Electron. **33**, 1499-1509, 1990

Invited Talks

Strained Layer Lasers in the InGaAs/GaAs/AlGaAs Heterostructure System

Presented at *NATO Advanced Research Workshop on Condensed Systems of Low Dimensionality*, Marmaris, Turkey, April 23-27, 1990

Strained Layer FETs, Lasers and Phototransistors in the InGaAs/GaAs/AlGaAs Heterostructure System

Presented at *1990 Seoul Int'l Symposium on the Physics of Semiconductors and Applications*, Seoul, Korea, August 20-21, 1990.

Heteroepitaxy of Compound Semiconductors on Elemental Substrates

Presented at *The Third Annual Materials Research Symposium*, American Chemical Society, Corning, NY, October 5, 1990

PhD Graduates

Jen-Inn Chyi, Post-doc, University of Illinois
Daming Huang, Post-doc, U. of Southern Florida-Tampa

C.P. Flynn

Publications

X-M. Zhu, H. Zabel, I. K. Robinson, E. Vlieg, J. A. Dura and C. P. Flynn
Surface Induced Heterophase Fluctuations
Phys. Rev. Lett. **65**, 2692 (1990)

Huang, J. C. A., R. Du and C. P. Flynn
Nucleation Processes in the Growth of HCP Titanium
Phys. Rev. Lett. (in press)

J. Mayer, C. P. Flynn and M. Rühle
High Resolution Studies of Nb/Al₂O₃ Interfaces
Ultramicroscopy **33**, 51 (1990)

J. Mayer, W. Mader, F. O. Phillipp, C. P. Flynn, and M. Rühle
Structures of Nb/Al₂O₃ Interfaces Produced by Different Experimental Routes
Int. Phys. Conf. Ser. **98** (EMAG 89) 349 (1989)

J. Mayer, J. Dura, C. P. Flynn and M. Rühle
High Resolution Electron Microscopy of Interfaces
Between Al₂O₃ Substrates and MBE Grown
Nb Films
J. Mat. Res. (in press)

C. A. Lee, K. S. Laing, F. S. Shieu, S. L. Sass and
C. P. Flynn
Interface Structure of Epitaxial Nb Fibers on
Sapphire Grazing Incidence X-ray
Diffraction and X-ray Reflectivity Studies
J. Mat. Res. (in press)

J. F. Ankner, H. Zabel, D. A. Neumann, C. F.
Majkrzak, A. Matheny, J. A. Dura and C. P.
Flynn
Neutron Reflectivity Study of the Interfacial
Magnetism of tan Y/Gd Film
in *Neutron Scattering in Materials Science*, ed.
Shapiro, Moss and Jorgensen, MRS
Symposium Proc. Vol. 166 (MRS, Pittsburgh,
PA 1990)

J. F. Ankner, H. Zabel, D. A. Neumann, C. F.
Majkrzak, J. A. Dura and C. P. Flynn
Grazing Angle Neutron Diffraction
J. Phys. Colloq. 50 C7-189 (1989)

J. F. Ankner, C. F. Majkrzak, D. A. Neumann, A.
Matheny and C. P. Flynn
Grazing-Angle Magnetic Diffraction Using
Polarized Neutrons
(in press)

M. H. Zhu, I. K. Robinson, E. Vlieg, H. Zabel, J.
A. Dura and C. P. Flynn
Surface Phase Transition and Kinetics of
Cu₃Au(111)
J. Phys. Colloq. 50 C7-283 (1989)

R. Du and C. P. Flynn
Asymmetric Coherent Tilt Boundaries Formed by
MBE
J. Phys. CM2, 1335 (1990)

R. O. Simmons

Publications

K. W. Herwig, J. C. Gavilano, M. C. Schmidt and
R. O. Simmons
High-energy spectroscopy of compressed solid
hydrogen
Phys. Rev. B 41, 96-102 (1990)

D. A. Peek and R. O. Simmons
Single-particle kinetic energies of noble-gas
solids and liquids: Xenon, krypton and argon
J. Chem. Phys. (in press)

Honors

Member, Illinois Governor's Science Advisory
Committee, 1989-present

Invited Talks

"Neutron and x-ray scattering studies of
condensed noble gases"
Department of Physics and Astronomy
Michigan State University, East Lansing,
Michigan
January 16, 1990

"Momentum Distributions in Condensed Matter by
Neutron Scattering"
Department of Physics, University of Illinois at
Urbana-Champaign, Urbana, Illinois
April 12, 1990

"Deep Inelastic Neutron Scattering Studies of
Condensed Matter Systems"
Department of Energy Discussion Meeting on
Neutron Scattering
Gatlinburg, Tennessee
May 16, 1990

Ph.D. Graduates

John C. Thorpe (Ph.D. in Physics, January 1991)
"Thermal vacancies in hcp Helium-4"
(As of January, 1991, has not yet accepted a
position)

C.P. Slichter

Publications

P.-K. Wang, C. P. Slichter and J. H. Sinfelt
The Similarities and Differences in the C-C Bond
Scission of Ethylene and Acetylene on
Supported Ir and Pt Clusters
J. Phys. Chem. 94, pp. 1154-1157, (1990)

J. H. Ross, Jr., Z. Wang, and C. P. Slichter
NMR Studies of NbSe₃: Electronic Structures,
Static Charge Density Wave Measurements
and Observations of the Moving CDW
Phys. Rev. B **41**, pp. 2722-27344 (1990)

S. E. Barrett, D. J. Durand, C. H. Pennington, C. P.
Slichter, T. A. Friedmann, J. P. Rice, and D. M.
Ginsberg

⁶³Cu Knight Shifts in the Superconducting State
of YBa₂Cu₃O_{7-δ} (T_c=90K)
Phys. Rev. B. **41**, 6283-6296 (1990)

H. Monien, D. Pines, and C. P. Slichter.
Spin and Charge Excitations in YBa₂Cu₃O₇:
Constraints from Spin Relaxation Rates in the
Normal State
Phys. Rev. B **41**, pp. 11120-11127 (1990)

C. H. Pennington and C. P. Slichter
Nuclear magnetic resonance studies of
YBa₂Cu₃O_{7-δ}
*Physical Properties of High Temperature
Superconductors II*, D. M. Ginsberg, ed.
(World Scientific, NJ, 1990), pp. 269-367.

J.-Ph. Ansermet, C. P. Slichter, and J. H. Sinfelt
Solid State NMR Techniques for the Study of
Surface Phenomena
Chapter in *Prog. of NMR Spectroscopy*

S. E. Barrett, J. A. Martindale, D. J. Durand, C. H.
Pennington, C. P. Slichter, T. A. Friedmann, J.
P. Rice, and D. M. Ginsberg
Anomalous Behaviour of Nuclear Spin-Lattice
Relaxation Rates in YBa₂Cu₃O₇ Below T_c
Phys. Rev. Lett. **66**, 108 (1991)

C. H. Pennington and C. P. Slichter
Theory of Nuclear Spin-Spin Coupling in
YBa₂Cu₃O_{7-δ}
Phys. Rev. Lett. **66**, 381 (1991)

Invited Talks

NMR Studies of High T_c Superconductors
Physics Colloquium-University of Illinois at
Urbana-Champaign, Feb. 1990

NMR Studies on Single Crystals of YB₂Cu₃O₇
American Physical Society Meeting, March 12-
17, 1990, Anaheim, CA

DOE Catalysis and Surface Chemistry
Conference
Gaithersburg, MD, March 26-30, 1990

Probing Metal Catalysts by NMR
AMOCO, Naperville, IL, April 1990

NMR Studies of Catalytic Surfaces
ENI/Emerson Electric Symposium on Nuclear
Magnetic Resonance,
Washington University, St. Louis, MO

Nuclear Magnetic Resonance Studies of High
Temperature Superconductors
Tenth European Experimental NMR Conference,
Veldhoven - The Netherlands, May 1990

Probing High Temperature Superconductors by
NMR
Physics Colloquium, Michigan State University,
Oct. 1990

Probing High Temperature Superconductors by
NMR
Physics Colloquium, Ohio State University, Oct.
1990

Probing High Temperature Superconductors by
NMR
Physics Colloquium, University of Chicago, Nov.
1990

Somorjai Conference - The Mechanism of
Heterogeneous Catalysis
Department of Chemistry, University of
California at Berkeley, Nov. 1990, Invited
but unable to attend.

J.P Wolfe

Publications

D.R. Wake, H.W. Yoon, J.S. Preston, H. Morkoç,
and J.P. Wolfe
Picosecond Imaging of Photoexcited-carrier
Transport in GaAs/AlGaAs Multiple
Quantum Wells
in *Ultrafast Phenomena VII*, eds. C.B. Harris,
I.P. Ippen, A.H. Zewail, Springer Series in
Chemical Physics, Vol 53, p. 262 (1990)

H.W. Yoon, D.R. Wake, H. Morkoç, and J.P.
Wolfe
In-plane transport and spectral bleaching of
photoexcited carriers in GaAs quantum wells
Phys. Rev. B. (submitted)

Invited Talks

Picosecond Imaging of Photoexcited-carrier
Transport in GaAs/AlGaAs Multiple
Quantum Wells

Seventh International Conference on Ultrafast
Phenomena, Monterey, CA, May 14-17, 1990

Picosecond Imaging
Annual Review of Electronics, University of
Illinois at Urbana-Champaign, September
12, 1990

H. Zabel

Publications

J.F. Ankner, H. Zabel, D.A. Neumann, C.F.
Majkrzak, J.A. Dura and C.P. Flynn
Total Reflectivity and Grazing Angle Diffraction
of Neutrons
Electrochemical Society, Montreal, May 7 (1990)

X-M. Zhu, H. Zabel, I.K. Robinson, E. Vlieg, J.A.
Dura and C.P. Flynn
Surface Induced Heterophase Fluctuation
Phys. Rev. Lett. 65, 2692 (1990)

J.F. Ankner, H. Zabel, D.A. Neumann, C.F.
Majkrzak, A. Matheny, J.A. Dura and C.P.
Flynn
Neutron Reflectivity Study of the Interfacial
Magnetism of Y/Gd Film
In *Neutron Scattering for Materials Science*,
Materials Research Society Symposia
Proceedings, Vol. 166 (Materials Research
Society, Pittsburgh, 1990), edited by S.M.
Shapiro, S.C. Moss and J.D. Jorgensen

H. Zabel
X-Ray and Neutron Scattering of Thin Films
*Festkörperprobleme (Advances in Solid State
Physics)*, ed. by U. Rössler (Vieweg,
Braunschweig), 1990, p. 197

X-M. Zhu, R. Moret, H. Zabel, I.K. Robinson, E.
Vlieg, and R.M. Fleming
Grazing-Incidence X-Ray Study of the Charge
Density Wave Phase Transition in $K_{0.3}MoO_3$
Phys. Rev. B (Rapid Communication) 42, 8791
(1990)

P.F. Miceli, H. Zabel, J.A. Dura and C.P. Flynn
Anomalous Lattice Expansion of Metal-hydrogen
Thin Films
J. Mat.Res., submitted

S.F. Fang, K. Adomi, H. Morkoç, H. Zabel, C.
Choi, and N. Otsuka
Gallium Arsenide and Other Compound
Semiconductors on Silicon
J. Appl. Phys. 68(7), R31 58 (1990)

Invited Talks

Structure and Magnetism of Thin Epitaxial
Layers
Deutsche Forschungsanstalt für Luft und
Raumfahrt, Köln, Jan. 10

Hydrogen in Thin Films and Superlattices
Hahn Meitner Institut, Berlin, Feb. 12

X-Ray and Neutron Scattering at Thin Films
Plenary Talk, Spring Meeting of the German
Physical Society, Regensburg, March 30

Structure and Phase Transitions in Epitaxial
Films
Physics Colloquium, University of Dortmund,
April 4

Total Reflectivity and Grazing Angle Neutron
Diffraction
Electrochemical Society Meeting, Montreal, May
7 (presented by J.F. Ankner)

Structure and Magnetism of Thin Epitaxial Films,
Materials Science Colloquium, Ruhr University,
Bochum, June 11

Phonons, Magnons, and Librons in Graphite
Intercalation Compounds
Condensed Matter Colloquium, Technical
University Munich, June 21

X-Ray and Neutron Scattering at Thin Films and
Multilayers
Condensed Matter Symposium of the Austrian
Physical Society, Salzburg, Sept. 18

High Resolution X-Ray Scattering at Thin Films
and Heterostructures
Philips Research Symposium, Wirsberg, Sept. 26

Spin Structure and Excitations in a 2D KT System:
 $CoCl_2$ in Graphite

Internal Workshop on Kosterlitz - Thouless
Systems, Tokyo, October 11

Magnetism in Two Dimensions
Physics Colloquium, University of Bayreuth,
Nov. 13

Present Status of Surface Neutron Scattering
Forschungszentrum, Institut for Solid State
Physics, Julich, Dec. 3

Ph.D. Graduates

John F. Ankner
Postdoc
National Institute of Science and Technology,
Gaithersburg, MD

Xiaomei Zhu
Postdoc
University of Washington, Seattle

A.V. Granato

Publications

B. Colluzzi, C. Costa, F. M. Mazzolai, B.
Igarashi and A.V. Granato
Magnetic Anelastic Effects in Ni₃Al at Ultrasonic
Frequencies
*Proceedings of the Ninth International
Conference on Internal Friction and Ultrasonic
Attenuation in Solids*. Beijing, China.
International Academic Publishers. Ed. T.S.
Ke, Beijing and Pergamon Press, Oxford
(1990), p. 429

Ward L. Johnson and A.V. Granato
Ultrasonic Relaxation of Interstitial Aluminum
in Silicon
Phys. Rev. (Accepted)

E.C. Johnson, B. Igarashi and A.V. Granato
Configuration and Dynamics of an Interstitial
Impurity Complex in a Dilute Al-Li Alloy
(Submitted to Phys. Rev.)
Co-sponsored with the Aerospace Corporation

B. Igarashi, E.C. Johnson and A.V. Granato
The Diaelastic Susceptibility of Iron Containing
Self-Interstitials
Co-sponsored with the Aerospace Corporation

E.2 SIGNIFICANT ACCOMPLISHMENTS FOR SOLID STATE PHYSICS KC-02-02-02

Theory of Solids, Surfaces and Heterostructures

Scientific Achievement:

A systematic method has been developed to incorporate accurately correlations of core and valence electrons by Greens function methods. The calculations can be done on atoms and used to define an effective potential that can be employed in solid state calculations. Potentials have been calculated 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.

Significance:

Because 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, recent work has used only single particle (local density or Hartree Fock) methods to treat core electrons. Martin and coworkers have shown this leads to serious errors in some very important cases, in particular 3d states crucial to transition metals and the high temperature superconductors. They have shown how to use diagrammatic expansion to treat relaxation and correlation of core electrons and incorporate these in a potential which can then be used in molecular and solid state calculations. Tests on many atoms and the Na₂ molecule have shown the results are significant improvements over all previous pseudopotentials and all other ways of treating core electrons. The new potentials can be used as easily as previous less accurate potentials and can be used as either norm-conserving pseudopotentials or as effective potentials added in all-electron calculations.

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

Nuclear Magnetic Resonance in Solids

Scientific Achievement

Slichter has employed ^{13}C , ^1H , and ^2H nuclear magnetic resonance (NMR) and ^{13}C - ^1H spin echo double resonance (SEDOR) to study chemical reaction kinetics of simple hydrocarbon molecules on the surface of supported metal catalysts.

For example, with the molecule acetylene (HCCH) made with ^{13}C atoms, ^{13}C NMR plus SEDOR is used to show that the structure, at room temperature, is a CCH_2 molecule attached to the metal by the C which is not bonded to H atoms. The C-C axis is inclined at an angle to the surface. If the temperature of the catalyst is raised to several hundred degrees Celsius, it is found that the molecule breaks up into isolated C and H atoms adsorbed on the metal, plus methane gas. The temperature of the break-up depends on which metal (eg Pt vs. Ir) is used for the catalyst, thus giving a measure of the effectiveness of the particular metal for catalytic action. Slichter is able to follow the details of the break-up by starting at room temperature and following what happens at progressively higher temperatures. For CCH_2 on Ir, it is found that the molecule remains intact until the C-C bond breaks. Once that happens, the C-H bonds also break. But for CCH_2 on Pt, it is found that the C-

H bonds break at a lower temperature than the C-C bonds. This is revealed by the observation of two ^{13}C resonance lines, one from species containing hydrogen (CCH_2 , CCH) the other from species (C_2 , or C) which have lost their hydrogen. (See Fig. 1). Study of these processes versus temperature enables Slichter to characterize quantitatively the reaction pathways involved in the break-up of the molecule.

Significance:

One of the most important fields of surface science is investigation of mechanisms of catalysis. Many of the most powerful techniques of surface science however can only be applied to highly idealized systems, (such as single crystal surfaces). NMR, however, enables one to study real catalysts in a quantitative manner. The ability to study the pathways of chemical reactions on real catalysts in a quantitative manner is an essential prerequisite to developing a theoretical understanding of catalytic mechanisms. The NMR technique will not only enable one to study real catalysts, but will also allow one to relate results of studies of idealized systems by other experimental methods to real catalysts.

Performer: C. P. Slichter, University of Illinois at Urbana-Champaign

Figure 1

Figure 2

Fig. 1: The ^{13}C NMR of acetylene on Pt at 25 C, showing two absorption peaks. For Fig. 2, the H nuclei is also flipped in a double resonance experiment. It is possible to destroy the ^{13}C signal of ^{13}C atoms in a molecule containing H atoms. The fact that the signal at 100 ppm is greatly reduced in Fig. 2 relative to Fig. 1 shows that it arises from molecules containing H. The peak at 370 ppm is unaffected, showing that it comes from C_2 or C species.

F. RESEARCH SUMMARIES FOR MATERIALS CHEMISTRY

F.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.

HIGHLIGHTS

During the last year or so the major accomplishments of the group in the application of "pressure tuning spectroscopy" include the following:

(1) Using a complex of Ni^{2+} Professor Drickamer demonstrated for the first time a system where the ligand field decreases with increasing compression so that a transformation from low to high spin occurs.

(2) Drickamer has developed a set of principles involved in pressure-induced molecular conformation changes which introduces systematics and some predictability into solid state chemistry (see Significant Accomplishment Section below).

(3) Two sets of apparatus have been developed for making thermoluminescence measurements at high pressure, one operable from 77-320K and one from 300-600K. Each can be operated at two different constant heating rates. No such studies have been previously performed anywhere.

(4) Working with L. Faulkner, Drickamer has developed an apparatus for making a variety of electrochemical measurements under high pressure. It contains three electrodes and two sample compartments separated by a metal frit so one can contact two solutions under pressure with minimal mixing.

FUTURE DIRECTIONS

Current plans for the future include:

(1) The completion of the set of studies of molecular rearrangements at high pressure with some studies involving large metal clusters and proton transfer in molecules over large distances.

(2) A concentrated effort in thermoluminescence. In the apparatus operating from 77-320K, the electron is excited into the trapping state at 77K with a UV or visible laser. Drickamer plans to study initially two classes of materials; inorganic crystals like doped zinc chalcogenides and doped polymer films. The apparatus, operating between 300-600K uses samples in which electron and hole traps are introduced by x-rays or gamma rays under ambient conditions, then heating releases the trapped electrons or holes. Initial studies involve the alkali halides, but these will be extended to a variety of glasses. It is felt that high pressure studies of the properties of electron and hole traps will permit the better characterization of these defects and the design of improved phosphors.

Increase in intensity of high spin absorption peak relative to low spin peak with pressure, indicating a decrease in the local field at the Ni^{2+} ion with compression for $[\text{Ni}(\text{diethylthiourea})_4\text{X}_2]$ [X = Cl (■), X = Br (○).]

(2) The electrochemical studies will be initially concentrated on the properties of conducting polymer films deposited on electrodes. Further studies will involve characterization electron transfer processes at electrode surfaces.

SIGNIFICANT ACCOMPLISHMENT

High Pressure Studies of Molecular and Electronic Phenomena

Significant Accomplishment

Over the past several years Professor Drickamer has been studying pressure induced changes in molecular geometry in organic molecules like anils, spiropyrans and bianthrone, in metal cluster compounds, and in complexes of Cu(II) and Ni(II) with organic ligands or counterions in the solid state. From these studies a set of rules or generalizations which provide a systematic picture of such reactions has been developed.

(a) Molecular rearrangements in liquids are stochastic processes involving only nearest neighbor interaction. In a tightly bound solid it may be necessary for all molecules to transform together, i.e. the cooperativity is macroscopic and one has a first order phase transition. In molecular crystals, glasses, polymeric media and intercalates the extent of cooperativity may be at either extreme or at some intermediate value. In the language of physics, a higher order phase transition may be involved.

(b) The extent of cooperativity depends on the nature of the rearrangement and on the medium. A rearrangement which is discontinuous in the crystal may involve a lesser extent of cooperativity in a polymeric matrix or glass.

(c) The probability that a given rearrangement is induced by pressure depends more on differences in intermolecular (interionic) interactions and packing than on differences in bond lengths between configurations.

(d) Temperature and pressure are not, in general, conjugate variables. Pressure may act either to inhibit or accelerate the effect of temperature.

(e) In general there appear to be two modes by which pressure induced isomerizations and consequently, piezochromism, can occur. There can be a transformation from one distinct conformation to another due to the relative stabilization of the potential well associated with conformation B with respect to that of A. This process may be either an equilibrium process if the energy barrier is small, or involve a first or

higher order phase transition depending on the extent of cooperativity demanded by the type of transformation and the environment. Such transformations are characterized by a change in the electronic character of the ground state. If there is no distinct change in the electronic character of the ground state, a series of compounds may follow each other along a reaction pathway as they undergo a similar piezochromic transformation over different pressure ranges.

(f) Frequently a given complex, e.g. CuCl_4^{2-} exists in a wide range of geometries at ambient pressure depending on the extent of hydrogen bonding, van der Waals forces etc. provided by the surroundings. At high pressure the range of geometries is much smaller as packing and repulsion dominate over the weaker attractive forces at higher compression.

These rules are not necessarily a complete set, but they supply a significant degree of regularity in an area where there has been little or none, and they can provide some extent of predictability in solid state chemistry.

Performer: H.G. Drickamer, University of Illinois at Urbana-Champaign

Organometallic Polymers

GOALS

Organometallic clusters are used to build new new types of polymeric materials. Synthetic strategies explored in this program include cluster charge transfer salts and clusters linked by inorganic and organic backbones. These species are characterized by chromatographic, spectroscopic, electrochemical, and crystallographic methods

HIGHLIGHTS

In the past year Professor Rauchfuss has succeeded in preparing the first vinyl-substituted organometallic cluster. Using a three step procedure, vinyl groups can be attached to $[(C_5H_5)Fe(CO)]_4$. The modified cluster copolymerizes with methyl acrylate upon free radical initiation. The resulting pale green polymer is thermally stable. Both high performance liquid chromatography and UV-vis spectroscopy demonstrate that the Fe_4 cluster has been incorporated into the polymer.

A study on the preparation and redox properties of organometallic compounds of the type $(C_5R_5)MX_3$ has been completed. These species have been shown to serve as electron acceptors which can give rise to novel charge transfer salts. They are, in essence, analogs of the difficult to handle oxyhalides MOX_n (M is a metal, X is a halide). A single crystal X-ray diffraction study of $(C_5H_5)VI_3$ shows that it forms a chiral polymer of paramagnetic ($S = 1/2$) centers held together by weak $I \cdots I$ interactions. This substance undergoes a phase transition near 23 K to a diamagnetic state.

The bifunctional reagent $Fe_2S_2(CO)_6^{2-}$ was found to form a step polymer upon treatment with α, α' -dibromo-p-xylene. Preliminary results suggest that the oligomers, which consist of alternating p-xylene and Fe_2S_2 subunits, are quite soluble in organic solvents. In related work the ferrocene compound $Fe(C_5H_4)_2S_3$ was shown to polymerize upon chemical removal of a sulfur atom.

FUTURE DIRECTIONS

The hybrid Fe_4 -polymethylmethacrylate copolymer will be further characterized. The structure and processing characteristics of the ferrocene and Fe_2S_2 polymers system are soon to be studied. Experiments are about to commence on several new polymers based on (chiral) ferrocenyl-amino acids, and the reactive cobalt-containing polymer $[(C_2H_3C_5H_4)Co(CO)_2]_n$.

SIGNIFICANT ACCOMPLISHMENT

Functionalized Organometallic Clusters

Scientific Achievement:

Methods have been developed for functionalizing organometallic clusters in ways that allow them to be incorporated into organic polymers. Using a three step procedure a vinyl group can be attached to the organometal cluster $[(C_5H_5)Fe(CO)]_4$. The copolymer derived from the vinyl-substituted cluster and methylmethacrylate is green, soluble, and thermally robust. This is the first example of a covalently attached organometallic cluster. The methodology could be used for the preparation of other hybrid cluster copolymers.

Significance:

This work has shown how two large families of compounds, organometallic clusters and organic polymers, can be combined so as to give new hybrid materials. The new materials exhibit properties of the constituent parts, for example organic polymers are typically not redox active (i.e. they cannot be doped with mild oxidizing and reducing agents), whereas the cluster polymers display this property. Organometallic clusters tend to crystallize and thin films cannot usually be prepared while this is a possible with the hybrid materials. The new methods define routes for the incorporation of other organometallic clusters into polymers. Thus it appears that this will be the first in a large family of structurally novel materials.

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

F.1.b PUBLICATIONS AND HONORS FOR
CHEMICAL STRUCTURE
KC-02-02-02

H.G. Drickamer

Publications

H.G. Drickamer
High Pressure Luminescence Spectroscopy in
Polymer
in *Photochemistry and Photophysics*, Vol. I, pp
137-175, J. F. Rabek ed. CRC Press, New York.
(1989)

H.G. Drickamer and K. L. Bray
Pressure Induced Molecular Rearrangements in
the Solid State
International Rev. of Phys. Chem. 8, 41-64 (1989)

H.G. Drickamer
Recent Applications of Pressure Tuning
Spectroscopy
CHEMTRACTS (Physical and Anal. Ed), 1, 272-
87 (1989)

H.G. Drickamer and K. L. Bray
Piezochromism: Pressure Induced Isomerizations
in the Tetrachlorocuprate Anion in the Solid
State with Various Cations
J. Phys. Chem. 94, 2154-59 (1990)

H.G. Drickamer, J. L. Coffey, J. T. Park, R. T.
Roginski and J. R. Shapley
Infrared Spectra of C₂ Hydrocarbon Ligands
Coordinated to a Triosmium Framework: The
Effect of High Pressure as a Tool for
Assignment
J. Phys. Chem. 94, 981-85 (1990)

H.G. Drickamer and K. L. Bray
Pressure Tuning Spectroscopy as a Diagnostic for
Pressure Induced Rearrangements
(Piezochromism) of Solid State Cu(II)
Complexes
Acc'ts. of Chemical Research 23, 55-61 (1990)

H.G. Drickamer, J. L. Coffey and J. R. Shapley
The Effect of Pressure on the Surface Plasmon
Spectrum of Colloidal Gold and Silver
Particles
J. Am. Chem. Soc. 112, 3736-42 (1990)

H.G. Drickamer, J. L. Coffey and J. R. Shapley
Pressure Induced Skeletal Isomerization of
[(Au)₉(PPh₃)₈] (PF₃)₃ in the Solid State.
Inorg. Chem. 29, 3900-01 (1990)

H.G. Drickamer and K. L. Bray
Pressure Induced Spin State Isomerizations in
Weakly Tetragonal Nickel (II) Complexes
with Thiourea
J. Phys. Chem. 94, 7037-40 (1990)

H.G. Drickamer, J. L. Coffey and J. R. Shapley
Effect of High Pressure on the Vibrational
Frequencies of the α -Pyridyl Moiety in
HOS₃(CO)₁₀(μ , η^2 -NC₅H₄)
J. Phys. Chem. 94, 5208-10 (1990)

H.G. Drickamer
High Pressure Since P. W. Bridgman - A Personal
View
in *High Pressure Research* 5, 955-62 (1990)

H.G. Drickamer
Forty Years of Tuning Spectroscopy
Ann. Rev. of Materials Science, 20, 1-17 (1990)

H.G. Drickamer and W. W. Ley
Pressure Tuning Spectroscopy of Two
Phospholipids and Their Common Fatty Acid
J. Phys. Chem. 94, 7367-71 (1990)

H.G. Drickamer and K. L. Bray
Pressure Induced Isomerizations in Five
Coordinate Copper (II) Complexes
J. Phys. Chem. (in press)

H.G. Drickamer
Pressure Effects in Molecular and Related
Luminescence
J. Luminescence (in press)

Honors and Awards

Department of Energy Award for Outstanding
Sustained Materials Chemistry

Invited Talks

David A. Mason Lectures (two)
Stanford University, Stanford, CA - May 1990

Opening Lecture and Plenary Lecture, Workshop
on Pressure Effects on Molecular Crystals
Catania, Italy - May-June 1990

Plenary Lecture - International Luminescence
Conference
Lisbon, Portugal - July 1990

PhD Graduates

W. W. Ley (Ph.D.)
Kraft Research Laboratories

K. L. Bray (Ph.D.)
Assistant Professor of Chemical Engineering
University of Wisconsin
Madison, Wisconsin

T.B. Rauchfuss

Publications

D. B. Morse, T. B. Rauchfuss, and S. R. Wilson
Main Group Transition Metal Chemistry. The
Pentamethylchromium Iodides Including
[(C₅Me₅)₂Cr₂I₃][I₁₆]
J. Am. Chem. Soc., **112**, 1860, 1990

D. B. Morse
Organometallic Acceptors in Molecular-based
Materials: Field Dependent Magnetic
Behavior on an Organovanadium Charge
Transfer Salt
Chem. Mat., **2**, 33, 1990

D. B. Morse, T. B. Rauchfuss, and S. R. Wilson
Organometallic Oxidants. The Chemistry,
Structures, and Redox Properties of
(C₅H₅)VX₃ (X = Br, I)
Inorganic Chem. **30**, 0000, 1991

G. K. W. Freeman, X. Yang, T. B. Rauchfuss, and
S. R. Wilson
Reactions of Tetrathiometalates of Molybdenum
and Tungsten with Dithiocarbonates and the
Redox-Dependant Reactivity
Inorganic Chemistry, submitted

Honors and Awards

Editorial Advisory Board for the journal
Organometallics

Editorial Advisory Board for the journal
Chemical Reviews

Editorial Advisory Board for the series Inorganic
Syntheses

Invited Talks

Invited Speaker at Symposium on
Desulfurization Catalysis, National Meeting
of the American Chemical Society, Boston

Invited Speaker at Symposium on
Organometallic Electrochemistry, National
Meeting of the American Chemical Society,
Washington, D. C.

Coorganizer of and Speaker at Symposium on
Soluble Metal Chalcogenides, National
Meeting of the American Chemical Society,
Washington, D. C.

Invited Speaker at Dept of Chemistry, Michigan
State University

Invited Speaker at Gordon Conference on
Organometallic Chemistry

Invited Speaker at Dept of Chemistry, West
Virginia University

Invited Speaker at Shell Development
Laboratory

F.2.a. RESEARCH SUMMARIES FOR
CHEMISTRY OF MATERIALS SURFACES
KC-02-03-03

THEODORE L. BROWN

**Synthesis and Characterization of
Organometallic Liquid Crystal Polymers**

GOALS

The goals of Professor Brown's effort are to:

(a) Synthesize liquid crystal polymers containing organometallic functional groups. Few such compounds have been prepared and characterized. It is expected that the new substances will have novel electrical, magnetic and optical properties that will provide useful applications.

(b) Characterize newly synthesized materials to determine whether they exhibit liquid crystalline behavior, and to determine other physical and chemical properties.

HIGHLIGHTS

In FY 1991, excellent progress was made in the synthesis of copper-schiff base complexes exhibiting liquid crystalline behavior. These materials were prepared because they have the potential to form the basis of main-chain polymeric systems. Three distinct series of compounds were prepared, each containing several members with varying carbon chain lengths. Throughout each series several members exhibit liquid crystalline behavior over wide temperature intervals. The liquid crystalline phase is nearly always smectic in nature, as determined from the optical microscopic properties. The results of this work suggest that the copper centers exert a significant influence on the intermolecular alignments. The smectic phases may be favored because they optimize interactions between the copper centers on adjacent molecules.

FUTURE DIRECTIONS

Professor Brown's group will continue to develop a "chemical tool kit" of low molecular weight units that have the potential to form liquid crystalline polymers. The possibilities for copolymerization of the copper systems with organic monomeric units to form main chain polymeric systems will be investigated. However, the major emphasis will be on the

development of side chain systems with organometallic functionality. Although such systems pose significant synthetic challenges, they have the potential to yield novel liquid crystalline polymeric materials. Finally, the properties of the copper-containing liquid crystalline materials that have been synthesized will be further studied. Because these materials are of quite high molecular masses, they may have properties intermediate between those expected for low molar mass liquid crystals and polymeric systems. Among the approaches employed will be incorporation into oriented polymer films, to determine whether the copper systems orient, as determined from IR and UV-visible spectra.

SIGNIFICANT ACCOMPLISHMENT

**Synthesis and Characterization of
Organometallic Liquid Crystal Polymers**

Scientific Achievement:

A significant accomplishment this year has been the synthesis and characterization of an extensive series of copper-containing schiff base complexes that exhibit mesogenic behavior above their melting points. These are not the first copper-containing liquid crystalline materials, but our results add substantially to the extant body of data for such systems. Professor Brown has observed for the first time a characteristic luminescence from solutions of all the copper complexes synthesized.

These have been characterized materials through use of optical microscopy and differential thermal analysis. The results clearly point to the formation of mesophases, nearly all of which appear to be smectic in character, rather than nematic. The nematic phase is less ordered than the smectic phases, because the molecules are not aligned into sheets, but only maintain generally parallel orientation. The strong tendency to adopt the smectic phase suggests that the copper centers in adjacent molecules possess some degree of interaction that provides a driving force for alignment of the molecules into sheets. There has until now been no recognition of this possibility in metal-containing liquid crystals. The nature and extent of the interaction is not clear as yet, but will be the subject of further study.

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

Surface Chemistry of Boundary Layer Films

GOALS

The goal of this program is to obtain an understanding of the chemistry of molecular films adsorbed to metal surfaces. Such adsorbed films are important in tribological technologies such as lubrication, in catalysis, and in corrosion passivation. Professor Gellman's work focuses both on the study of surface chemistry and on the development of methods for study of adsorbed surface films.

HIGHLIGHTS

During the past year progress has been made in the study of two types of surface reactions. Straight chain carboxylic acids ($\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{H}$, $n=0-5$) have been adsorbed on silver surfaces to determine orientation and heats of interactions with the surface. These appear to behave in a fashion similar to alcohols, orienting themselves parallel to the surface with heats of interaction with the surface of ~ 1.0 kcal/mole/ CH_2 group.

EXELFS has been used to study the surface structure of NiO films grown on both Ni(100) and Ni(110) surfaces. These studies have revealed similar structures on both surfaces with Ni-O bond lengths of ~ 2.08 Å. In addition, the structure of N atoms on the Cu(100) and Cu(110) surfaces have been examined. Although these form structures with different long range order, the local structure about the nitrogen atoms appears to be common, having Cu-N bond lengths of 1.84 Å and 1.81 Å respectively.

Previously Gellman had determined the mechanism of a surface reaction in which acetylene heterocyclizes with sulfur atoms to yield thiophene. This is important chemistry since it serves to remove sulfur from the metal surface. During the past year Gellman has been able to show that this reaction is occurring at defects in the sulfur overlayer. These defects are models for anion vacancies that occur in compound catalysts and it is possible to form the defects by heating of the surface.

FUTURE DIRECTIONS

A future direction in the study of straight chain acids on the silver surface is to use these molecular films as surface modifiers in

measurements of interfacial friction. Our study of heterocyclization chemistry will employ an STM to image the surface defects at which this reaction is occurring. Finally, a new project will be started as part of the DOE Solid-Liquid Interfaces Initiative in the Illinois MRL. The surface chemistry of acetylenic alcohols used as corrosion passivation agents will be examined to determine what types of species actually exist on metal surfaces following adsorption of such compounds.

Desorption of straight-chain carboxylic acids (acetic-hexanoic) from a clean Ag(110) surface. The desorption temperature is incremented by 20K per methylene group (CH_2). This translates into an increment of ~ 1 kcal/mole/ CH_2 in the heat of adsorption to the surface.

SIGNIFICANT ACCOMPLISHMENT

Determination of Heterocyclization Reaction Sites

Scientific Achievement:

During the past year Professor Gellman has been able to demonstrate that the heterocyclization reactions on the sulfided Pd(111) surface occur at defect sites in the sulfide films. These defects occur as a result of heating of the surface or during sulfiding of the surface as the sulfur coverage approaches saturation. It has been possible to determine the coverage of surface defects and to correlate the surface heterocyclization reactions directly with defect density.

Significance:

There are many compound catalysts such as oxides and sulfides on which the active surface sites are thought to be anion vacancies. The present observations open the way to the use of surface methods for the study of surface reactions occurring at anion defects in compound catalysts, and to the formation of model anion vacancies on single crystal surfaces. While surface science methods have been applied with great success to metallic surfaces and the study of surface reactions occurring at steps and kinks on metal surfaces, much less work has been done with compound surfaces. This is due in part to the low concentrations of active defects and a lack of approaches to characterizing defects. On the sulfided Pd(111) surface it is possible to create defects in controlled concentrations at high coverages.

Performer: Andrew J. Gellman, University of Illinois at Urbana-Champaign.

E. G. SEEBAUER

Optical Spectroscopy of Surface Processes in Thin Film Deposition**GOALS**

Professor Seebauer's investigations are intended to examine the surface chemistry of interest in the deposition of semiconductors such as GaAs. The main techniques employed are photoreflectance (PR) and surface second harmonic generation (SHG). Being photon-based instead of electron or ion-based techniques, PR and SHG are relatively nonintrusive and avoid some of the severe surface perturbations that are often encountered with these other methods. Furthermore, experiments may be carried out if necessary in situ under reaction conditions. Surface diffusion measurements with SHG are of particular interest because essentially no reliable measurements of diffusion on semiconductors currently exist.

HIGHLIGHTS

Professor Seebauer's PR experiments have shown for the first time that this technique can be used to extract quantitative adsorption/desorption parameters at pressures well above the ultrahigh vacuum range. In PR, the optical reflectance of a GaAs surface is changed slightly with a low-power laser. The magnitude of this change is measured as a function of wavelength and varies strongly with adsorption. During the past year Professor Seebauer has isolated by trial-and-error the optimum conditions of a carrier concentration and surface preparation for measuring heats of adsorption of on GaAs(100).

Using SHG, Professor Seebauer has this year been able to image for the first time the evolution of a step concentration profile in response to surface diffusion on a semiconductor. For experimental ease, the system chosen was Sb adsorbed on Ge(111), although the method is quite general. The initial step 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 with the second harmonic light generated by a pulsed laser. The yield of this light varies upon adsorption, and is imaged to 10 μ resolution and a precision of 0.03 monolayer with a photodiode array. A schematic diagram is attached. The activation energies and pre-

exponential factors for diffusion, along with their concentration dependence, are being extracted.

Create step concentration profile at low temperature

Image relaxation of step concentration profile

FUTURE DIRECTIONS

Professor Seebauer intends to continue PR experiments on GaAs to obtain heats of adsorption of the weakly adsorbed metallorganic species used in deposition processing. The SHG will be employed primarily for surface diffusion measurements of Ga, As, and related molecular compounds on GaAs and other semiconductors. The wavelength dependence of SHG will be investigated in order to improve signal-to-noise ratios. Ultimately, Professor Seebauer intends to make these measurements under the gaseous ambients typical of real processing conditions.

SIGNIFICANT ACCOMPLISHMENT

Imaging of Surface Diffusion Profiles with Nonlinear Optics

Scientific Achievement:

The surface diffusion of antimony on germanium has been measured using the nonlinear optical reflectance technique of surface second harmonic generation (SHG). SHG is used to monitor directly the evolution of a step concentration profile in ultrahigh vacuum with a spatial resolution of 10 microns. On the Ge(111) surface, the diffusion coefficient of Sb is 4×10^{-9}

cm^2/s at 400°C . These experiments represent the first use of SHG to perform highly controlled imaging with this resolution. It is now possible to image diffusion profiles with this technique down to surface concentrations of a few percent of a monolayer.

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 by chemical vapor deposition or molecular beam epitaxy. Slow diffusion results in highly defected, poor-quality material. We have invented a method using SHG that measures diffusion with high spatial resolution and without causing surface damage. Our technique can be employed in a wide variety of adsorption systems and can measure surface diffusion under a gaseous ambient or even under a liquid. Such experiments will be critical for developing rational approaches to enhance diffusion and thereby improve thin-film quality.

Performer: E. G. Seebauer, 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 we discovered a reaction that yields two-dimensional polymers from chiral high molar mass monomers. These systems yield chiral molecular sheets which order into layered structures and exhibit remarkably stable nonlinear optical susceptibility. We have monitored the intensity of the second harmonic laser beam for one year and no changes have been detected so far. Our data indicate that the two-dimensional structures form through the "double stitching" of two covalent backbones in a system that experiences molecular recognition. In the area of nematic polymer-organic dye alloys we were able to show that second order susceptibilities can be tripled when magnetic fields are used to achieve high macroscopic order parameters before electric fields eliminate the center of inversion. This year we also faced the first challenges in the area of field-responsive organometallic polymers which are to synthesize structures that are at least soluble but preferably fusible as well. Our work has been concentrated on the synthesis of polymers containing tetradentate metal complexes as structural units. Following a number of failed attempts we were able to prepare new highly substituted polymers which were soluble in methanol.

FUTURE DIRECTIONS

We propose to study the reaction yielding the 2D structures in order to understand its mechanism and generality. One of our objectives is to carry

out the reaction in controlled states of monomer orientation. We plan to use magnetic fields to orient the layered structures of the monomeric precursor and electric fields to align the functional groups that yield the stitching backbones of the newly discovered molecular sheets. Our main probe for structure-properties correlations will continue to be the measurement of the second harmonic intensity as a function of temperature, time and electric field intensity. The objective in the study on organic alloys will be to understand how various molecular environments restrict the motion of organic dye molecules in electric fields. With regard to organometallic polymers our main objective will be to synthesize and characterize the properties of paramagnetic comb polymers containing the organometallic structures as side chains.

SIGNIFICANT ACCOMPLISHMENT

Two-Dimensional Polymers

Scientific Achievement:

This year we discovered a reaction that leads to the synthesis of two-dimensional polymers from chiral high molar mass monomers. The products are new materials which can be described as chiral molecular sheets forming through the "double stitching" provided by two polymerization reactions. The essence of the discovery is that of monomers with special architecture that react in configurations controlled by molecular recognition phenomena. The specific systems studied this year form the two-dimensional structures through a conjugated polyimine chain and an all carbon backbone resulting from the polymerization of nitrile groups and acrylate groups, respectively. The newly discovered materials exhibit a strong nonlinear optical signal of remarkable temporal stability; we have monitored the intensity of the second harmonic laser beam for one year and no changes have been detected so far. The two-dimensional polymers form smectic phases which undergo an isotropization transition, possibly a "crumpling" transition at a temperature which is 140°C higher than that of the precursor monomer.

Significance:

The new materials discovered in this research program can have impact in technological

applications related to nonlinear optics. In this emerging area new materials are utilized to double the frequency of laser beams or change the refractive index of light through electrical pulses. The materials that have the nonlinear properties must be shaped as waveguides in electro-optical devices that store, transmit and process information. These devices could play a role in the development of powerful computers as well as new telecommunication systems. One critical property that materials for these technologies must have is temporal stability of their nonlinear properties. Industrial laboratories have specified that materials must remain field-responsive for periods of five years or more. The only materials known so far that have reasonable but not ideal stability are glassy crosslinked polymers such as epoxies but these would present a number of difficulties in terms of processing and aging. The materials we have synthesized recently have potential because their nonlinear optical activity is remarkably stable and also because the layered structures they form can be processed into monodomains with external magnetic fields. These monodomains are important because they reduce the light scattering that must be avoided in the waveguides of opto-electronic devices.

Performer: 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 O₂ 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

Professor Suslick has succeeded in preparation of polymeric porphyrins. The first ligand bridged one-dimensional polymers with a non-symmetric bridge has been isolated and crystallographically characterized. There are several structural types in which these polymers might be expected to crystallize: disordered, anti-parallel, and polar (aligned) orientations of the polymer chains. There are now examples of all three groups. Of special interest, is our structure of $[\text{Fe}^{\text{II}}(\text{tetraphenylporphyrinato})\mu\text{-(1-(4'-phenolato)imidazole)}]$ which has fully aligned chains in a polar space group. Suslick has succeeded recently in making thin films from such formulations and will actively pursue examination of their ferroelectric, piezoelectric, and optical dichroic behavior in poled films.

FUTURE DIRECTIONS

Up to this point, Suslick's efforts have been principally synthetic, with full spectroscopic and crystallographic characterization of pure isolated solids. Initial screening for ferroelectric and optical dichroic and nonlinear behavior will become a necessary and routine part of this characterization. To this end collaborative efforts for such characterization have now been

A 1-dimensional porphyrin coordination polymer.

established with the research groups of Professors Stupp and Bohn, both participants in the UIUC MRL, and with Dr. G. R. Meredith and his group at duPont Central Research.

Suslick will continue to develop the synthesis of metalloporphyrin assemblies as non-linear optical materials in the near-infrared (where porphyrins do not absorb). The ability to use the porphyrin as a synthetic platform on which one can erect optical activity (as either a molecular or a crystallographic property), large dipole moments, and high polarizability will be explored. The promise which organic polymers have for large optical nonlinearities has been discussed in great detail. Porphyrinic materials have not been explored for such a use, but are excellent candidates for such an effort.

SIGNIFICANT ACCOMPLISHMENT

A New Class of Polymers

Scientific Achievement:

A new class of polymers has been made from metalloporphyrins, materials closely related to the central units found in both photosynthesis and in the oxygen carrying protein hemoglobin. Long asymmetric chains made from flat disks

bridged by molecular rods have been assembled and characterized.

Significance:

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. The class of polymers that are under development here can potentially serve as molecular switches, responsive to applied electrical fields. This is the basis for electronic memory storage, as well as having potential application for extremely small scale sensors.

Performers: Kenneth S. Suslick, University of Illinois at Urbana-Champaign

F.2.b. PUBLICATIONS AND HONORS FOR
CHEMISTRY OF MATERIALS AND SURFACES
KC-02-03-03

Theodore L. Brown

Publications:

K. P. Reddy and T. L. Brown
Synthesis and thermal Behavior of Mesomorphic
Copper (ii) Schiff Base Complexes
J.Mat.Chem. (submitted)

Invited Talks

Visiting Distinguished Scientist Program,
National Science Council, Taiwan, July 1990.

Lectures at:

National Taiwan University, Taipei
National Tsing Hua University, Hsinchu
National Cheng-Kung University, Taichung
National Sun Yat Sen University, Kaoshiung
Annual Meeting, Inorganic Chemists of
Taiwan

DeGussa Lectures, University of South Alabama,
April 1990

Departmental Chemistry Colloquium,
University of South Florida, January, 1990

A.J. Gellman

Publications

Dai Qing, A.J. Gellman
Spectral Transformation of EXELFS Data - NiO
on Ni(100) and Ni(110)
Surf. Sci. 235 (1990) 217

Dai Qing, A.J. Gellman
A Structural Examination of Nitrogen on Cu(100)
and Cu(110) Surfaces
Surf. Sci., in press

A.J. Gellman
Heterocyclization Reaction Sites on the Sulfided
Pd(111) Surface
Langmuir, in press

A.J. Gellman
Surface Induced Heterocycle Formation - Sulfur
Atom Abstraction During Cyclization
J. Am. Chem. Soc., (submitted)

A.J. Gellman
Heterocyclization of Acetylene to Thiophene at
Defects on the Sulfided Pd(111) Surface
Defects in Materials, MRS Proc. 209 (in press)

Dai Qing, A.J. Gellman
Spectral Transformation of EXELFS Data and a
Structural Examination of
Nitrogen on Cu(100) and Cu(110) Surfaces
Advances in Surface and Thin Film Diffraction
MRS Proc. 208, (submitted)

Honors and Awards

Packard Fellowship in Science and Engineering -
David and Lucile Packard Foundation, 1989 - 94

Chairman-Elect, U. of Illinois Local Section of
the ACS, 1990-91

Editorial Advisory Board, "Critical Reviews in
Surface Chemistry"

Invited Talks

Exxon Chemical Co., Baytown, TX - Jan. 1990

Lawrence Berkeley Laboratory, Berkeley, CA -
Apr. 1990

University of California, Dept. of Chemistry,
Riverside, CA - Apr. 1990

Aerospace Corp., Los Angeles, CA - Apr. 1990

Columbia University, Department of Chemistry,
New York, NY - Nov. 1990

Dow Chemical Co., Midland, MI - Feb. 1991

Iowa University, Department of Chemistry, Iowa
City, Iowa - March 1991

ACS National Meeting, Symposium on
"Applications of Surface to Problems in
Tribology", Atlanta, GA - Apr. 1991

ACS National Meeting, Symposium on "Surface
Reaction Mechanisms and Kinetics", Atlanta,
GA - Apr. 1991

Electrochemical Society Meeting, Symposium on
"Critical Issues in the Structure and
Chemistry of Organic Monolayers at
Electrode Surfaces", Washington, DC - May
1991

Chairman - American Chemical Soc. Central
Region Meeting Symposium on "Mechanisms
and Intermediates in Surface Reactions",
Indianapolis, IN - May, 1991

E.G. Seebauer

Publications

P. L. Jackson and E. G. Seebauer
Accurate methods for calculating electro and
photoreflectance lineshapes for GaAs
J. Appl. Phys. (in press)

Honors and Awards

Presidential Young Investigator Award from
National Science Foundation, 1988

Dow Teaching Excellence Award, 1988

DuPont Young Faculty Awardee, 1989

Observer for U.S. Delegation, 35th General
Assembly, Lund, Sweden, 1989

Invited Talks

Chair, Kinetics of Deposition Session, Amer. Inst.
of Chem. Engrs. Annual Meeting, Chicago, IL,
1990

Co-Chair, Kinetics of Etching Session, Amer. Inst.
of Chem. Engrs. Annual Meeting, Chicago, IL,
1990

MS Graduate

Kent A. Schultz, M. S., Jan. 1990 (continuing as a
Ph.D. student)

S.I. Stupp

Publications

J.S. Moore and S.I. Stupp,
Room Temperature Polyesterification
Macromolecules, **23**, 65 (1990).

J.S. Moore and S.I. Stupp
Cleavage of Aldehyde Hydrazone Iodides
Under Mild Conditions. A Convenient Route
to Chiral Nitriles of High Enantiomeric
Purity
J. Organic Chemistry, **55**, 3374 (1990).

J.S. Moore and S.I. Stupp
Materials Chemistry of Chiral Macromolecules.
1.Synthesis"
J. Amer. Chem. Soc. (submitted)

S.I. Stupp
Synthesis of Materials with Self-Ordering
Chiral and Functionalized Macromolecules
Proceedings US-Japan Seminar on Polymer
Synthesis, Tokyo, November 1990.

F. Zuo, I. Yu, M. B. Salamon, X. Hong, and S.I.
Stupp
Magnetic Studies of Cu-Based Organometallic
Monomers and Polymers
J. Applied Physics (submitted)

Honors

Visiting lecturer for three weeks at the Max
Planck Institut fur Polymerforschung, Mainz

Chairman, ACS symposium "Interactions of
Polymers with Electric and Magnetic Fields"

Invited Talks

Hoechst-Celanese

Polymer Processing Society, France

American Chemical Society

Max Planck Institut fur Polymerforschung, Mainz

ETH, Zurich

Technion, Israel

Weizmann Institute, Israel

Institute of Macromolecular Chemistry, Prague

Bulgarian Academy of Sciences

Dow Chemical

IUPAC, Montreal

Alcoa Symposium

US-Germany Polymer Symposium (NSF-DFG),
Germany

University of Minnesota

Nippon Steel, Tokyo

Kyoto University

Seikisui Chemicals, Kyoto

US-Japan Seminar on Polymer Synthesis, Tokyo

American Chemical Society, Polymer Chemistry
Division

K.S. Suslick

Publications

K.S. Suslick and C-T. Chen
Polymeric Metalloporphyrins for Field
Responsive Materials
Polymer Material Sci. Engin. Preprints (ACS
Polym. Div., Washington, D.C.), 1990, xx, in
press

G. S. Girolami, S.N. Milam, K.S. Suslick, and
S.R. Wilson
Mono(porphyrinate) Actinide Complexes
Submitted

K.S. Suslick and C-T. Chen
Metalloporphyrin Coordination Polymers as
Field Responsive Materials
Submitted

Honors and Awards

Beckman Associate, UIUC Center for Advanced
Study, 1991-1992

NIH Research Career Development Award, 1985-
1990

Instructor, Royal Society of Chemistry
Residential Course on Sonochemistry,
Coventry, U.K., 1991

Guest Editor, Special Issue on Sonochemistry,
Ultrasonics, Butterworth Publishing, 1990

Finalist Mentor (of Mr. Chin-Ti Chen, DOE
supported graduate student on this project),
1990 Sherwin-Williams Student Award of
the American Chemical Society Polymer
Materials, Science and Engineering Division

Invited Talks

Symposium on New Catalysts, National
Materials Research Meeting, Boston,

Plenary Lecturer, Symp. on Cavitation, National
Center for Physical Acoustics, Oxford, MS.

Sherwin-Williams Symposium, Polymer
Materials Science and Engineering Division,
200th ACS National Meeting, Washington,
D.C.

Symposium on Oxidation Catalysis, 199th ACS
National Meeting, Boston

Union Carbide, Bound Brook

University of Delaware

University of New Mexico

Central New Mexico ACS Section

University of Illinois, Biophysics

Argonne National Laboratory

Nazarene-Olivetti University, Kankakee

duPont & Co., Wilmington

Hoechst-Celanese, Corpus Christi

Carleton University, Ottawa

**F.3. SIGNIFICANT ACCOMPLISHMENTS FOR
MATERIALS CHEMISTRY
KC-02-03**

SIGNIFICANT ACCOMPLISHMENT

Two-Dimensional Polymers

Scientific Achievement:

This year we discovered a reaction that leads to the synthesis of two-dimensional polymers from chiral high molar mass monomers. The products are new materials which can be described as chiral molecular sheets forming through the "double stitching" provided by two polymerization reactions. The essence of the discovery is that of monomers with special architecture that react in configurations controlled by molecular recognition phenomena. The specific systems studied this year form the two-dimensional structures through a conjugated polyimine chain and an all carbon backbone resulting from the polymerization of nitrile groups and acrylate groups, respectively. The newly discovered materials exhibit a strong nonlinear optical signal of remarkable temporal stability; we have monitored the intensity of the second harmonic laser beam for one year and no changes have been detected so far. The two-dimensional polymers form smectic phases which undergo an isotropization transition, possibly a "crumpling" transition at a temperature which is 140°C higher than that of the precursor monomer.

Significance:

The new materials discovered in this research program can have impact in technological applications related to nonlinear optics. In this emerging area new materials are utilized to double the frequency of laser beams or change the refractive index of light through electrical pulses. The materials that have the nonlinear properties must be shaped as waveguides in electro-optical devices that store, transmit and process information. These devices could play a role in the development of powerful computers as well as new telecommunication systems. One critical property that materials for these technologies must have is temporal stability of their nonlinear properties. Industrial laboratories have specified that materials must remain field-responsive for periods of five years

or more. The only materials known so far that have reasonable but not ideal stability are glassy crosslinked polymers such as epoxies but these would present a number of difficulties in terms of processing and aging. The materials we have synthesized recently have potential because their nonlinear optical activity is remarkably stable and also because the layered structures they form can be processed into monodomains with external magnetic fields. These monodomains are important because they reduce the light scattering that must be avoided in the waveguides of opto-electronic devices.

Performer: S. I. Stupp, University of Illinois, at Urbana-Champaign

G. FACILITIES OPERATION

G.1 OPERATIONAL HIGHLIGHTS

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 Center for the Microanalysis of Materials

This is the largest of the M.R.L. facilities and is very closely linked to support of the D.O.E. research program. The primary role of the Center is to develop and support microcharacterization methods which are required by the M.R.L. research programs. One of the basic philosophical underpinnings of this facility is that the variety of techniques available, coupled with the expertise of the staff allow users the possibility of considering the most appropriate technique to be applied and the possibility of applying multiple methods of characterization and analysis. Faculty and staff of the three MRL programs, other faculty members and students at the University of Illinois, faculty and students at other Universities, the staff of the National Laboratories, and researchers from industrial laboratories are all users of the Center for the Microanalysis of Materials.

UPGRADING OF EQUIPMENT

The past year has seen a continuation of the process of renewal and upgrading of the facilities. This is a continuing effort required to keep the capabilities of the Center at the cutting edge of science; as it must be to maintain the utility of the systems for researchers. Funds supplied by the D.O.E. have been heavily leveraged to allow the purchase of these equipment items. This is indicated by the fractions of D.O.E. support for each major item. Clearly, the other programs of the MRL are paying their share of the capital equipment costs.

A new Zeiss 960 Scanning Electron Microscope has been installed to replace an old JEOL 35c which is

being used as a test bed for instrument development. The new instrument is equipped with an advanced energy dispersive x-ray detector to allow microanalytic studies. The cost of this instrument was shared between the various sources available to the MRL with 33 % being supplied by the D.O.E.

We have equipped the SEM with a Raith electron beam writing instrument which allows the SEM to be conveniently used for microlithography at the 0.1 micron level. This technique is being used for the development of novel materials structures for research on the electron behavior in mesoscopic solids. The D.O.E. shared in the cost of this addition to the extent of 0 %.

Completion of the installation of the Philips EM 12 Analytic TEM occurred during this past year. This instrument was acquired at no cost to the D.O.E.

During the past year we have initiated the purchase of an atomic resolution TEM, a JEOL 3010 which is capable of 0.16 nm resolution. This purchase was made possible by the addition of Professor J. Murray Gibson to the Departments of Physics and Materials Science and Engineering as he will provide the expertise required for atomic resolution microscopy by many of the other faculty and students in the MRL. This microscope will be delivered in the spring of 1991 for installation in the Center for the Microanalysis of Materials. The DOE contribution to this purchase was 38 %.

Another instrument development associated with Professor Gibson joining the MRL is the design and construction of a true UHV electron microscope/surface analysis instrument; the SHEEBA. This instrument will combine UHV surface preparation, surface analysis techniques, and surface electron microscopy to allow the structure and chemistry of important surfaces to be studied in a truly clean environment. The electron optics part of the instrument is being constructed by JEOL to the design specifications of Gibson. The electron optics part of the instrument will be delivered to MRL in the spring of 1991. The D.O.E. did not contribute towards the purchase of the electron optics column as the funds were obtained from the University of Illinois. We will support the development of the remainder of the instrument with D.O.E. funds in FY91.

The capabilities of the Environmental Cell TEM have been increased with the addition of a **double tilt high temperature stage**. This instrument was acquired at no cost to the D.O.E.

A high resolution, **small spot XPS** has been obtained from the **Surface Science Corp.** and is being installed in the Center for use in conjunction with the present high resolution XPS. The new XPS will be applied for long time experiments such as gas doping and adsorption studies. This instrument was obtained in connection with the addition of Ralph Nuzzo to the Department of Materials Science and Engineering. The DOE was required to contribute 0 % to the purchase of this instrument.

The funds for installation of a **PIXIE** line on the Van de Graaf accelerator have been obtained and the necessary equipment has been ordered. Design of the apparatus is underway and installation will be completed in FY91. The contribution of the DOE to this purchase is 0 %.

INSTRUMENT AND TECHNIQUE DEVELOPMENT

Design and construction of a **high temperature SEM straining stage** was completed in FY 91. This stage has the capability of carrying out straining experiments in situ in the SEM at temperatures of up to 1200 C. The upper temperature limit is actually set by the temperature at which thermal emission of electrons exceeds the intensity of the secondary and back scattered electrons.

A **double tilt straining stage** has been designed and constructed for use in the Environmental Cell TEM. This instrument is based on a design developed in the MRL and constructed in the MRL shops. It has unique capabilities.

A **high temperature straining stage** capable of operation to temperatures of 1000 C has been designed and is being constructed for use with the Environmental Cell TEM.

An **environmental chamber** has been designed and built for the **PHI XPS** which allows treatment of specimens in high pressure gases at various temperatures, ion bombardment at various temperatures, etc., and then transfer of the specimen into the UHV chamber of the XPS. A similar **environmental chamber** has been built for the **Scanning Auger Spectrometer** which allows

ion bombardment and treatment of the surfaces with gases at temperatures up to 1200 C.

Development work with SNMS and SIMS has shown that compound semiconductors show pronounced topography development when sputtered. Surface diffusion appears to be the process responsible for ripple formation and also, in the case of InP, for cone formation as both are inhibited by sample cooling. These processes have also been shown to affect XPS and Auger analyses.

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 FY91 the number of users trained in the various techniques of Center for the Microanalysis of Materials was 201.

USER ACTIVITIES

The Center provides a heavily used resource available to scientists at the M.R.L., at the Universities within the U.S., at National Laboratories, and in Industrial Laboratories. In the past year, we have had about **20 outside users**, many of whom made repeated trips to use our facilities. These users include the scientists from the following organizations:

Argonne National Laboratory
 Southern Illinois University
 Northwestern University
 Purdue University
 Anderson Laboratories
 Yugoslav A.E.C.
 University of Illinois (Chicago)
 E.G.G. Idaho/INEL
 University of Nevada (Reno)
 University of Colorado
 Haynes International
 Caterpillar Tractor Co.

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	5790
STEM	333
SEMs	2022
X-Ray	4850
SAES	2074
SNMS	594
SIMS	2525
XPS	1323
Accelerator	507
Ion millers	16939

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 underfunded 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. People in

the areas of electronics, U.H.V., and computer programming are needed. Addition of support staff will have the added benefit of allowing the professional scientists more time for innovative research on techniques and instruments.

We would also like to add Research Associates to the Center to support the efforts in instrument science which are carried out. A particular need is for an additional professional staff member in the area of microchemistry as we have added several new instruments in microchemistry without being able to add any staff.

Carefully considered plans have been laid for continuing capital purchases based on input from the Facility Advisory Committee and are being reported to the D.O.E. as a Ten Year Development Plan. The Center operates about 19 major instruments, each of which has a useful life expectancy of about ten years. Funds equal to 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 major equipment items required in the next few years are:

FY 1991	Replacement of the Secondary Ion Mass Spectrometer with a Cameca 4f Completion of the UHV SHEEBA instrument
FY 1992	Replacement of the Secondary Ion Mass Spectrometer with a Cameca 4f (if this is not accomplished in FY91) Rigaku D1 x-ray diffractometer Upgrade of HB 5 STEM Cathodoluminescence detector for the SEM Electron backscatter detector for the SEM
FY 1993	Replacement of STEM with a modern analytic version (this will utilize the upgrade items from the HB 5 STEM)

As a result of support by the University, additional space will be available to the Center

for the Microanalysis of Materials. This will allow us to pursue a long planned effort to develop a research and teaching program in Instrument Science which will focus on developing the science which underlies instrument development and on allowing instrument development to be carried out in conjunction with M.R.L. research programs. We hope to begin to educate scientists and engineers in the subject of instrument science as a beginning of an effort to restore the vitality of the instrument industry in the U.S.

The EpiCenter (Molecular Beam Epitaxy Center)

All the basic instrumentation in the EpiCenter has been installed, specifications have been met, and the facility is in full operation. The interactive mode of research is being developed in a gradual manner but appears to be working well. The M.R.L. (in cooperation with the C.S.L.) has installed a gas handling system which will allow the use of toxic gases safely and therefore will allow the development of **Gas Beam Epitaxy and MOCVD**. These techniques, which are complementary to M.B.E. crystal growth, allow great flexibility in crystal growth and in the systems which can be studied.

The cost of this upgrade was borne by University of Illinois funds.

The Center for Computation

The Center for Computation provides computer facilities for the M.R.L. 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 modelling, there is an impending shortage of supercomputer capacity available to researchers in Materials Science. In the past year the M.R.L. has completed an upgrade of the Computer Facility to meet these needs. We have 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 D.O.E. contribution to this upgrade amounted to 48 % of the total cost.

The Laser Facility

During the past year we have upgraded the Laser Facility to begin to acquire the equipment needed for **femtosecond pulsed laser studies**. The facility has moved to expanded and upgraded quarters. The non-linear optics systems are in regular use, principally by the researchers in the "Field Responsive Polymeric and Organic Materials" group.

The D.O.E. contribution to the added equipment amounted to 20 % of the total.

The Ceramics Fabrication Facility

The Ceramics Fabrication Facility continues to operate efficiently to meet the needs of the ceramic researchers for specimen preparation. No major change in the facility occurred during this past year.

The Low Temperature Facility

This facility has undergone a transition in the past two years. Usage of the Millikelvin Cryostat has fallen to the point where we decommissioned the instrument as a facility operation. This decrease in use is the result of the onset of interest in high T_c materials. The cryostat operation has been placed on a "standby status" and will be activated as a facility when the demand warrants it.

The SQUID magnetometer is in full operation. Its usage is very high due to the interest in high T_c materials.

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 is closely linked to the CMM through the use of the SEM as an electron beam writer and for

this purpose the Raith electron beam control unit was purchased during FY90. The D.O.E. contribution to this purchase was 0 %.

G.2 CONSTRUCTION OF FACILITIES

Experimental Facilities in the Interpass

The MRL program has grown considerably since the construction of the initial building in 1966. While the present building offers adequate accommodation for some of the D.O.E. supported program, there is not sufficient space to house all of the supported work. Consequently, much of the research supported in recent years is housed in other buildings. The major concern about this arrangement is that it decreases the amount of interaction between components of the research effort. It has been shown repeatedly, that close scientific interactions occur most readily when the researchers meet each other at relatively frequent intervals. This is not possible with our present building arrangement.

An excellent solution to this problem appears to be at hand. The Coordinated Science Laboratory building, adjacent to the MRL building, will be vacated in about two years as that laboratory moves to new quarters. The University has agreed that the present CSL building will then be occupied by Physics and MRL. At that point the MRL will gain about 24,000 square feet of laboratory space and the opportunity to house most of its programs in contiguous space.

Construction of the Interpass Building between MRL and CSL is scheduled for the spring of 1992 and will be largely funded by the State of Illinois. The three story office structure will provide needed office space as well as acting as the corridor between the two buildings. The MRL offices will be moved to the Interpass in order that the three buildings comprising the MRL be joined into a single unit.

Most of the funding for this project is in hand. The State of Illinois has committed \$3,100,000 of construction funds, which is sufficient to complete the structures and to finish the first and second floor space. The Engineering College has agreed to complete the third floor offices. An additional \$600,000 is required to complete the basement into finished laboratories.

The basement laboratories are intended to house the Central Facilities. This would provide

needed additional space for the Center for the Microanalysis of Materials, allow us to move the Laser facility to the basement and allow us to establish the Polymer Facility in a suitable laboratory. Contiguous location of the Central Facilities has a number of major advantages; principal among these is the ability to share technical manpower between them.

We propose that the basement laboratory space be completed with the assistance of the D.O.E. The MRL can borrow the funds necessary for completion of this space; an amount estimated to be about \$600,000. We are requesting that the D.O.E. reimburse the MRL for this cost over six years, FY 1992 to FY 1997, at the rate of \$100,000 per year added to the MRL budget. If this suggestion is favorably received we will proceed with the development of a full construction proposal.

A.P.S. SYNCHROTRON BEAM LINES

The Materials Research Laboratory has taken an active interest in the development of the Advanced Photon Source at Argonne National Laboratory. Many of our programs have a need for the capabilities of this unique facility and our staff is planning to take an increasingly active role in the development of new science made possible by this unique x-ray source. The M.R.L. is actively interacting with the staff of the A.P.S.; H.K. Birnbaum is a member of the A.P.S. Proposal Evaluation Board and H. Chen is serving on the Users Steering Committee.

The M.R.L. is planning to participate in the development of one sector of the A.P.S. in cooperation with Oak Ridge National Laboratory and the Allied-Signal UOP Corporation. A Collaborative Access Team partnership has been developed between these three organization for the purpose of building and operating the sector beam lines, with equal participation and contribution from each of the organizations. Haydn Chen has been elected as the Director of the sector organization and will be coordinating the activities at the institutions. A Letter of Intent has been accepted by to the APS, giving permission to develop a full proposal for the sector development. Active discussions are presently taking place for the development of this proposal which will include an undulator beam line and a bending magnet beam line. The undulator line will be devoted to scattering experiments (including time resolved scattering)

while the bending magnet line will be designed for spectroscopy (including time resolved spectroscopy). It appears that the needs of the cooperating organizations are well matched and suited for development of the sector.

At the present time, the agreement between the partners in the CAT is that each institution will have a 1/3 share in the CAT and will pay for 1/3 of the cost. We estimate that the Illinois share of the CAT development over the period FY 1991 to FY 1995 will be \$3,000,000 (\$600,000 per year).

The M.R.L. has obtained \$750,000 of State of Illinois funding in a Scientific Challenge Grant competition in FY 90-91. These funds are being used to begin the Beam Line group effort and have been used for the purchase of end-station equipment, support of graduate students and Research Associates, and for the expenses of operating research programs in synchrotron scattering. In order that this group of M.R.L. researchers can begin to use synchrotron radiation prior to the operation of the A.P.S., we have entered into an agreement with Oak Ridge National Laboratory to assist in the operation of and to utilize their NSLS beam line X-14 for M.R.L. research. This will assist the M.R.L. programs to develop and use the end station equipment on an accelerated time scale.

The MRL is requesting continued funding from the State of Illinois. In addition, it will be submitting a proposal to the NSF Instrumentation Program and to the DOE for assistance in developing the APS sector. We will ask that the D.O.E. provide \$ 500,000 per year for the period of FY 1992 to FY 1995 for the expenses associated with the M.R.L. share of the A.P.S. Sector development.

END

**DATE
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01/27/92