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Nineteenth Annual Report

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MATERIALS RESEARCH

AT

STANFORD UNIVERSITY

July 1, 1979 - June 30, 1980

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Nineteenth Annual Report

on

MATERIALS RESEARCH AT STANFORD UNIVERSITY

Information concerning research activities related to the science of materials during the period July 1, 1979 through June 30, 1980.

This research was supported primarily by one or more of the following agencies of the United States Government:

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Department of Health, Education and Welfare
Department of the Interior
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SECTION A

INTRODUCTION

SECTION A

INTRODUCTION

This Nineteenth Annual Report includes the total research activity related to the science of materials at Stanford University during the period July 1, 1979 through June 30, 1980. It contains brief descriptions of research programs active during this period.

The report of the research programs is organized into two groupings: (1) the research programs of CMR Members who have participated in one of the five major Thrust group programs supported by the NSF-MRL block grant including their work on the Thrust program and other related research, and (2) individual research programs; when appropriate, members are included in both the Thrust and individual programs. As indicated in their descriptions, some of the research programs were supported by private sources. However, most received support from one or more of the following agencies of the United States government.

- Defense Advanced Research Projects Agency
- Department of the Air Force
- Department of the Army
- Department of Commerce
- Department of Energy
- Department of Health, Education and Welfare
- Department of the Interior
- Department of the Navy
- National Aeronautics and Space Administration
- National Bureau of Standards
- National Science Foundation
- Veterans Administration

The reports of the individual programs are organized by Principal Investigator arranged in alphabetical order, since many programs are cooperative and arrangement by subject would be cumbersome. Also included are compilations of publications, doctoral dissertations, faculty and senior staff members, research associates, graduate students and degrees awarded. Finally, a name index has been added for convenience in locating references to the activities of specific individuals. From this compilation, it can be seen that research on materials and related problems is being conducted within eleven

different academic departments as well as in the Hansen Laboratories.

In addition to the direct support of individual research programs by the agencies mentioned above, broad-base core support was furnished by the National Science Foundation through its Materials Research Laboratory (MRL) Program under Grant No. DMR 77-24222, administered by the Center for Materials Research (CMR), during this past year. Of particular importance has been the financial assistance for the establishment and operation of a group of important Central facilities for the Synthesis and Characterization of new materials.

SECTION B

THRUST RESEARCH PROGRAMS

1. THRUST PROGRAM ON ACOUSTIC NONDESTRUCTIVE TESTING

G. S. Kino, Professor, Electrical Engineering and, by Courtesy,
Applied Physics
B. A. Auld, Adjunct Professor, Hansen Labs
G. Herrmann, Professor, Mechanical Engineering, Applied Mechanics,
Civil Engineering
A. M. Nur, Professor, Geophysics
C. F. Quate, Professor, Applied Physics, Electrical Engineering
J. C. Shyne, Professor, Materials Science
C. R. Steele, Professor, Mechanical Engineering, Aerophysics and
Astrophysics

Professional Associates:

S. D. Bennett
A. G. Herrmann
D. B. Ilić
B. T. Khuri-Yakub

Graduate Students:

R. B. King	D. Rugar
W. F. Murphy	N. Shaikh
M. T. Resch	F. E. Stanke
M. Riazat	

Agency Support:

An associated program, AFOSR F49620-79-C-0217
An associated program, EPRI RP 609-1
NSF-MRL through CMR - Thrust Program on Acoustic Nondestructive
Testing

Technical Objective:

To establish new techniques for nondestructive testing of materials. We are particularly interested in measurement of stress by acoustic means and in measurement of stress intensity factor at a crack. We are also interested in new techniques for measuring the size and type of cracks and flaws.

Approach:

The measurement of stress in metals by measuring changes in acoustic velocity due to stress, and the measurement of stress intensity factor using this technique and using reflection of acoustic waves from

a crack. The development of new techniques for eddy current testing. The development of acoustic microscopy for observation of metal surfaces and integrated circuits. Research on applications of nondestructive testing ideas in the field of Geology.

Research Report:

During the last year, some new projects have been added to this program. The stress measurement technique itself has proven to be extremely successful, and the development of shear wave measurement methods is making good progress, under both CMR and other support. A new acoustoelastic theory has been derived which should make it possible to extrapolate the measurement technique to use with surface acoustic and Lamb waves and to a rigorous study of non-uniform applied stresses. The measurement technique has led to a major breakthrough in the measurement of residual stress of extruded aluminum samples. This work is reported under the thrust project on metals and plasticity. Other associated projects involve measurement of microstructure and hardness under AFOSR support, and measurement of the J and M energy integrals and the stress intensity factor of cracks under AFOSR and EPRI support.

The work on eddy current testing has been proceeding well, and initial successful tests have now been made to detect open and closed fatigue cracks, and for detecting metal inclusions in dielectrics.

The work on measuring cracks in glass has been completed, and excellent agreement between our predictions of fractures stress by acoustic techniques and measurements of fracture stress have been obtained. The theory has been extended to cover a larger range of crack sizes. It has proven more accurate than we expected to predict the breaking stress for fairly large crack sizes. The measurements have been repeated for structural ceramics on an associated ONR project, and a great deal has been learned about plastic flow in ceramic materials. Work has begun on the measurement of fatigue cracks in metals and the opening and closing of fatigue cracks observed acoustically for the first time during the fatigue cycle.

A small seed project has been begun on the possibilities of using high intensity acoustic waves or microwaves to improve the flow and recovery of oil using some the the NDT and microwave probe concepts.

Another project to study materials with the acoustic microscope using sophisticated processing of the images obtained has been supported in part by a grant for a microprocessor.

(1) Acoustoelasticity

Professional Associates: S. D. Bennett
A. G. Herrmann
G. Herrmann
D. B. Ilić
G. S. Kino
C. R. Steele

Graduate Students: N. Shaikh
F. E. Stanke

The acoustoelastic scanning of an inhomogeneous plane stress field using a scanned longitudinal wave transducer in water has been successfully accomplished under CMR support (Johnson, Ph.D. thesis, April 1979). The change of longitudinal wave velocity is proportional to the first stress invariant, $(\sigma_1 + \sigma_2)$.

Shear wave analysis is necessary to determine the separate values of σ_1 and σ_2 and the principal directions and for direct determination of the J and M energy integrals of fracture mechanics. Scanning with shear waves is more difficult, primarily because the transducer must be in direct contact with the specimen. To obtain satisfactory contact, previous investigators have resorted to strong bonding or the application of very large pressures (~ 140 MPa). To alleviate this difficulty, we have developed a transducer with a spherical front face of large radius (10 - 20 cm) that requires a contact force of only around 40 N to give a Hertzian contact of about 1 ~ 2 mm diameter.

The major accomplishments in this year's activity has been the development of mechanical equipment and a computer controlled system necessary for automated scanning, and rotation of the transducer to excite shear waves at an arbitrary angle of polarization. The specimen

to be tested is stressed by a hydraulic ram system, and the applied force measured with a thrust cell.

The calibration test consists of pulling a plate of constant cross-section in uniform tension. Automatic recording of load value and corresponding null frequency are done **both on the loading** and unloading cycles at a large number of intermediate points. The graph of $\Delta f/f$ versus stress is then made for two specific polarizations, one along the direction of tension and another normal to it. The results are straight lines whose slopes are a complicated function of elastic constants but a compact representation of the acoustoelastic characteristics of the material. The slopes obtained from a tensile test of Al6061-T6 compare well with the results of Johnson (1979) as well as those of Smith et al. (1966) from a bonded transducer. The reproducibility of measurements both on loading and unloading is very good.

We have accomplished the first goal of proving the feasibility of such a system and obtaining the desired reproducibility of scanning with the movable contact transducer. There are still significant questions concerning the effects of material anisotropy and texture. As we progress, specimens with interesting stress fields due to holes and cracks will be examined. For the eventual practical application, the contact shear scanning, in addition to the complete determination of the stress field, offers distinct advantages in eliminating the water bath and increasing the resolution near boundaries where peak stresses usually occur.

The theory of acoustoelasticity developed by Murnaghan, Thurston, and others is extremely difficult to apply when the applied stress is non-uniform. It is also inconvenient to use for acoustic waves with a non-uniform profile such as surface acoustic waves, Lamb waves, etc. We have formulated a new theory based on energy conservation principles; this employs a variational expression to determine the propagation constant of the wave. This makes it possible to work with the equation for internal energy of the material directly without having to go through several differentiations, and the final Murnaghan acousto-elastic equations can be derived far more quickly by this method. The

use of this technique is the start of the development of a perturbation theory based on normal mode or coupled mode theories, which are themselves closely related to energy conservation theories. Such theories should make it relatively simple to predict the effect of stress on propagation of arbitrary kinds of waves, such as surface or Lamb waves.

(2) Improvement of the Scientific Base of Eddy Current Testing

Professional Associates: B. A. Auld
J. C. Shyne

Graduate Students: M. T. Resch
M. Riazint

This program is directed toward providing part of the theoretical base for a Rockwell-supported development study of ferromagnetic resonance (FMR) probes for detecting surface cracks in metals and supporting feasibility studies of unconventional types of electromagnetic probes, such as capacitive probes. This activity relates to two other electromagnetic flaw detection projects (EPRI and Garrett Airresearch) where it provides scientific insight and conceptual cross-linking.

Theoretical study of FMR probes is being carried out under the thrust program and compared to experimental results. A normal mode theory of FMR probe behavior is being developed that is better adapted to interpreting and explaining the rather complex dependence of lift-off/flaw signal discrimination on the mode structure of the probe. Our aim in developing this theory, partly under Rockwell support, is to better understand the nature of multimode probe operation so as to arrive at an optimal probe design.

Another aspect of FMR flaw detection probe operation currently under joint study with the Rockwell program is an investigation of the behavior of fatigue cracks in aluminum under load. Under this joint activity a mechanical scanner has been constructed for the FMR probe and used to examine fatigue cracked specimens under load in the MTS machine and in a small laboratory bending device constructed for this purpose. All fatigue crack samples have been easily detected, even when tightly closed. The experiments, which are still in progress,

have as a goal the verification of theoretical relations between crack opening compliance and stress intensity factor, as well as testing feasibility of using the FMR probe for monitoring fatigue crack growth and making J integral type measurements of fracture toughness. The crack opening displacement (COD) is being measured optically, and results are correlated with the FMR probe results.

In the previous report it was noted that the basic theory of electromagnetic flaw detection probes had been extended to include specifically the capacitive probe, and a probe figure of merit (Electric test field/Probe input current) was defined. We have constructed a probe, with sharply-pointed electrodes, using a special high-impedance bridge and differential amplifier circuit for detection. The circuitry includes a phase discriminator unit that permits a two-dimensional display of the complex probe impedance. At the present time, this system has been tested using short sections of the through wire as test objects. A metal test object of volume equivalent to a 0.2 mm diameter sphere has been detected, at a signal level within 6 dB of the theoretical prediction, based on an approximate analysis of the electric field distribution of the probe.

(3) Characterization of Cracks by Acoustic Scattering

Professional Associates: B. T. Khuri-Yakub
G. S. Kino
J. C. Shyne

Graduate Students: M. T. Resch

Surface acoustic waves are being used quantitatively to assess the effect of surface flaws on the mechanical behavior of cracked solids. The measured reflection coefficient of acoustic surface waves reflected from a surface flaw is analyzed to yield such information as the predicted fracture stress of a cracked plate. This work has provided experimental confirmation for the theoretical ideas proposed by Budiansky and Rice which have been extended by Kino and Auld to cover the use of surface acoustic waves to examine surface cracks, and it demonstrates the practical NDE potential of the technique. During the year, the theory was extended to take account of image effects at the surface.

Semi-elliptical surface cracks are introduced into flat, Pyrex glass discs. After measuring the acoustic reflection coefficient for 3.4 MHz Rayleigh waves using specially developed wedge transducers, the acoustic data is analyzed to predict the fracture strength of the glass plate. This prediction is then compared to actual fracture test results. These experiments on glass are now essentially complete. A large number of specimens has been tested with crack depths varying from 50 to 500 μ . The correlation between acoustically predicted fracture behavior and the mechanical test results is good. Better than anticipated correlation is observed with larger cracks that deviate from the theoretically required condition that crack dimensions be much smaller than acoustic wave length. Figure 1 compares the acoustic predictions with measured fracture stresses.

Currently we are extending the Rayleigh wave scattering experiments to fatigue cracks in metals. The intent is to detect and measure the early stages of fatigue crack growth at the microcrack stage. Initially we experienced considerable difficulty due to scattering from the surface microstructure caused by machining. By growing cracks perpendicular to the very fine machining grooves which occur, we were able to minimize this effect and detect cracks 300 μ long and 20 μ deep, or 50 μ diameter semicircular cracks with 3.5 MHz surface acoustic waves. For the first time, we have been able to observe the opening and closing of such cracks on an MTS testing machine during the crack growth process.

In our experiments, we grow the cracks by starting them at a highly focused laser burned region. Our intention is to put these measurements on a quantitative basis and observe crack growth during fatigue. We also intend to instrument to observe second harmonic generation of acoustic waves at cracks during fatigue growth. Following the work of Buck at Rockwell, this should provide additional information on the crack properties.

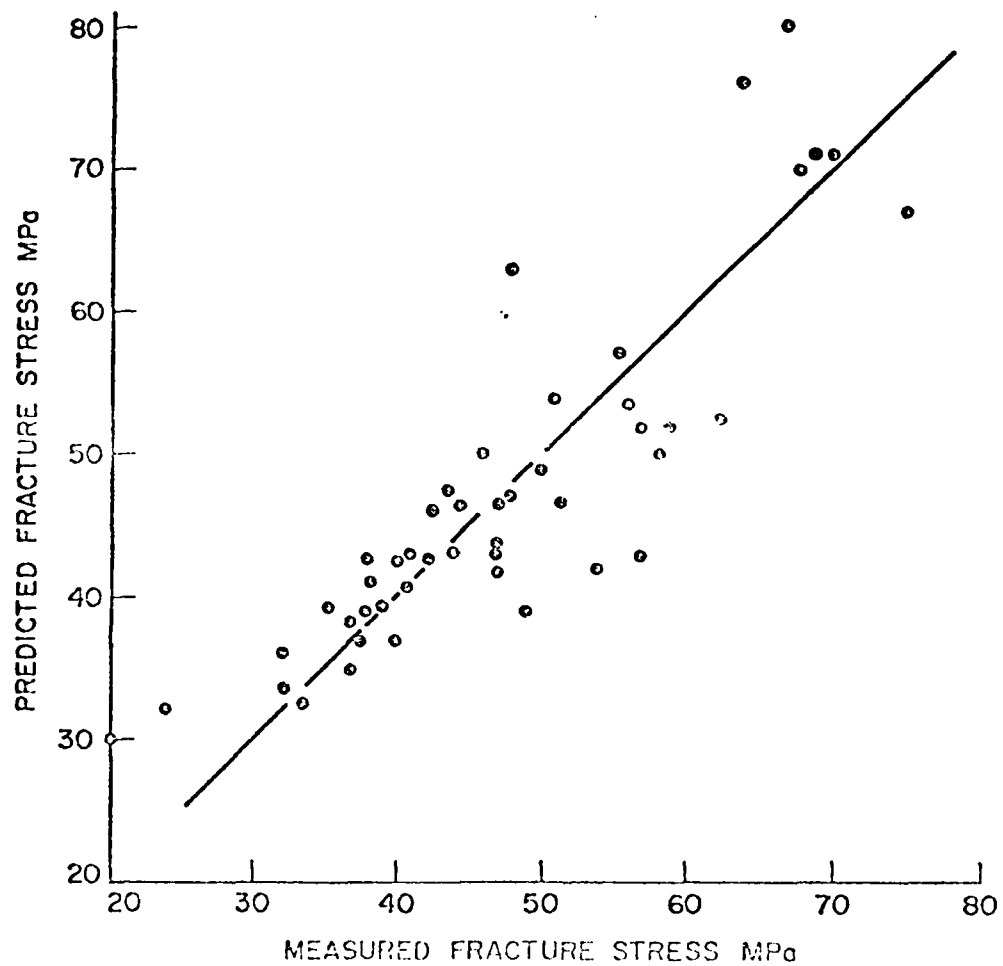


Figure 1. Acoustically predicted fracture stress versus measured fracture stress in Pyrex glass plates containing a single semi-elliptical surface crack.

(4) Acoustic Microscope

Professional Associate: C. F. Quate

Graduate Student: D. Rugar

With funds from the Thrust Program, we purchased a Cromenco Z-2 microprocessor with 64 kilobytes of memory and dual 8-inch floppy disk drives. The computer system has been interfaced to the cryogenic acoustic microscope. It serves a variety of control functions for the microscope and allows high resolution (512 pixels x 512 pixels) digital storage of micrographs. Innovative features of the system include:

1. Conversion of non-raster microscope scans to raster scans. This eliminates degradation of images due to vibration that is coupled into the microscope's mechanical scanning system from external sources (room vibration, pump vibration, etc.)
2. Signal averaging of microscope image information. The computer keeps a running average of image information for each pixel. As many as 60 samples per pixel may be averaged together. This results in a factor of eight improvement of signal-to-noise ratio in the micrographs. This will prove useful for analytical interpretation of acoustic micrographs.
3. Rayleigh velocity mapping. By scanning the acoustic lens in the Z (focusing) direction, we can, using the computer, estimate the Rayleigh velocity of materials on a microscopic scale. The computer controls the Z-axis scanning, measures a quantity which is a function of the Rayleigh velocity, and outputs a Rayleigh velocity map to the television monitor. This system is insensitive to height variations of the sample - a problem that has plagued other methods of analysis.

(4) Physical Properties of Porous Rocks

Professional Associate: A. M. Nur

Graduate Student: W. Murphy

We have begun to consider the role which the physical properties of the internal surfaces of porous rocks play in controlling bulk rock behavior. This includes, in particular, effects on wave propagation

and attenuation and single and two phase fluid flow. The goals of the study are twofold: one is to understand the effects at low wave amplitudes and low flow rates to develop diagnostic tools for geophysical exploration purposes, and second, we wish to explore the possibilities for using high intensity waves for improved flow and recovery from porous rocks. All processes involved are strongly associated with surface phenomena and require much input from concepts in material sciences and surface sciences.

Results to date include (1) the effects of acoustic wave amplitudes on increased wave attenuation and dispersion, (2) the effects of clay mineralogy, surface area density, and bound water on microwave heating of rocks, and (3) attempts to study cavitation in porous media.

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2. THRUST PROGRAM ON POLYMERS

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Agency Support:

NSF ENG 7822167
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AF AFOSR-77-3386
NSF-MRL through CMR

Technical Objectives:

To study the piezoelectric and pyroelectric properties of poly(vinylidene fluoride) (PVF₂) from the point-of-view of establishing the relationship between these properties and the molecular, crystalline, and microstructural properties of this polymer; and applying insights gained by such studies to the development of techniques for polymer synthesis, thermomechanical treatment, and electro polarization which will optimize the piezoelectric and pyroelectric properties of this unique material for various device applications. Yet another long-range objective of this research is to gain sufficient understanding of the fundamental relationships between polymer chemical composition, microstructure, and electrical behavior to permit the design, selection, and ultimate development of novel synthetic polymers or polymer

combinations displaying superior electrical behavior.

Approach:

Samples of PVF_2 of well-characterized molecular structure (average molecular weight, molecular weight distribution, intramolecular atomic arrangement as determined by IR and NMR spectrometry) are thermoformed into uniform, thin films under carefully-controlled conditions; the film samples are then electrically polarized by holding at high voltage-gradients while the sample is subjected to a controlled heating/cooling schedule, and the appropriate piezoelectric coefficients of the resulting polarized film samples measured. The determination of piezoelectric coefficient and charge-leakage as functions of time and temperature are also studied. Infrared spectrophotometry and X-ray diffraction analysis of polymer samples both before and after poling are used to characterize the crystalline morphology of the polymer, and the morphological changes which take place upon thermal or electrical processing, or mechanical deformation.

Research Report:

(1) Background

Polyvinylidene fluoride (PVF_2) has captured the attention of polymer physicists and chemists, materials scientists, chemical and electrical engineers around the world because of its unique material properties. The major reason for the widespread current interest in the scientific community is that PVF_2 is strongly piezoelectric with properties similar to crystalline quartz. Furthermore, it is also pyroelectric and has a large nonlinear optical coefficient, as well as a high dielectric breakdown strength. These interesting bulk electrical properties are coupled with favorable bulk mechanical characteristics. First, since it is a good injection molding medium and is essentially inert chemically, it may be easily processed into flexible thin films. In addition, the material has very low acoustic wave velocity and impedance. This combination of electrical and mechanical properties raises exciting technological possibilities for the development of transducer arrays using low cost, highly accurate, planar integrated circuit techniques from the

solid state electronics industry. This set of features is not available using current ceramic and crystalline piezoelectric materials.

Recently, some understanding of the role of crystalline structure of PVF_2 in influencing piezoelectric properties has been developed: Polyvinylidene fluoride is a semicrystalline polymer the crystalline phase of which can exist in at least three lattice-structures or polymorphs called the α , β , and γ phases. The polymer microstructure consists of individual α , β , or γ crystallites which are imbedded in an amorphous phase of the same chemical composition. The individual vinylidene difluoride units have a very strong transverse dipole moment which aligns differently within the three types of polymorphs. All three phases behave like classical ferroelectrics, although to varying degrees: the dipole orientations can be aligned by a poling procedure. If, prior to poling, the polymer chains are caused to lie in parallel orientation within a thin film (a consequence of uniaxial stretching of the film below its crystalline melting temperature), the resulting film displays high piezoelectric and pyroelectric activity. Of the three polymorphs, the orthorhombic (β) form displays the highest piezoelectric activity. On cooling from the melt, the (α) form is the stable phase obtained. The (γ) form is obtained only after a drawing or stretching procedure which causes molecular alignment and recrystallization. The electrical properties of PVF_2 films are believed to be dependent upon the cooperative interaction between individual crystallites.

Despite this understanding, the underlying physicochemical relationships between the molecular structure of the polymer and its macroscopic electrical behavior remain in question. Thus, the primary objective of the Polymer Thrust Program is to attempt to unravel these complex and controversial internal processes and their dependencies on thermal and mechanical processing history. To this end, materials efforts have been developed in the Department of Chemical Engineering under C. W. Frank and A. S. Michaels, and the Center for Materials Research under R. S. Feigelson. These programs encompass the complete spectrum of materials development, including synthesis of the basic homopolymer and selected copolymers, characterization of the configurational properties of the chain backbone arising from the chemical

synthesis, characterization of the morphological, thermal, mechanical, and electrical properties of bulk polymer as a function of the processing history, and mechanistic studies directed toward understanding the relationship between the polymer microstructure and the bulk electrical and mechanical properties.

A unique feature of the Polymer Thrust Program is its close interaction with device programs in Stanford's Departments of Applied Physics and Electrical Engineering. These latter groups are involved in research on ultrasonic imaging systems for nondestructive testing of materials and structures, and nonintrusive medical diagnosis, as well as reading aids for the blind. These device efforts are independently funded, and receive no direct support from the Thrust Program. A mutually supportive relationship exists between the materials and device groups: The materials effort aims to quantify the electrical properties of the polymers and their relationship to polymer composition and processing history, while the device-development team evaluates samples of such well-characterized materials for specific electronic applications. Hence the Thrust program on materials, taken in conjunction with the related work on device development, constitutes a fruitful interdisciplinary collaboration. The importance of this cooperation in the solution of the overall research problem should be apparent.

(2) Polymer Synthesis and Molecular Characterization

In almost all other PVF₂ research programs around the world, the polymers studied may be traced back to one or two commercial sources in which synthesis was performed by free-radical suspension polymerization at high temperatures and pressures. These synthesis processes yield polymers of highly variable molecular architecture, and which are difficult to characterize. By including polymer synthesis as a major element of the Thrust program, it should be possible to obtain complete control over the chemical variables which affect polymer microstructure. Such variables include the molecular weight and its distribution, the number of statistical defects such as "head-to-head" structures or branches, and (in the case of copolymers) the amount and sequence distribution of dissimilar monomer units in the chain backbone. Through

such control of the polymer chemistry, it may be possible to tailor the chain structure to achieve specific bulk mechanical and electrical properties. In addition, a reliable, local source-of-supply of polymer is essential for state-of-the-art applications work, in which the device performance may hinge on subtle variations in materials properties.

After the polymer has been synthesized, it must be characterized by instrumental methods outlined above. The first methodology involves the study of the polymer chain-length and chain-configuration, all measurements being performed in solution. Three techniques have at this point been developed: These are: (1) intrinsic viscosity measurement to estimate the viscosity-average molecular weight; (2) ^{19}F nuclear magnetic resonance to obtain the percentage of head-to-head defects in the polymer backbone; and (3) gel permeation chromatography as a means for determining the molecular weight distribution.

The second methodology involves the utilization of experimental techniques which elucidate the polymer microstructure in solid, bulk samples. The principal microstructural features to be determined are (1) the degree of crystallinity, (2) the specific crystal lattice structure, and (3) the size, perfection, and spatial orientation of the crystalline domains. Extensive development work has been done to apply Bragg X-ray diffraction methods to determine quantitatively the degree of crystallinity of this semicrystalline polymer. A small amount of work has been done to assess qualitatively the degree of crystalline orientation in mechanically-deformed films, using Laue X-ray techniques. In addition, infrared spectroscopy has been used to determine the relative properties of α - and β - crystalline phases present in that polymer. Finally, differential scanning calorimetry has been used to study fusion and crystallization kinetics. These techniques are the primary methods currently available for determining the effect of thermal and mechanical processing history on the macroscopic morphology of bulk polymer.

Now being initiated are yet more fundamental studies designed to yield information on the detailed interaction between the microstructure and the bulk electrical and mechanical properties. The first study is directed toward relating chain configuration to charge storage and

release characteristics. Previous workers have indicated that a reduction in head-to-head defects, and an increase in the degree of crystallinity, will lead to different polarization behavior and electrical activity. To test this, an apparatus for the measurement of thermally stimulated depolarization (TSD) currents has been designed and assembled. In a typical experiment, the electroded polymer film is converted to an electret by poling for two hours at 130°C and 80 kV/cm. This is followed by cooling the sample below the glass transition temperature to -60°C, thereby freezing in the charge. At this point, the poling field is removed. The film is subsequently heated from -60°C to 130°C at a linear heating rate of 3°C/min, while the current generated by the randomization of charge is measured. Through correlation of the discharge current with known molecular relaxation mechanisms, we hope to assess the relative contributions of the amorphous and crystalline regions to the bulk piezoelectricity.

The second study, which is only in the preliminary stages, involves the examination of gas sorption and permeation in homopolymer and copolymer films. We are assembling a high-precision system for measuring the sorption dynamics and equilibria for various gases and condensable vapors in semicrystalline homo- and copolymers. Measurement of gas/vapor equilibrium sorption isotherms should permit estimates of the amorphous phase content of the polymer, as well as of the freedom of backbone segmental motion within the amorphous phase. Determination of the unsteady state sorption/desorption kinetics should permit determination of penetrant diffusivities, which reflect the microcrystalline texture and inter- and intramolecular relaxation processes within the polymer. These parameters, when combined with independent measurements of gas and vapor permeation through thin films and with results of the TSD studies, are expected to provide valuable new insight into the microstructural features of PVF₂ which are important in determining its electrical behavior.

The homopolymer synthesis, adapted from a method described in the literature, employs a low-pressure, free-radical polymerization in which the reaction is initiated by trisobutyl boron activated by oxygen. The initiator is prepared by a Grignard reaction between isobutyl bromide-

magnesium Grignard reagent, and distilled boron trifluoride etherate. The major accomplishment this year has been the development of this method as a reproducible homopolymerization procedure. The resulting polymer has several unique features! First, the Stanford PVF₂ has 4.1% head-to-head defects in contrast to 6.3%, as measured by ¹⁹F NMR, for commercially supplied polymer. Secondly, the melt temperature determined by differential scanning calorimetry of Stanford PVF₂ is 450°K, compared to 432°K for commercial polymer. Finally, while the charge-storage characteristics in the amorphous phase are similar for both the Stanford-synthesized and commercial polymers, the total amount of charge released consequent to crystalline relaxation at high temperature is much higher with the Stanford material. Although a cause-and-effect relationship for this difference has not yet been established, the discovery of these unique morphological and electrical properties in PVF₂ with modified chemical constitution is quite exciting.

3. Electrical Properties Measurement and Microstructural Characterization Studies

As mentioned above, one important objective of the program is to study the relationship between polymer microstructure and electrical properties such as piezoelectric and pyroelectric behavior. Microstructure (crystallinity, lattice-form, crystalline texture, domain size, etc.) is profoundly influenced by processing history, which includes such fabrication variables as cooling rate from the melt, annealing conditions, stress-strain history, and poling time/temperature and voltage. A major goal is to optimize certain important properties such as the piezoelectric modulus by controlling the appropriate processing steps in film fabrication.

A secondary objective of this program is the fabrication of high quality piezofilm for device research. In this activity, the CMR group fabricates and supplies piezofilm (both poled and unpoled) to the device group, which in turn provides metallization services, and performs electrical measurements on devices fabricated from the films supplied. By comparing device performance characteristics with piezofilm properties and microstructure, the effects of critical processing variables

can be evaluated.

During the first two years of this program, we developed the capability reproducibly to fabricate piezoactive polymer films, starting with bulk polymer resin obtained from commercial sources. The fabrication steps include melting, pressing, oriented recrystallization by uniaxial drawing, annealing, electroding (metallization), and poling in a dc field at elevated temperature. IR spectrophotometry and X-ray diffraction analysis have been used to identify crystallite morphologies, and to assess changes in crystallinity and crystallite perfection during each processing step.

Having established a reproducible processing capability, a broad survey of all commercially available polymer sources was undertaken to determine which materials gave optimum piezoelectric properties. In addition, a program was undertaken to systematically vary individual processing steps and to evaluate their effects on both the microstructure (as evidenced by IR spectrophotometry and X-ray diffraction analysis) and the piezoelectric behavior.

During the past year, we have developed a reliable method for the direct dc measurement of the piezoelectric activity in PVF_2 films, and have also developed a technique for poling and measuring the electrical properties of these films without the need for metallization. This has considerably simplified the procedure required to evaluate the effects of changes in processing parameters upon piezoelectric behavior. Also, we have completed a comparative evaluation of the piezoelectric properties of PVF_2 films fabricated (under equivalent conditions) from polymer samples procured from a variety of commercial sources; no significant differences in electrical behavior was found to exist between these materials.

Post-strain annealing of drawn films at elevated temperature was found to shift (θ) polymorph unit cell parameters, and to sharpen the X-ray diffraction pattern. These crystal-morphological changes were accompanied by a 10-15% reduction in piezoelectric activity, suggesting that crystalline- or chain-uniaxial orientation, which is probably partially sacrificed upon annealing, may be a more important parameter than crystalline perfection in determining electromechanical response.

In contrast, films prepared from homopolymeric PVF₂ synthesized by our in-house procedure display 10-15% higher piezoelectric activity than films fabricated from commercial polymer under similar conditions; the effects of annealing these high-activity films upon their piezoelectric coefficient remain to be determined.

Finally, thermal decomposition (as evidenced by discoloration and/or gas-evolution) of PVF₂ is observed to occur at temperatures approaching 200°C. The nature of the decomposition (which is presumed to involve dehydrofluorination, chain-scission, and/or crosslinking) appears to depend upon the environment in which the material is heated; in vacuo or in inert gas (N₂, He), the polymer blackens, while in air (and presumably, in oxygen) little discoloration occurs. A more detailed understanding of the decomposition process (in view of its possible impact upon film electrical properties during melt-manipulation) is now being sought by instrumental analysis (IR/UV spectrophotometry).

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4. Invited Paper, "PVF₂ Transducers," IEEE Ultrasonics Symposium (1980).

3. THRUST PROGRAM ON INTERSTITIAL ALLOY CATALYTIC MATERIALS

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Agency Support:

NSF-MRI through CMR
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Research Report:

There were several significant developments in the program during the past year. These included: (1) a new procedure for synthesizing a molybdenum carbide catalyst of high specific surface area and high catalytic activity, (2) the theoretical prediction of a dangling bond at the surface of WC and its observation on the basal plane of single crystal WC by UPS, and (3) the observation that the surface reactivity of molybdenum surface carbide parallels that of tungsten and that the reactions are extremely sensitive to the metal, oxygen, carbon ratios at the surface. These developments are discussed, briefly, in turn, below.

The new synthesis of the unsupported molybdenum carbide powder was accomplished by the simultaneous reduction of molybdenum trioxide in a flowing CH_4/H_2 mixture in a temperature programmed manner. This method affords close control of the carburizing potential of the reacting gas and the rate of carburization. Previously, samples were prepared at a fixed temperature. The chemisorption properties of this new molybdenum carbide material are remarkable and are listed in Table I.

The temperature programmed reduction results in an increase in the capacity of CO chemisorption of nearly an order of magnitude over the other catalyst. This result is due partly to an increase in total surface area and partly to an increase in site density, presumably due to the increased control over carburization afforded by temperature programming the reduction. The large uptake of CO indicates that the surface is not contaminated with amorphous carbon or graphite which are known from previous work in this program to decrease catalyst performance.

TABLE I

H ₂ Chemisorption			
Catalyst	H ₂ uptake $\mu\text{mol g}^{-1}$	BET surface area $\text{m}^2 \text{g}^{-1}$	
Mo ₂ C (fixed temp red)	37.7	13.9	
Mo ₂ C (temp prog red)	59.7	48.4	
CO Chemisorption			
Catalyst	CO uptake $\mu\text{mol g}^{-1}$	BET surface area $\text{m}^2 \text{g}^{-1}$	Site density cm^{-2}
Mo ₂ C (fixed temp red)	37.0	12.5	1.8×10^{14}
Mo ₂ C (temp prog red)	287.6	39.1	4.4×10^{14}

Work has been carried out to determine the reactivity of molybdenum carbide and molybdenum oxycarbide in: (1) the Fischer-Tropsch synthesis, and (2) the hydrogenolysis of n-butane. The results of these studies show that the carbide is comparable in reactivity to both palladium and ruthenium.

Major theoretical advances have been made in the past year which point toward the calculation of the electronic state of the surface for the carbides. Much of our effort has been directed at obtaining simple theoretical methods which are transparent enough to give physical insight, but accurate enough to be meaningful and thus contact all other phases of this program. Such calculations for semiconductor and insulator surfaces have been possible for some time using minimal-basis-set, nearest-neighbor LCAO theory. During this year the theory giving the interatomic matrix elements involving d-states was developed, and the d-state energies were obtained self-consistently. The parameters needed for the immediate analysis of systems, such as tungsten carbide in which some of the important states are of d-character.

On a qualitative basis it can be argued that tungsten carbide should have a dangling orbital at the surface. We were fortunate to obtain on loan a large WC single crystal grown by accident. Making significant use of CMR's central facilities, the bulk properties of this crystal were characterized; then, LEED and AES measurements were used to prepare a surface free of sulfur or graphite contamination. It was found that graphitic carbon, detrimental to catalytic activity of powdered samples, could be burned off with molecular oxygen. This result has possible practical importance for removing graphitic carbon from the powdered catalysts. Angular resolved photoemission revealed a state sharply peaked along the surface normal. It appears possible to follow this surface state from pure W, to the W(100)(5x1)C surface carbide and finally to the surface of the WC single crystal. Preliminary work suggests that CO adsorption involves this orbital. In addition to these results, the electronic properties of the surface of bulk WC crystal and W(100)(5x1)C show very similar features. However, additional work is necessary for the W(100)(5x1)C surface. This result strengthens our hypothesis that surface carbide structures can be used to model the surface chemical behavior of the bulk carbide.

The surface reactivity of several molybdenum surface carbides was studied. The major result was that the chemical properties of a surface carbide with a Mo:C ratio in the surface of 1:1 were very similar to the W(100)(5×1)C surface studied extensively in the preceding year. It was conclusively shown that the formation of the surface carbide reduced the chemical reactivity of the surface so that atomization of hydrocarbons to adsorbed carbon, oxygen and hydrogen did not occur as on clean Mo. Instead, subtle bond rearrangements occurred which, for example, produced CH₃O (methoxy), CH₃CH₂O (ethoxy) and methoxy-hydride complexes from methanol and ethanol, respectively. An easily reduced adsorbed form of oxygen was also observed. Basically, the molybdenum surface carbide showed the capacity for breaking and reforming carbon-hydrogen and carbon-oxygen bonds.

In addition to these results the general features of the surface reactivity were found to be very sensitive to the surface C/O/Mo ratio. The fully oxidized surface was very inert. Strong ligand effects on the adsorption of CO were noted with changing composition. These effects may be useful for observing the composition of the surfaces of the powdered catalysts by monitoring CO desorption peaks.

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4. THRUST PROGRAM ON METASTABLE MATERIALS

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NSF-DMR 79-08554
NSF-CHE-7809317

Technical Objectives:

To synthesize new amorphous and other metastable phases and composite structures; to investigate their atomic arrangements; to relate preparative parameters and structural properties to electronic and electrochemical properties; and to develop a theoretical understanding.

Approach:

Identify and study metastable materials of common interest to the Thrust members. Employ vapor phase synthesis to prepare samples using newly-developed magnetron-sputtering and electron-beam-evaporation techniques. Make structural determinations using x-ray diffraction and

techniques using the synchrotron light source such as EXAFS, anomalous scattering and small angle scattering. Correlate structural characteristics with electric and electrochemical behavior. Make molecular dynamic computer simulations of condensed phases to gain further understanding of the relationship between kinetics and growth.

Significant Accomplishments:

During the past year there were significant accomplishments connected with (1) development of anomalous scattering to obtain a unique type of RDF; (2) an understanding of the relationship between the sputtering procedures employed and the occurrence of phase separation in the Cu-Zr system; confirmation of phase-separation by small angle scattering and TEM work; and a strong correlation of electrochemical behavior with the existence of phase-separation; (3) the development of new ways of performing molecular dynamics computer simulation; (4) a quantitative understanding of the crossover from 3D to 2D dimensional behavior in the magnetic field behavior of finely layered superconducting Nb-Ge composites below T_c ; (5) an experimental determination of the phonon density of states in amorphous Nb and Mo by tunnel junction spectroscopy and the evidence that both topological and force constant disorder are needed to describe the vibrational properties of amorphous transitional methods. Further details of the above are given in the following sections.

THRUST PROGRAM ON METASTABLE MATERIALS

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Agency Support:

NSF-MRL through CMR

NSF CHE-7809317 (an associated program)

Research Report:

To understand the formation and stability of metallic glasses from a theoretical point of view, two new ways have been developed of performing molecular dynamics computer simulation of condensed phases that will be useful in the theoretical study of amorphous metallic materials. The first new method allows one to simulate the behavior of an atomic liquid at constant external pressure. Previous methods could only deal with constant density. The second new method allows one to simulate the behavior of a liquid at constant external temperature. These two techniques put together allow one to simulate the cooling of a liquid at constant pressure. One can also calculate the temperature, energy, and structure of the material as a function of time, observe the glass transition or nucleation to a crystal, and calculate the properties of the low temperature glass or crystal that is formed. The dependence of the results on cooling rates can also be determined. So far, extensive calculations have been performed only on the one-component model atomic fluid using several hundred atoms. Preliminary calculations for model two component fluids which resemble the metallic glasses in a more realistic way have been started. Simulation of the cooling of a one-component Lennard-Jones fluid into the glass state did yield a glass transition. However, the glass transition occurs over a range of temperatures, not sharply at one temperature. The transition temperature depends on the external pressure but is independent of cooling rate. No relaxation processes or hysteresis effects were observed for cooling rates thus far achieved.

Publication receiving substantial support from CMR/NSF-MRL;

H. C. Andersen, "Molecular Dynamics at Constant Pressure and/or Temperature," J. Chem. Phys. 72, 2384 (1980).

SUPERCONDUCTIVITY:

M. R. Beasley, Professor, Applied Physics and Electrical
Engineering

Professional Associates:

T. Claeson
R. H. Hammond
T. W. Barbee, Jr.

Graduate Students:

S. J. Bending
J. M. Graybeal
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D. A. Rudman
S. T. Ruggiero
R. B. van Dover

Agency Support:

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JSEP N00014-75-C-0632
ONR N00014-77-C-0439
NSF DMR79-11117
NSF-MRL through CMR - Thrust Program on Noncrystalline Metals

Technical Objective:

To extend and deepen the understanding of the electromagnetic behavior of superconductors of superconducting structures and devices.

Approach:

The response of superconductors to currents, magnetic fields, and electromagnetic radiation under a wide variety of conditions are studied and related to the basic properties, structure, material parameters, and geometry of the superconductors. Tunneling studies of high- T_c superconducting materials to determine microscopic electronic properties of superconductors and to explore device possibilities.

(1) Superconducting Tunneling and Tunneling Applications in High- T_c Al5 Superconductors

Graduate Student: D. Rudman

Tunneling junctions exhibiting both quasiparticle and Josephson tunneling are being made on the high- T_c Al5 superconductors deposited by means of electron beam coevaporation. The junctions have been found to be superior to any obtained previously and are making possible detailed study of the basic electronic properties (e.g. energy gaps Δ and electron phonon spectral function $\alpha^2F(\omega)$) of these superconductors. Josephson device potential is also being investigated. During the past year we have been attempting to understand better the nature of the tunneling barriers in our successful junctions.

In particular we have been investigating the use of oxidized amorphous silicon as a tunneling barrier. The results have been extremely gratifying. Following up on our earlier work, we find that these barriers work on all the Al5 superconductors (Nb_3Sn , V_3Si , Nb_3Al , Nb_3Si) with which we have tried them. They also were successful on amorphous Mo-Ge films. In view of this success we have undertaken a systematic study of the properties of these tunneling barriers as a function of base electrode and a-Si layer thickness. We find that for $d_{Si} > 30 \text{ \AA}$ the barriers universally lead to excellent tunnel junctions and have barrier and conductances which are independent of the electrode. A model of these barriers has been developed which is in accord with our results and which provides some predictive powers for under what circumstances these barriers should be effective. Further applications and device implications are under study.

(2) High- T_c Superconducting SNS Microbridges

Graduate Student: R. B. van Dover and A. de Lozanne

The objective of this project is to make SNS planar microbridges incorporating high- T_c superconductors. Our previous work has shown that the high- T_c materials are extremely sensitive to damage during processing. To alleviate these problems we have developed a plasma etching process

that can successfully form small ($\sim 0.3 \mu\text{m}$) SNS bridges with no apparent damage (e.g. reduction of T_c).

These techniques have now been successfully applied to Nb/Au/Nb SNS bridges. The electrical characteristics (e.g. T_c , $I_c R$ product and resistance) are all superior to any previous weak-link Josephson devices. Moreover they operate over the entire temperature range $0 < T < T_c$. The electrical behavior of these devices (critical currents and I-V curves) are found to be in accord with existing theories providing that a more realistic model of the S/N and bridge/bank interfaces were introduced.

(3) Superconducting Layered Structures and 2-D Superconductivity

Graduate Students: S. Ruggiero and J. Graybeal

We have been studying the electric and magnetic behavior of finely ($8 \text{ \AA}$ to $100 \text{ \AA}$) layered periodic SNS composites formed by vapor deposition. These are of interest because of the information they provide about SN interfaces and because of the novel superconducting properties expected in Josephson coupled 2-D systems. During the past year we have unequivocally observed the 3-D to 2-D dimensional crossover predicted for layered superconductors as the temperature is reduced below T_c . This novel crossover is different from those commonly seen in lower dimensional systems in the fluctuation regime above the phase transition temperature. The crossover observed in superconductors manifests itself in a dramatic increase in the critical magnetic field and critical current of the superconductor (in parallel magnetic fields) when the coherence length becomes comparable to the layer separation as the temperature is decreased. Excellent quantitative agreement with theory is obtained. We have also extended our measurements to include the fluctuation conductivity above T_c where dimensional crossover behavior is also seen. These data are also in accord with available theory using material parameters consistent with those deduced from the critical data below T_c . Finally we observe an anomalous temperature dependence in the perpendicular critical fields. Such behavior has been reported previously in the layered compound superconductors. Its presence in

these more ideal artificial systems strengthens the evidence that this anomaly is intrinsic to quasi-two-dimensional superconductors and not due to sample imperfections.

(4) Critical Fields of Al5 Superconductors

Graduate Student: T. P. Orlando and S. Bending

As we have previously reported the upper critical field behavior of Nb_3Sn and V_3Si are being studied as a function of disorder (as measured by residual resistivity) and the results analyzed within the framework of the GLAG theory including the effects of the electron-phonon interaction. A surprising conclusion of this study is that the apparent absence of Pauli paramagnetic limiting in clean Nb_3Sn and by contrast its presence in clean V_3Si results significantly from the stronger electron-phonon interaction in Nb_3Sn . In the past this has been attributed to a large spin-orbit scattering rate. The present materials are too clean for this to be possible. We have developed a simple physical argument showing that the electron-phonon interaction increases the Pauli limit above the BCS value, thus decreasing the required spin-orbit scattering. These corrections have heretofore been neglected in analyzing the behavior of high field superconductors. This is a major oversight since the corrections arise primarily from the electron-phonon renormalizations of the normal state parameters, and only secondarily from the strong coupling corrections to the superconductivity, thus making them non-negligible even in relatively weak coupled superconductors. This fact also appears not to have been appreciated previously.

More recently we have extended these measurements to include the behavior as a function of deviations from stoichiometry and for both A-site and B-site substitutions. We are also examining the theory from the microscopic point of view including electron-electron interactions which also appear to be playing a role.

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2. "Oxidized Amorphous-Silicon Superconducting Tunnel Junction Barriers," by D. A. Rudman and M. R. Beasley, to appear in Appl. Phys. Lett.
3. "Advanced Superconducting Materials for Electronic Applications," by M. R. Beasley, to appear in IEEE Transactions on Electron Devices on Superconductive Junctions.
4. "Refractory Superconductor S-N-S Microbridges," by R. V. van Dover, A. de Lozanne, R. E. Howard, W. L. McLean and M. R. Beasley, submitted for publication.
5. "Layered Superconductors," by M. R. Beasley, to appear in the Proceedings of the Inhomogeneous Superconductors Conference, Berkeley Springs, Virginia, 1-3 November 1979.
6. "Superconductivity in Quasi-Two-Dimensional Layered Composites," by S. T. Ruggiero, T. W. Barbee, Jr., and M. R. Beasley, submitted for publication.

THRUST PROGRAM ON METASTABLE MATERIALS

A. I. Bienenstock, Professor, Materials Science & Engineering and
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Professional Associates:

F. Betts
P. Eisenberger
W. Warburton

Graduate Students:

P. H. Fuoss*
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D. G. Stearns

*Received Ph.D. during report period.

Agency Support:

NSF-MRL through CMR (Thrust Program on Metastable Materials)
NSF-DMR 73-07692 (Stanford Synchrotron Radiation Laboratory),
an associated program.
NSF-DMR 79-08554, an associated program.

Technical Objectives:

The primary purpose of this work is to investigate atomic arrangements in amorphous materials and to relate them to preparative procedures as well as electronic and electrochemical properties associated with the work of others in the Thrust program. At the same time, we are developing new techniques for such structural studies, utilizing synchrotron radiation.

Approach:

The basic methods used during the past year were x-ray small angle scattering, x-ray diffraction, and extended x-ray absorption fine structure analyses.

Anomalous Scattering Studies of Amorphous Materials

Professional Associates: P. Eisenberger
W. Warburton

Graduate Students: P. Fuoss

During the past year, we have had a major success with the first demonstration¹ that a variation of the Shevchik [Phil Mag. 35, 1289 (1977)]

procedure can be used to effectively obtain a unique type of radial distribution function. In this procedure, one determines experimentally the derivative with respect to photon energy of the x-ray diffracted intensity from a polyatomic amorphous material, holding constant the scattering vector magnitude, $4\pi\sin\theta/\lambda$. The derivative is evaluated at photon energies just below the absorption edge of a specific element (denoted A) in the material, so that it arises from the change with photon energy of the atomic scattering factor of element A due to anomalous scattering. Fourier transform of the derivative yields a radial distribution function in which all the atomic pairs included contain at least one A atom. That is, it yields the average coordination of species A in the material.

We have used the tunability of synchrotron radiation to test and utilize this technique during the past year. Methods were developed for more accurate determination of the anomalous scattering factors, f' and f'' , than we have been able to achieve previously.² These were used with measurements of the scattering from amorphous GeSe_2 and GeSe near the Ge and Se edges. The GeSe_2 measurements indicate that reasonably reliable coordination numbers can be obtained with this approach. The GeSe measurements appear to resolve a long-standing question as to whether the Ge is threefold or fourfold coordinated in this material, indicating the former.

The method, in principle, supplies the same information as EXAFS. In practice, however, there are distinct differences. In this approach, the intensity can be measured at low k ($4\pi\sin\theta/\lambda$) values. As a result, one can obtain accurate coordination numbers and reliable information about second and more distant neighbors. On the other hand, one cannot examine the coordination of relatively dilute species, as one can with EXAFS. Consequently, we anticipate that the new method will become extremely important for the determination of atomic arrangements in polyatomic amorphous materials, joining EXAFS as one of the two major methods for determining the coordinations of individual atomic species.

During the coming year, we are hoping to increase still further the accuracy with which we measure f' and f'' at SSRL. In addition,

we expect to increase the accuracy with which the intensities are measured so that we may hope to obtain more reliable results from the three wavelength approach² in which the A-A, A-B and B-B pair correlation functions are determined separately.

Structural Studies of the Amorphous Ni-As System³

Professional Associate: F. Betts

Graduate Students: S. Laderman
D. Stearns

Interest in this system comes from the large increases in electrical conductivity of amorphous As which arise when Ni is cosputtered with it. The goal is to understand how the amorphous, covalent As accommodates the Ni atoms.

During the past year, the EXAFS data acquired at the end of the preceding year were analyzed. These indicate that the Ni is six-fold coordinated. It is not possible to tell uniquely whether the coordinating species are As, Ni, or a mixture of the two. Nevertheless, the EXAFS patterns and their Fourier transforms are quite similar to those obtained from crystalline NiAs_2 and considerably less similar to those from other related materials. Hence, our suspicion from the EXAFS results was that the Ni is coordinated in the amorphous materials as it is in crystalline NiAs_2 . An x-ray radial distribution analysis performed on a high Ni concentration sample was consistent with this view.

An implication of this coordination is that it is highly likely that the material is phase-separated into a NiAs_2 -like phase and an As-rich phase. Consequently, we have performed x-ray small angle scattering measurements which do show the presence of the scattering and an increase with increasing Ni concentration, consistent with the phase-separated picture.

Finally, at low Ni concentrations, it is possible to see two optical absorption edges corresponding, presumably, to two different bandgaps for the two phases. We are presently attempting to obtain a detailed interpretation of these results.

Small-Angle Scattering Studies of Binary Systems

Graduate Students: S. Laderman
D. G. Stearns

In addition to the Ni-As studies discussed above, we have undertaken small-angle scattering studies of other materials which were, during this past year, of primary interest to other members of the Thrust Program. In each case, properties discussed at meetings of the Program participants led us to suspect the existence of phase separation in some samples. SAS measurements were performed to see if that was the case. These include samples in the Mo-Ge, Cu-Zr, and Ag-Ge (on which EXAFS measurements were also made for one sample) systems.

Among the most interesting results was the observation that Mo-rich Mo-Ge alloys sputtered directly onto Kapton do show strong small-angle scattering which is due, presumably, to phase separation. This may be the beginning of an explanation of why these alloys are not superconducting when sputtered onto Kapton, but are when sputtered onto sapphire or silicon. Samples of the latter are presently being prepared for SAS analysis.

These studies of phase separation on the metal-semiconductor systems, which were started because of the work of others in the Program, have become a major focus of our structural studies.

Publication: (Received substantial support from CMR/NSF-MRL).

1. P. H. Fuoss, W. K. Warburton, and A. Bienenstock, "Anomalous Scattering Determinations of the Pair Distribution Functions in Amorphous GeSe," J. Non-Cryst. Solids 35&36, 1233 (1980).

SYNTHESIS AND LOW TEMPERATURE PROPERTIES OF NEW MATERIALS

T. H. Geballe, Professor, Applied Physics and Materials Science and
Engineering

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S. J. Poon	
T. Claeson	

Graduate Students:

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R. D. Feldman	W. P. Lowe
K. E. Kihlstrom	F. Hellman
	J. J. Talvacchio

Undergraduate:

J. Marshall

Agency Support:

DOE DE-AT03-76ER71043 (with M. R. Beasley)
AF F49620-78-C-0009
NSF-MRL through CMR - Thrust Program on Noncrystalline Metals

Technical Objective:

To prepare new or unusual superconducting and magnetic compounds and composite structures and to study their mechanisms and interactions responsible for their behavior.

Approach:

Techniques such as electron-beam evaporation, sputtering, arc melting, and vapor transport are used to prepare crystals, compounds or materials of interest. Their electronic properties are then correlated with their structural properties by investigating superconducting transitions, heat capacities, optical and transport properties including tunneling.

(1) New and Unusual Composites and Amorphous Phases by Vapor Deposition

Professional Associates: T. W. Barbee, Jr., and S. J. Poon

Graduate Students: S. R. Early, W. L. Carter, W. Lowe and
D. B. Kimhi

The superconducting properties of amorphous Mo-Ru, Mo-Ru-Si, and Mo-Ge alloys have been investigated. Tunneling into amorphous Mo and Nb has been carried out when the films are evaporated on Al oxide at 50°K. Microscopic parameters in the conventional alloy theory of superconductivity have been determined from specific heat (θ_0 , $N(0)$) and tunneling measurements (Δ , $\hbar^*$, $\langle\omega\rangle$). It is found that the trend of superconductivity in the 4d series can be correlated with the electronic density of states at the Fermi surface. The Eliashberg functions $\omega^2 F(\omega)$ in amorphous Mo and Nb are found to resemble the theoretical phonon spectrum of amorphous tight binding metals obtained from computer simulation when both topological and force constant disorder are included. The enhancement of electron-phonon coupling at low energy is insignificant as compared with amorphous simple metals. This is consistent with the weak-coupling behavior of amorphous transition metals. Appreciable enhancement of upper critical field above the prediction of the Landau-Ginzburg-Abrikosov-Gorkov theory is observed. The critical field gradient near T_c is found to be related to the magnetic susceptibility function in the theory of indirect exchange interaction demonstrating that the upper critical field measurement can give a more relevant range of magnetic interaction than the free-electron value.

A number of systems involving compositionally-modulated periodic structures prepared by the technique of depositing onto a rotating substrate using magnetron sputtering which has previously been developed at CMR (by Barbee and Keith) are being studied. The structural and superconducting properties of binary composites involving metals which are immiscible in the liquid state such as Nb-La as well as those which form complete solid solutions are being compared.

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2. "Amorphous Superconductors Based on the 4d Series," by S. J. Poon and W. L. Carter, to be published in Solid State Commun.
3. "Superconductivity of Amorphous Mo and Nb," by D. Kimhi and T. H. Geballe, Bull. Am. Phys. Soc. 25, 169 (1980); Phys. Rev. Lett. (in press).
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5. "Superconducting Properties of Amorphous Mo-Ru Thin Films," by S. R. Early, W. L. Carter, S. J. Poon, and T. H. Geballe, Bull. Am. Phys. Soc. 25, 432 (1980).
6. "Eliashberg Function in Amorphous Superconductors," by S. J. Poon submitted for publication.

(2) Synthesis and Properties of Superconducting Compounds

Professional Associates: R. H. Hammond and S. J. Poon

Graduate Students: K. E. Kihlstrom, S. R. Early, R. D. Feldman,
J. Kwo, F. Hellman and J. Talvacchio

Metastable compounds primarily with the Al5 phase are being synthesized by codeposition using beam-techniques. The three colinear electron-beam source facility has been improved so that the deposition parameters and the growth process can be controlled more carefully. Efforts are being made to extend the phase boundaries of the high superconducting transition temperatures (T_c 's) of the compounds Nb_3Al , Nb_3Ge , and Nb_3Si toward the metalloid-rich side. The heat capacity technique has been developed to the degree that it is now possible to deposit the film to be measured directly onto the silicon-on-sapphire thermometer which makes possible the routine measurement of

films as thin as one micron. Tunneling into the metastable Al5 compounds is being employed using the thin Si-barrier technique developed by Professor Beasley's group. The data show that the more nearly stoichiometric high-gap Nb_3Al which can be prepared by epitaxial methods onto especially prepared substrates can only maintain itself for a few hundred angstroms of film growth before relaxing. Analysis obtained by deconvoluting the Nb_3Al tunneling data shows pronounced low-frequency phonon structure not found in related neutron scattering experiments. Nb-rich Nb_3Si films with the Al5 structure have been epitaxially grown onto prepared substrates in which the Si concentration has been extended to 20% Si with T_c 's as high as 12 K. Efforts are being made to characterize and control chemical dopants such as carbon and residual gases present during the film growth, and to understand the role of O_2 or Cl_2 in stabilizing the high T_c phases.

Nb_3Sn has been codeposited with Al_2O_3 to form a very small microstructure with strong pinning. The measurements are being extended to Nb_3Ge to see if Al_2O_3 or some other inert 3rd source can stabilize the high- T_c composition with a microstructure suitable for strong pinning and high critical currents.

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THRUST PROGRAM ON METASTABLE MATERIALS

W. D. Nix, Professor, Materials Science & Engineering

Professional Associate: J. C. Gibeling

Graduate Student: D. T. Guidry

A Study of the Mechanical Properties of Metallic Glasses

During the past two years we have conducted a study of the creep properties of METGLAS 2826 (nominal composition: 40% Ni, 40% Fe, 14% P, 6% B). Tension creep experiments were conducted and the strain rate-stress relation was found to be highly nonlinear, but could be described by a power law relationship. The temperature dependence of creep flow has also been measured but sufficient information to identify a mechanism for creep was not obtained. The measured creep ductilities were found to be as high as 20% with very high local ductilities indicated on the fracture surfaces. Room temperature tensile fracture stresses were found to be highly dependent on sample preparation with properly prepared specimens having a fracture stress three times greater than unprepared samples.

Annealing studies of as-received materials show no signs of crystallization at creep testing temperatures. Room temperature microhardness versus time after annealing at temperatures above the crystallization temperature show a pattern of initial crystallization followed by possible phase separation. The hardness for samples annealed below the crystallization temperature remain unchanged, suggesting that recrystallization does not occur under these conditions. Similar studies on copper-zirconium alloys show the same pattern with a possible microhardness dependence on sample thickness.

THRUST PROGRAM ON METASTABLE MATERIALS

D. A. Stevenson, Professor, Materials Science & Engineering

Graduate Student: R. G. Walmsley

Electrochemical Characterization of Amorphous Films

During the past year, major activity has been devoted to three areas: refinement of sputtering techniques for the synthesis of Cu-Zr, Cu-Ti, and Cu-Hf films the design and construction of a small area electrode corrosion cell; and the evaluation of phase spread deposited amorphous films using a new corrosion cell. A synopsis of each of these activities is given below.

Influence of Sputtering Parameters on the Structure and Properties of Amorphous Films:

There were several objectives in this activity: to determine the composition limits within which amorphous alloys may be prepared; to establish the conditions under which a single amorphous phase or a phase separated structure is obtained in 50-50 Cu-Zr alloys; and to establish generally the relationship between film structure and deposition parameters. The deposition parameters of interest are: deposition rate; substrate temperature; substrate material; and the nature of the excitation source (i.e., DC or RF). One of the more interesting results was the influence of the substrate on the X-ray diffraction response of the 50-50 Cu-Zr composition. The deposition of a 50-50 composition produced a broad X-ray maximum for deposition on a silicon substrate whereas a double peak was observed when a glass substrate was used. It is believed that the thermal conductivity difference between the two substrates exerts the major influence. It was also noted that the diffraction peak is sharper away from the 50-50 composition and that there is no sharp amorphous-crystalline boundary as the extreme compositions are approached. Samples of Cu-Ti and Cu-Hf have been prepared and also show similar behavior.

Design of a Small Area Corrosion Cell:

The use of a phase spread technique in the vapor synthesis of films is a powerful tool for preparing a broad range of compositions in one experimental run. Such spreads may be used to establish the composition limits for the amorphous-crystalline boundary in a binary system. In order to exploit such samples for surveying the influence of composition on the electrochemical behavior, we have designed and constructed a corrosion cell with a provision for accepting small area thin film samples; inserts with an area in the range of 1 mm^2 to 1 cm^2 are possible. We have used a 4 mm^2 area insert which allows the evaluation of a region of a phase spread that has a variation of composition less than 2%. The cell described above was used to evaluate a Cu-Zr phase spread. It was remarkable to see the gradual and continuous change in the potentiodynamic scans upon traversing the composition range from ~20% Zr to ~75% Zr.

Potentiodynamic Scans of Phase Spreads Using the Small Area Cell

At 20% Zr there is a significant degree of passivity, a classic transpassive oxygen evolution region, followed by a transpassive pit formation region; a highly reproducible repassivation potential is observed.

Publications:

D. A. Stevenson and R. G. Walmsley, "Structural Modifications of Amorphous Cu-Zn Alloys Prepared by Sputtering Techniques; Electrochemical Properties," (in preparation).

5. THRUST PROGRAM ON METALWORKING AND PLASTICITY

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I. INTRODUCTION AND OBJECTIVES

Advances in techniques in metal forming can enhance the properties of structural materials and reduce energy costs in the manufacture of contemporary and new products. At Stanford, we have a unique opportunity to do interdisciplinary research in this field through faculty in mechanical engineering and in materials science and engineering. The CMR-NSF Thrust program has allowed us to perform this type of research.

As a specific objective, the Thrust program in the years through 1978-79 focussed largely on the problem of room-temperature extrusion. The goal was to create and demonstrate an ability to understand and predict metal flow during extrusion, and its effect on subsequent mechanical properties. Specific sub-tasks included hydrostatic extrusion experiments, development of a finite-element analysis to

predict extrusion response, and experimental determination of residual stresses in the product as a means of checking the analytical predictions. In the following sections, accomplishments in these areas and a few other related areas are described.

During 1978-79, a major new direction was adopted as a goal for this Thrust program, namely warm rolling of steels. While still within the general area of metal working, the warm rolling problem presents several new challenges. The first and major one is that the elevated temperature environment requires that several additional deformation phenomena be considered: strain rate sensitivity, recovery, approach to steady-state flow, grain boundary sliding, grain size refinement, and, in general, the temperature and history dependence of plastic flow. The second new challenge is that fracture is a limiting factor during warm rolling: total or per pass reductions which are excessive can result in "alligatoring," "crocodiling," or edge cracking. Thus a useful analysis of warm rolling requires a prediction of fracture. Hence development of a local fracture criterion in order to predict the "forming limit" during warm rolling has become an objective.

II. APPROACHES

A. Finite Element Analysis

Large deformation analysis is used in the IFDEPSA code developed, in part, under this Thrust program. A unique ingredient in this code is that it keeps track of the elastic strains; these, although small compared to the large plastic strains play an essential role in determining the stress distribution throughout the work piece, and in particular the residual stresses. A number of other specific approaches used in the code are described under "accomplishments."

B. Constitutive Equations

The "MATMOD" constitutive equation, developed at Stanford over the past six years or so, are well suited to the task of predicting non-elastic deformation during forming operations. Although originally

optimized for structural analysis applications (such as predicting the behavior of Zircaloy fuel cladding in nuclear reactors, under EPRI sponsorship), the equations predict many of the key phenomena of importance in metal forming, especially warm forming. These include:

1. Strain rate sensitivity
2. Temperature sensitivity
3. History dependence
4. Work hardening
5. Steady-state flow
6. Static and dynamic recovery
7. Directional hardening (Bauschinger effect)
8. Anisotropy

Because of these general capabilities, the decision was made in Spring of 1979 to start to utilize the MATMOD equations in the Thrust program on Plasticity and Metalworking.

C. Materials

In the warm forming investigation, our approach is to concentrate on two different steels in order to assess the effects of metallurgical structure on warm formability. The first is mild steel, an alloy of very widespread usage. The second is high-carbon steel, developed recently at Stanford for its unique combinations of superplastic warm formability, high room-temperature strength, and low alloy content.

D. Residual Stress Measurements

The use of acoustoelastic techniques to measure residual stresses has been a major breakthrough of this Thrust program. These techniques are orders of magnitude better than destructive or x-ray methods, and have been very useful in comparing the analytical and experimental results.

III. SIGNIFICANT ACCOMPLISHMENTS

A. Acoustic Determination of Residual Stresses in Hydrostatically

Extruded Aluminum

D.M. Barnett, Professor of Materials Science and Engineering

M.P. Scott, Graduate Research Assistant

Using acousto-elastic measurements we have been able to quantitatively determine the state of residual stress in hydrostatically extruded aluminum billets. In essence, the acousto-elastic effect refers to the fact that the velocity (V) of a plane acoustic wave propagating through a solid deformed by either applied or residual stresses is different from that (V_0) of the same wave passing through undeformed materials. The relative velocity shift for a longitudinal wave is, under plane stress conditions, proportional to the sum of the in-plane principal stresses at a point, i.e.,

$$\frac{V - V_0}{V_0} = B(\sigma_1 + \sigma_2) \quad (1)$$

where B is the stress-acoustic constant for longitudinal waves (B may be experimentally determined from acoustic experiments on samples in simple deformed configurations such as uniaxial tension. For axi-symmetric residual stress states, such as that produced during hydrostatic extrusion, σ_1 and σ_2 may be separately deduced from a single set of longitudinal acoustic wave measurements. The advantages of this method for determining residual stress variations are that:

- (a) The method is non-destructive in nature.
- (b) The technique is computer-controlled and is extremely rapid; a typical experiment requires about one hour to obtain data over an entire sample cross-section.
- (c) The method yields bulk residual stresses, whereas slower, destructive techniques such as those employing x-rays yield only surface residual stresses.
- (d) The method works well for aluminum, which normally is not well-suited for x-ray methods because of its low yield strength (as compared with, say, high strength steels).

The acoustic technique for residual stress determination yields reliable and reproducible results, and these experiments represent, to our knowledge, the first successful use of acoustics to quantitatively determine residual stresses.

The importance of these measurements to the present thrust program is that a primary link between the actual behavior during hydrostatic extrusion and its computer simulation by finite element techniques is the comparison of measured residual stresses with those predicted by computer simulation. The residual stresses measured acoustically compare extremely well with the same residual stress variations predicted using finite element simulation. In this sense we feel that this phase of our thrust effort has been enormously successful. Both the acoustic determination of residual stresses and the computer simulation of residual stresses induced during extrusion are contemporary difficult problems; the thrust mode of funding allowed us to conduct a successful interactive approach to these problems which would not have been possible under conventional individual grants.

B. Finite-Element Analysis of Metalworking Operations

E.H. Lee, Professor of Mechanical Engineering

R. Mallett, Senior Research Associate

V. Lubarda, Graduate Student

T. Wertheimer, Graduate Student

a. Comparison of predicted and measured residual stress distributions

Stress and deformation distributions have been evaluated for extrusion of a cylindrical billet through a reducing die. Elastic-plastic theory utilizing the finite element method has been employed so that stresses in the unloaded (elastic) region are included in the evaluation, in particular, steady state residual stresses in the extrudate. The technologically important case of steady-state extrusion was chosen for comparison of predicted and measured residual stress distributions.

In axi-symmetric extrusion a distribution of longitudinal, radial and circumferential residual stresses arises which is uniform along the length of the rod, but which varies radially as shown in Fig. B-1 for a 25% area reduction. In order to carry out the acousto-elastic

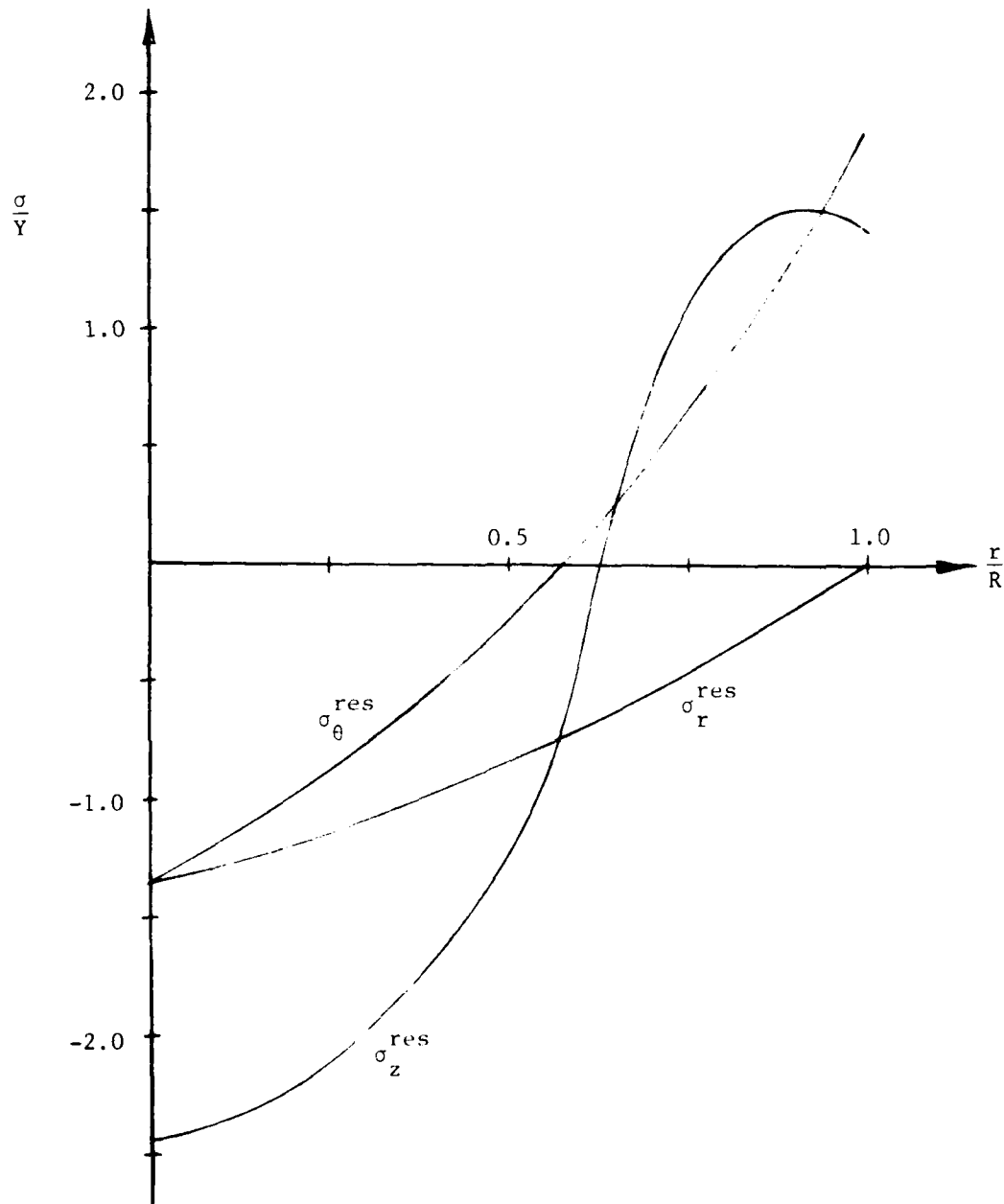
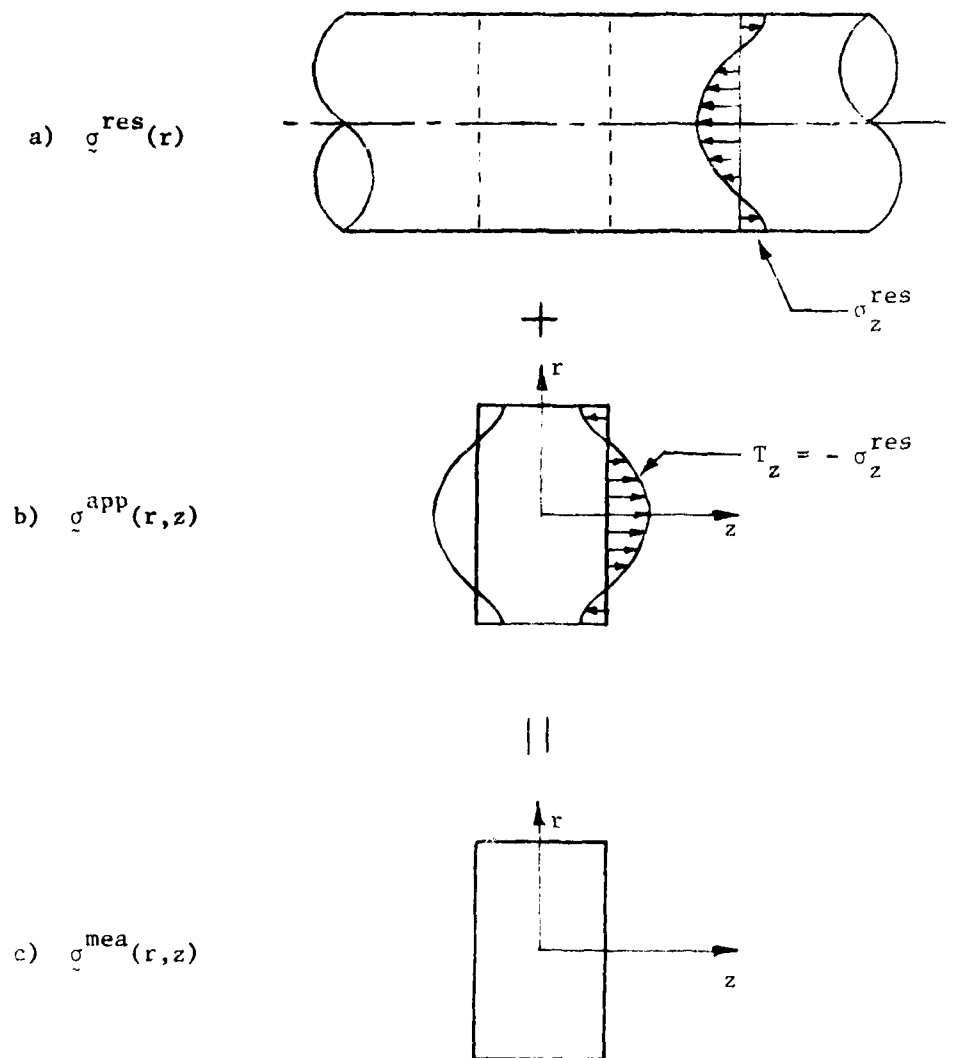


Figure B-1. Radial Distribution of Residual Stress.

measurements, a cylindrical specimen of finite length must be cut from the extruded rod by sectioning it on two planes normal to the axis as shown in Fig. B-2. Fig. B-2a shows the distribution of longitudinal residual stress, σ_z^{res} , before the specimen is cut. The change in the stress distribution in the specimen caused by the cutting will be given by the elastic solution corresponding to the application of tractions on the cut surfaces equal and opposite to the residual stress, σ_z^{res} . These stresses are termed "applied." The resultant of the residual and applied stresses gives zero surface tractions and the stress distribution locked in the specimen, Fig. B-2c, which is measured by the acousto-elastic method. Our prediction of this latter final stress distribution is denoted as σ^{mea} in Figures B-2-4 cause this predicted stress is the one which is expected to correspond to the stresses actually measured by acousto-elastic techniques on the finite-length specimen.

The applied stress distribution, corresponding to Fig. B-2b, will depend on the specimen thickness to radius ratio H/R , and this will determine a suitable H for accurate measurements. The acoustic waves travel axially and can be used to determine the stress components σ_r^{mea} and $\sigma_{\theta}^{\text{mea}}$ in the specimen so that one would like the longitudinal average of the corresponding "applied" stresses at each radius to be small to cause least modification of the residual stresses. The applied stresses were determined for four values of H/R ($H/R = 1/4, 1/2, 1, 2$) and their longitudinal variations along the centerline ($r=0$) are shown in Fig. B-3. The magnitude of H is also limited by the requirement of accurate acoustic wave measurement. Fig. B-3 shows that $H/R=1$ gives a relatively small longitudinal average σ_r^{app} (and similarly for $\sigma_{\theta}^{\text{app}}$) as well as a convenient height H for acoustic measurements and this H was selected for the experiment.

Fig. B-4 (main portion) shows that for $H/R=1$, the predicted residual stress distribution after cutting the specimen ($\sigma_{\theta}^{\text{mea}}$ and σ_r^{mea}) is fairly close to the original residual stress distribution in the uncut extrudate ($\sigma_{\theta}^{\text{res}}$ and σ_r^{res}). These predictions compare favorably with the actual acousto-elastic measurements shown in the insert to



$$\sigma_{ij}^{\text{meas}} = \sigma_{ij}^{\text{res}} + \sigma_{ij}^{\text{app}}$$

Figure B-2. Stress Redistribution in Specimen

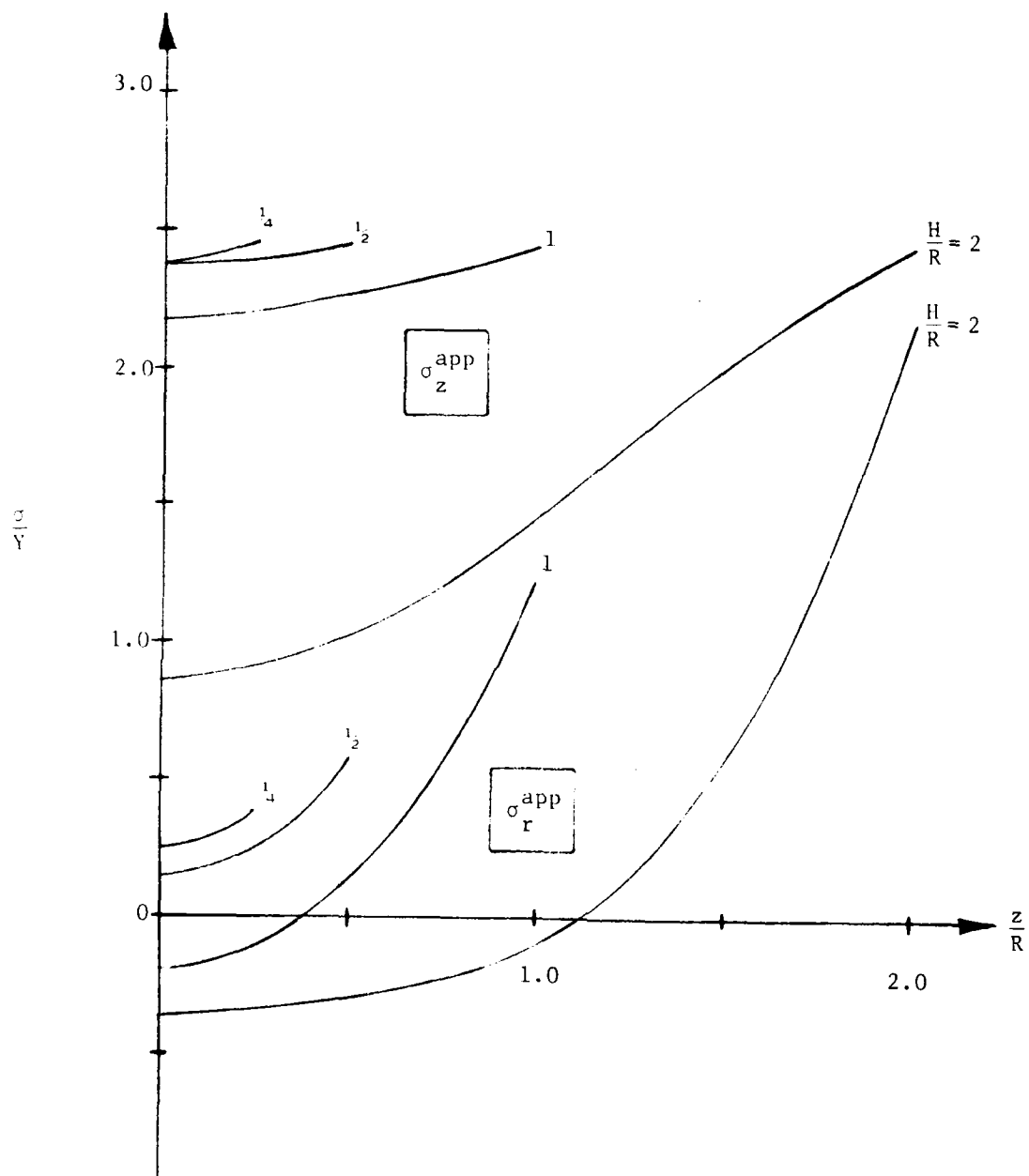


Figure B-3. Axial Variation of Applied Stress at $r = 0$ for Four Values of Specimen Thickness.

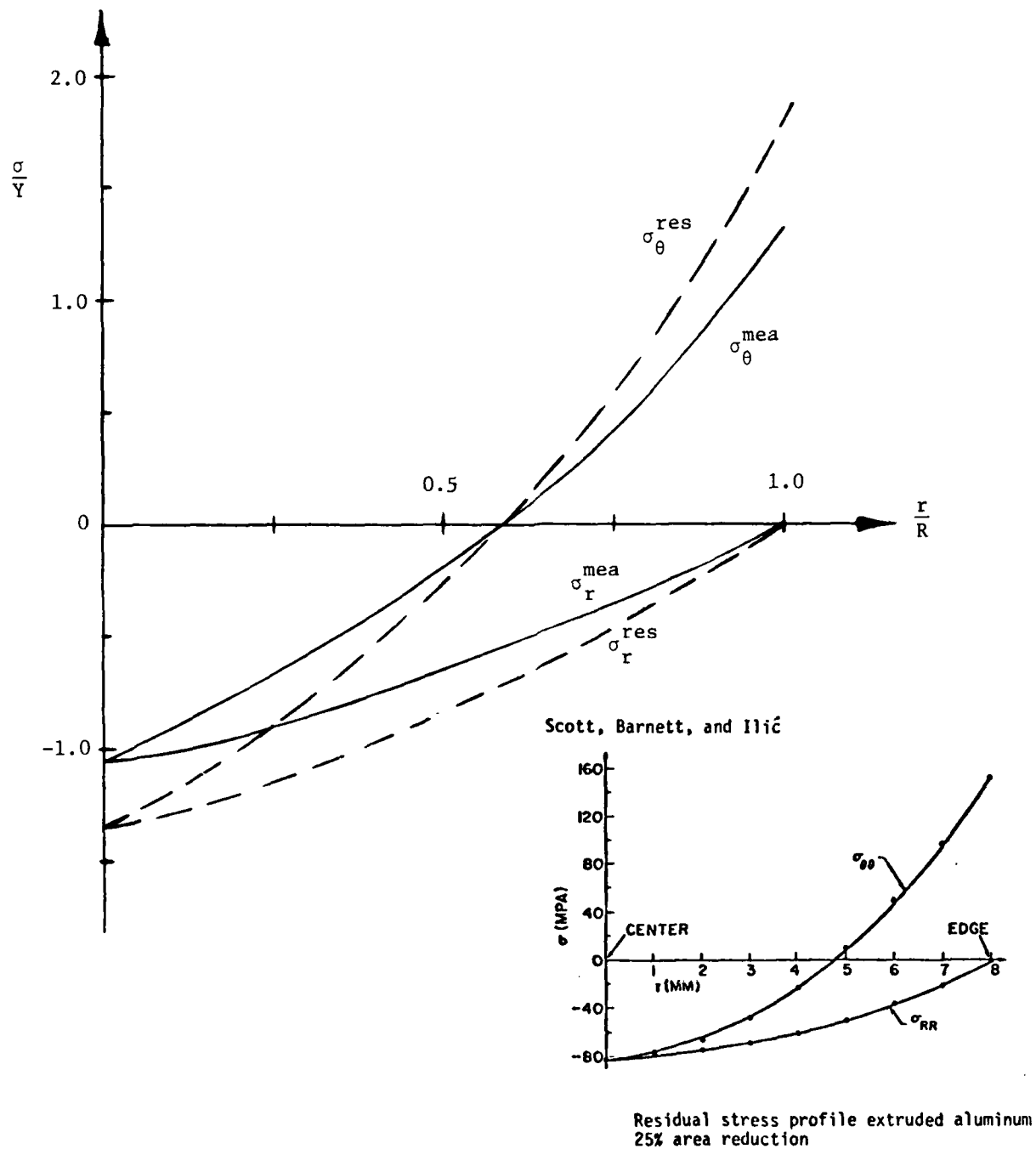


Figure B-4. Predicted Radial Variation of Stress.

Fig. B-4. These results indicate only qualitative agreement, since a softer aluminum was used in the experiments than assumed in the calculation. The latter is being repeated for the material actually tested.

b. Development of elastic-plastic finite-element program

The feasibility of carrying out the large deformation elastic-plastic analysis required for study of metal forming processes was demonstrated in our earlier work. The resulting finite-element digital computer code, IFDEPSA (Incremental Finite Deformation Elastic-Plastic Aalyzer), has undergone steady development in order to improve its efficiency and accuracy and to extend its capabilities for handling various boundary conditions which can arise in metal forming operations such as friction or loss of contact at curved metal-tool interfaces. During the past year improvements in IFDEPSA included: (1) the development of a procedure for exact tracking of the material strain hardening curve, (2) the conversion from an approximate to an exact rotation transformation in the stress updating procedure, (3) the incorporation of the initial load stiffness computation into the predictor-corrector loop, (4) the introduction of a partial stiffness technique to allow midstep yielding, (5) the adoption of new schemes for taking advantage of variable bandwidth and for imposing boundary conditions and, (6) the addition of several new element types.

Computations for plane strain chamber extrusion showed that a four noded constant dilation quadrilateral element gives more accurate stress fields than our initial element, the crossed triangle quadrilateral. However, the stress fields were found to be less than completely satisfactory for materials exhibiting saturation of strain hardening. The difficulty was traced to an inadequacy of the quadrilateral elements and thus led to an investigation of several higher order elements. The best results were obtained with an eight noded isoparametric quadrilateral with four point Gaussian integration. Considerable attention has been devoted to this problem because very accurate stress fields are required for metal forming defect analysis and because most of the materials used in our extrusion and rolling

experiments exhibit saturation hardening.

c. A Basic Error in Currently Used Elastic-Plastic Theory at Finite Strain

The plastic part of an elastic-plastic deformation is that remaining when the stress, and hence the elastic strain, is reduced to zero. Elastic deformation is that produced in this un-stressed, purely-plastically-deformed material by the action of stresses up to yield. The exact mathematical representation of the kinematics of elastic-plastic deformation at finite strain and rotation expresses the total deformation-gradient matrix as the plastic deformation-gradient matrix pre-multiplied by the elastic deformation-gradient matrix. The fact that this operation is not commutative immediately throws doubt on the almost universal assumption currently used in elastic-plastic theory that the total strain-rate is equal to the sum of elastic and plastic strain-rates, for this relation is commutative. The physical significance of this anomaly is documented in a paper to appear shortly in the International Journal for Solids and Structures. An exact analysis based on the non-linear kinematics was developed, which shows that the theory in current use is in error to the extent of not being objective, i.e. deductions from it may depend on the particular axes chosen by means of which to express the deformation. However, it is shown that an approximation to the exact theory does produce the commonly used expressions to a good degree of approximation in most cases of metal-forming. This development provides a more complete understanding of the computational process we are using for stress and deformation analysis.

C. Constitutive Equations for Analysis of Metalworking and Fracture During Forming

A.K. Miller, Assistant Professor, Materials Science and Engineering

T. Tanaka, Graduate Research Assistant

During the past year, the "MATMOD" approach was applied to mild steel (1020); specifically, an extensive literature search was conducted

to gather all pertinent data on its deformation properties, and from these data a set of material constants was calculated (not an insignificant task since so many facets of mechanical behavior are involved). Table I summarizes the behavior of 1020 steel which is now modelled. Figures C-1 and C-2 show some of the resulting fits to data: Fig. C-1 shows the way we can simulate the rather complicated interdependence among the flow stress, temperature, and strain, while Fig. C-2 for cyclic deformation illustrates the model's capability for dealing with reversals in the direction of deformation. The latter is important in predicting residual stresses. Thus we now have in hand the constitutive equations required for representing this alloy during analysis of warm forming.

Preliminary work was begun toward extending the MATMOD equations to cover superplastic high carbon steels. Specifically, suitable additions to cover grain boundary sliding and dynamic grain size refinement were outlined.

One of the major tasks requiring collaboration between ourselves and Applied Mechanics researchers is the implementation of advanced, unified constitutive equations into Finite-Element programs. Specifically, the MATMOD equations must be incorporated into the code which has been developed and improved in the Thrust program for analysis of extrusion. Previous experience has shown that numerical difficulties are legion in this area; accordingly detailed consideration was given to the numerical methods required for efficient computations. A new, unified approach was suggested which combines the tangent modulus and initial strain methods. This approach looks promising and is presently being explored further.

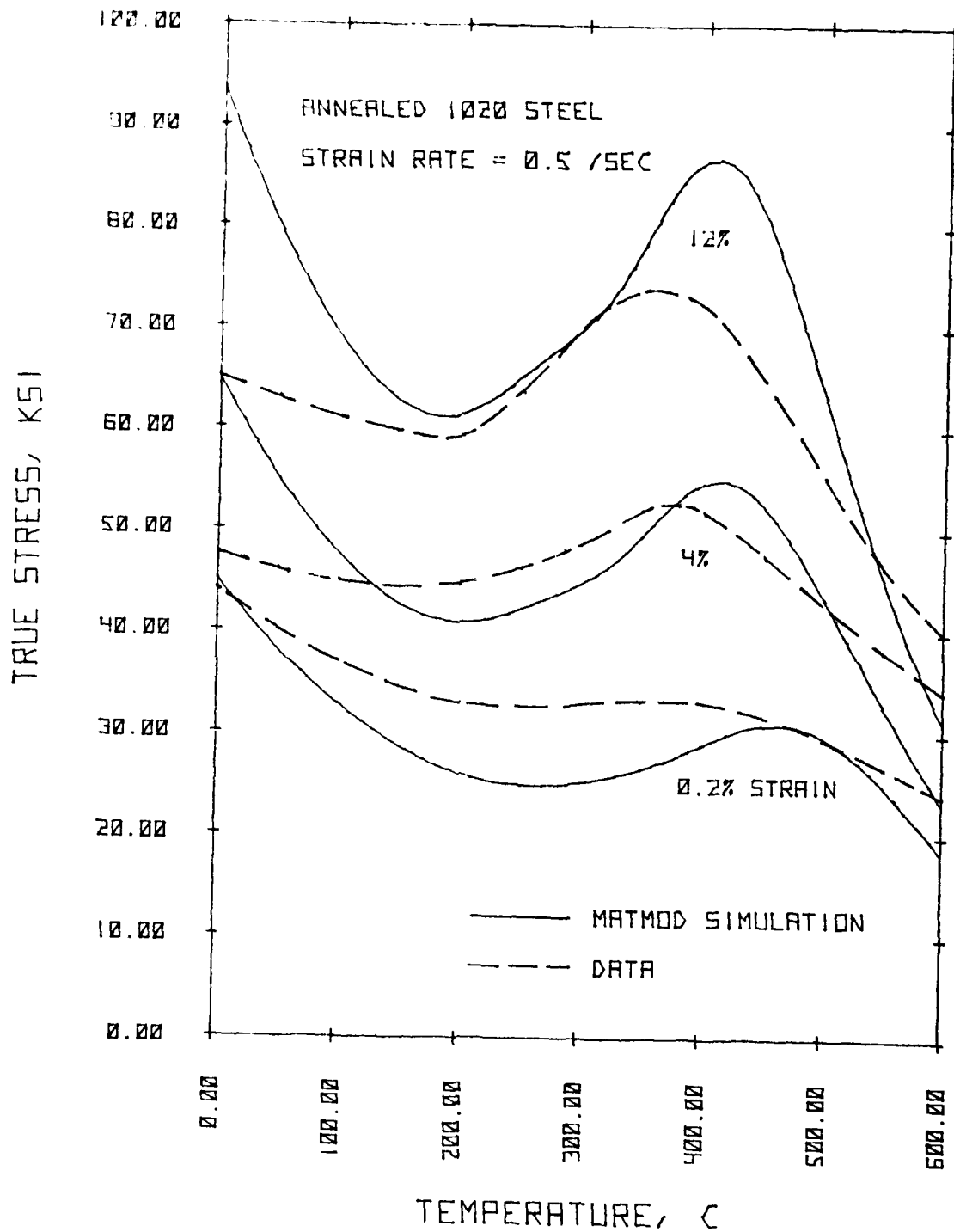


Fig. C-1 - Comparison of MATMOD simulations against data on the effect of temperature and strain on the flow stress of 1020 steel. The data (M.J. Manjoine, J. App. Mech., 1944, A-211) was used in calculating the material constants.

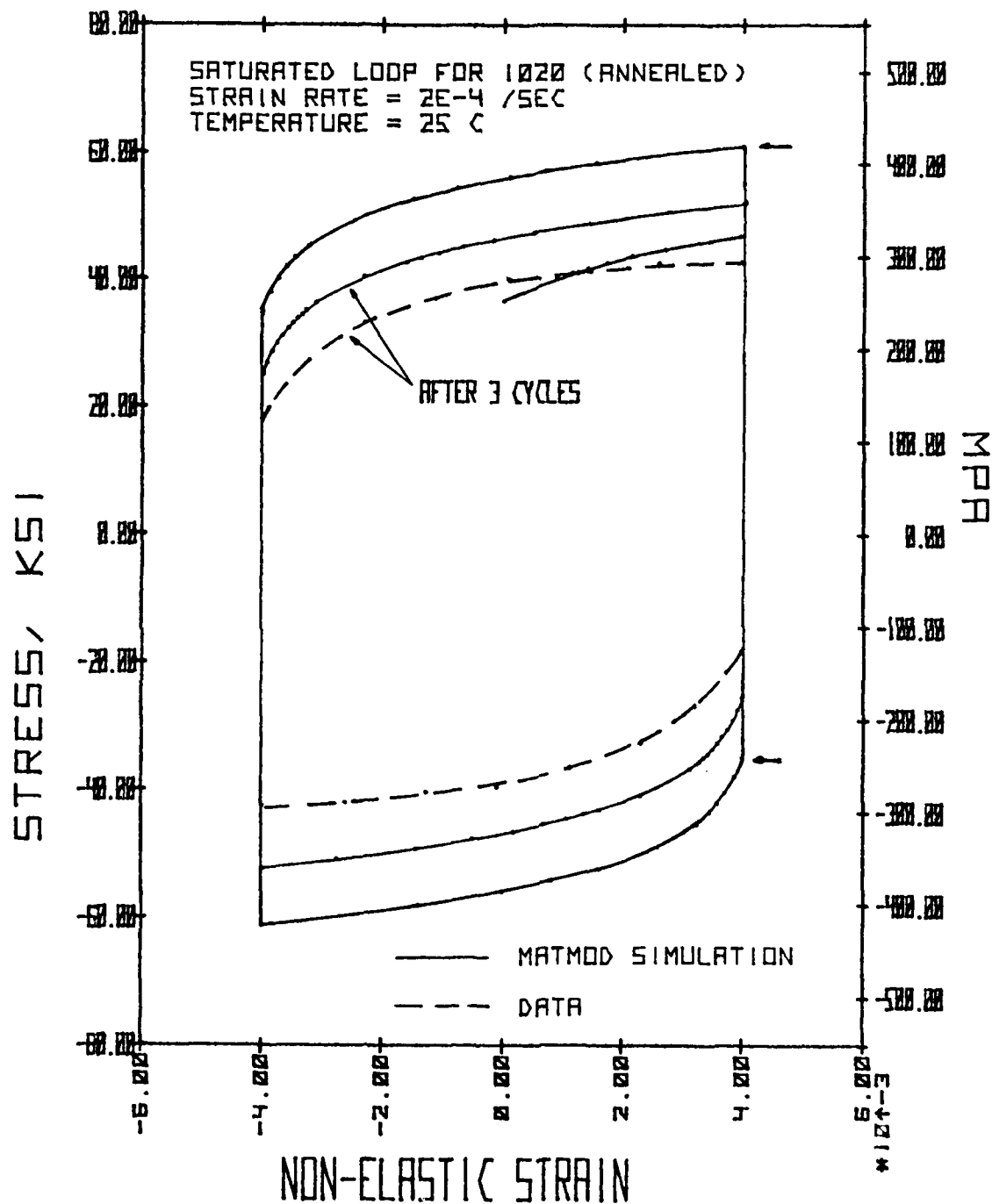


Fig. C-2 - Comparison of MATMOD simulation against data for cyclic deformation of 1020 steel. The curvature of the experimental hysteresis loops (M. Zohrei, "Cyclic Stress-Strain Behavior of A36 Steel," M.S. thesis, Stanford Un. Dept. of Civil Engineering, Dec. 1978) was used in calculating the material constants.

Table I

Data for 1020 Steel which was fit during the determination of its MATMOD constants:

1. .2% offset yield strength vs. temperature (0° - 650°C)
2. Strain hardening (0° - 650°C ; .2% offset to ultimate tensile strength)
3. Peaks in flow stress vs. temperature curve due to dynamic strain aging
4. Strain-rate dependence
5. Steady-state flow (of pure iron)
6. Bauschinger effect (hysteresis loop shape)
7. Cyclic hardening

D. Metal Working, Warm Forming, and Ductile Fracture

Oleg D. Sherby, Professor of Materials Science and Engineering

J. DeSimeon, Graduate Research Assistant

During the past year, Mr. David Bourell completed his doctoral thesis on the warm rolling of mild steel. Bourell showed that the subgrain structure developed during warm rolling does enhance mechanical properties. The yield strength of the warm rolled mild steel is increased by a factor of two over conventionally processed annealed mild steel. Furthermore, the impact characteristics of the warm-rolled steel are impressive, the transition temperature being reduced by 30°C over that for annealed mild steel. We illustrate these findings in Figures D-1A and D-1B.

Warm working as a means of enhancing properties of structural materials is a relatively new concept. Hirschvogel, in a recent review of this field, gave no references to American work -- an indication that little, if any, warm processing is done in this country. Warm rolling, as in any other temperature of rolling, can lead to defects during processing. These defects can result in undesirable features such as edge cracking and crocodiling. It is our objective to determine the environmental and metallurgical factors that can lead to such

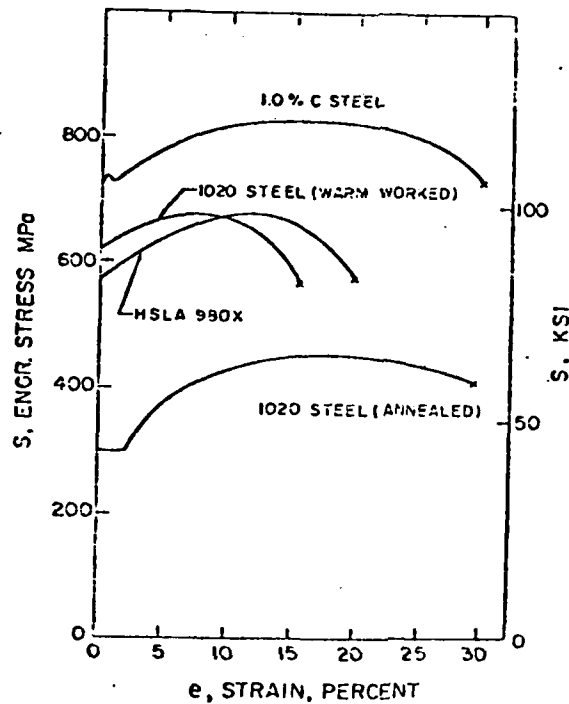


Figure D-1A.

Mild steel is the principal material used to make automobile bodies. In the annealed state, this steel is ductile (30% elongation) although its yield strength is not high (about 40 ksi). See bottom curve in above figure. There is a large effort in our country, as well as in Japan and Europe, to increase the strength of mild steel by dilute alloying and by special heat treatment. Steel 980 X (a high-strength-low-alloy steel, HSLA) is an example of one of these new materials (shown above) which exhibit double the yield strength of mild steel and yet retains fairly high ductility (20% elongation).

It is our contention that warm working conventional steels (a mild steel or a high carbon steel) can lead to properties that equal or exceed current HSLA steels. In the above graph, a warm rolled mild steel is seen to have about the same properties as HSLA 980 X. A 1% C steel (52100) is shown to have both high strength and high ductility.

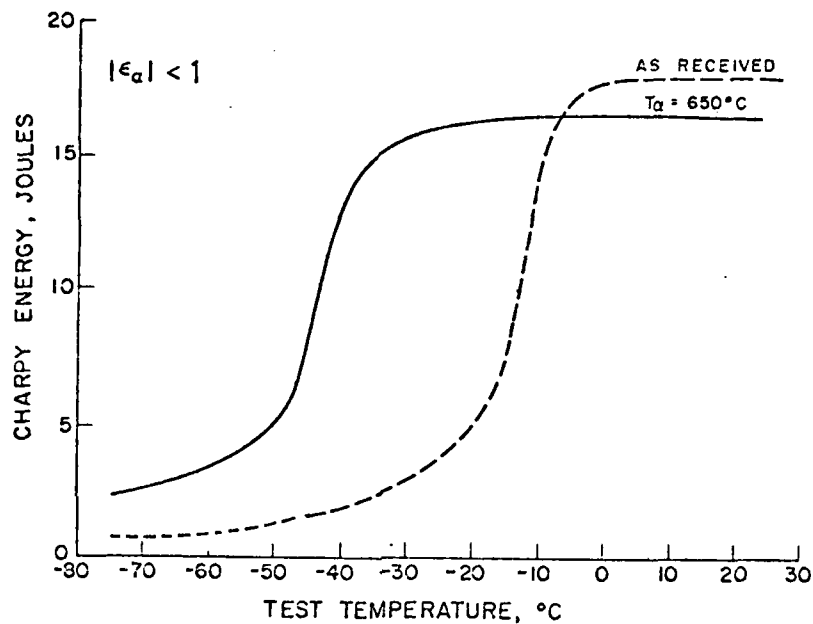


Figure D-1B.

The impact strength of a mild steel plate is enhanced by warm working. The above graph illustrates that the impact transition temperature is reduced by 30°C when a mild steel is extensively warm rolled at 650°C . This improvement in properties is attributed to the presence of subgrain boundaries in the warm rolled steel which inhibit fracture propagation.

failures. An example of crocodiling is shown in Figure D-2. The cause of such failures is the inhomogeneous plastic flow that occurs during rolling. This, in turn, leads to residual stresses, which, when built up to a sufficiently high value, will lead to failure of the material. Residual stresses can be determined by new analytical techniques using an elastic-plastic finite element approach and utilizing knowledge of the plastic flow behavior of the material (constitutive equations). It is here that an interdisciplinary approach is absolutely necessary to understand fully the process of rolling and its effect on properties.

S. DeJesus has prepared three dissimilar steels for study of their rolling characteristics (a mild steel, 1020; a bearing steel, 52100; and a super-plastic ultrahigh carbon steel). A thorough study of the rolling behavior of the mild steel at room temperature has been made. It has been determined that this material will crocodile when a strain of about 1.0 (3 to 1 reduction) is reached. Inhomogeneous plastic flow was readily observed to occur as seen by the development of inverse barrelling. We attribute inverse barrelling to the small bites taken per pass (about 1%). An example of inverse barrelling is shown in Figure D-3. If the percent deformation per pass is increased the degree of inverse barrelling is diminished. Even though more deformation occurs near the surface of the plate during inverse barrelling, the hardness profile after rolling indicates higher hardnesses in the center of the sample than near the surface. Such a hardness profile is shown in Figure D-4. The hardness in the center of the plate is an indication that residual stresses may be highest in the center and premature failure can be expected to occur there. This is because the build-up of hardness during cross-rolling is reduced compared to uni-directional rolling (see Figure D-4). For similar reasons, crocodiling can be delayed by warm rolling in comparison to cold rolling.

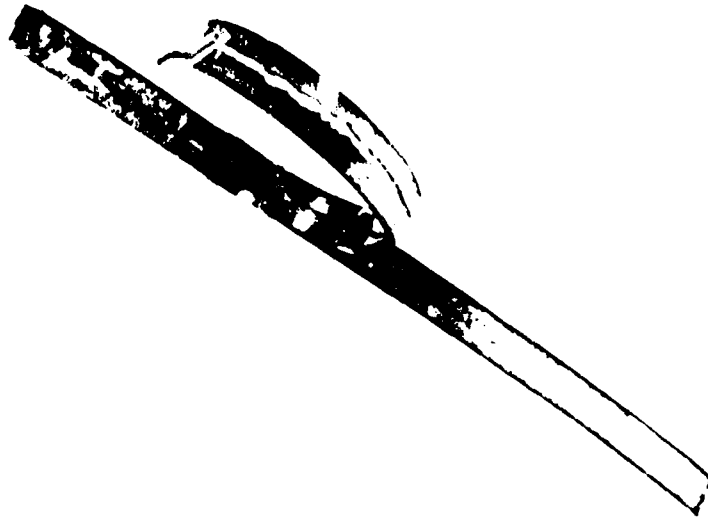


Figure D-2. An example of ductile failure during warm rolling of a mild steel. The separation begins at the end of the plate which first enters the rolls and always occurs in the center of the plate. This mode of failure is called crocodiling or alligatoring.

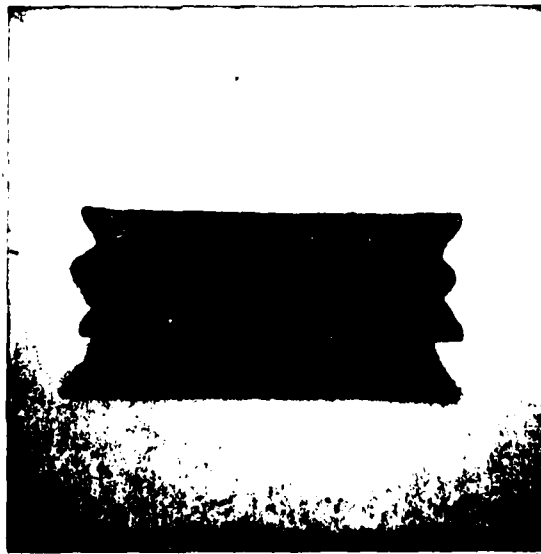


Figure D-3. Cross-section of a plate of a high carbon steel after extensive warm rolling. As can be seen, there is inverse barrelling, that is, the plate deforms in such a way that more deformation occurs near the surface of the plate than in the center of the plate.

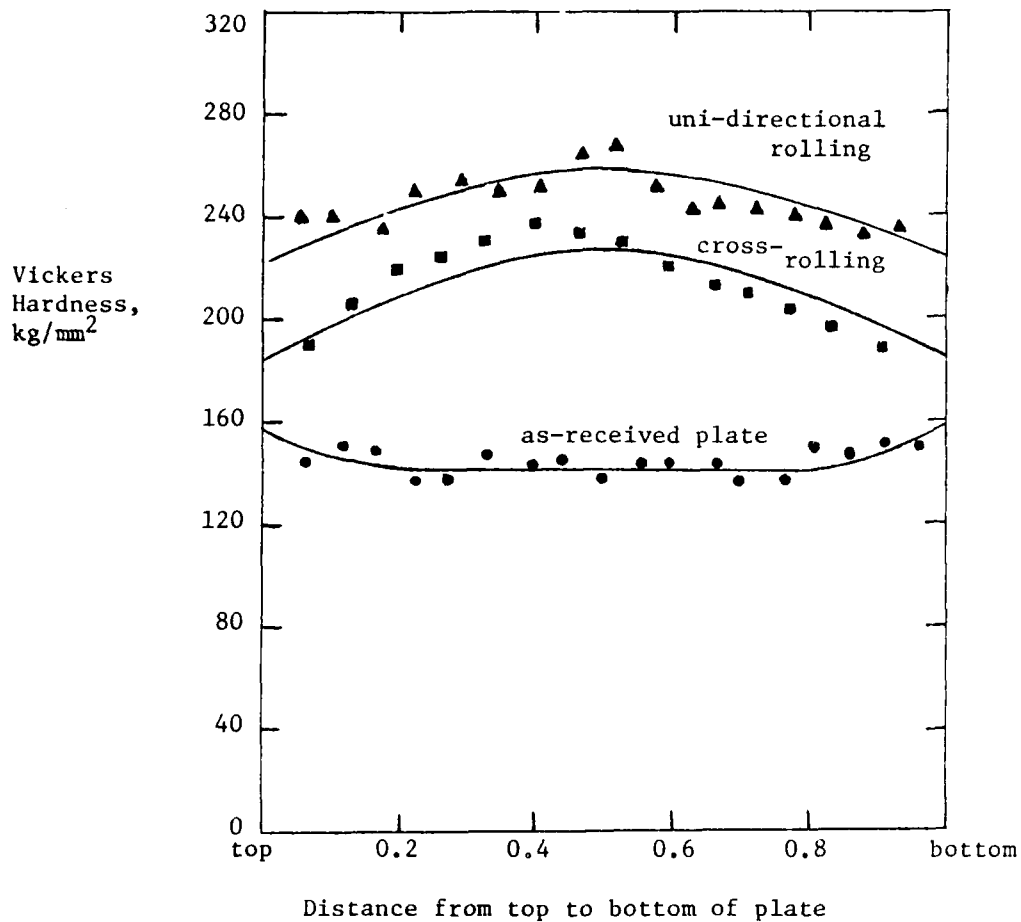


Figure D-4. Hardness profile of mild steel plate after rolling at room temperature to a strain of -1.14 (about 3 to 1 reduction). As can be seen, the hardness is highest in the center which is indicative of high residual stresses in that region. Failure of the uni-directionally rolled plate by crocodiling (a ductile separation of the plate at its center) occurs at a strain of about -1.2. Cross-rolling reduces the build-up of hardness in the plate and crocodiling does not occur.

Reference Publications:

1. M. P. Scott, D. M. Barnett, and D. B. Ilić, "The Non-destructive Determination of Residual Stress in Extruded Billets from Acoustoelastic Measurements," 1979 Ultrasonics Symposium Proceedings, IEEE. Cat. #79CH1482-9SU
2. E. H. Lee, F. L. Mallett and R. M. McMeeking, "Stress and Deformation Analyses of Metal-Forming Processes," Metal Forming Plasticity, E. H. Lippmann, 177-189, Springer Verlag 1979.
3. E. H. Lee and R. M. McMeeking, "Concerning Elastic and Plastic Components of Deformation," Int. J. of Solids and Structures 1980 (Stanford University SUDAM Report #78-5, 1979).

SECTION C

INDIVIDUAL RESEARCH PROGRAMS

1. ACOUSTIC AND MAGNETIC WAVES AND DEVICES

B. A. Auld, Adjunct Professor, Hansen Laboratories

Graduate Students:

S. Ayter	M. Riazat
M. M. Fejer	M. Tan
H. Kunkel	M. van Schilfgaarde
D. W. Pettibone*	C. P. Warren
F. G. Muennemann	

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Agency Support:

AFOSR 76-3059
EPRI RP-1395-3
Navy N00014-79-C-0222
Navy N00014-76-C-0632
NSF ENG 77-28541
Rockwell RISC BO-F01243-3
NSF-MRL through CMR - Thrust Program on Acoustic
Nondestructive Testing

Technical Objective:

To investigate acoustic and magnetic resonance and wave propagation phenomena and the use of new materials for device application in this area.

Research Report:

(1) Ferromagnetic Resonance Probe for Detecting Surface Flaws in Metals

Graduate Student: F. Muennemann

This work is in part related to a "Thrust" Program on Nondestructive Evaluation supported by the National Science Foundation's Materials Research Laboratory Program through the Center for Materials Research.

A new approach to microwave eddy current testing for surface cracks in metals involves the use of ferromagnetic resonance in a small yttrium iron garnet crystal placed close to the surface to be tested. It is well known that, in this situation, induced eddy currents on the metal surface cause a strong displacement of the ferromagnetic resonance

frequency. The presence of a crack on the surface produces, by disturbing the eddy current pattern, a perturbation of the garnet sample as it passes over the crack. Several models of such probes have been tested experimentally, demonstrating the principle and showing that a high detection sensitivity is possible.

Our studies of this probe have demonstrated that greater detection sensitivity can be achieved by directly measuring the amplitude and phase of the probe input impedance, rather than simply observing the shift in resonant frequency as in the past. This type of operation provides, as in conventional probes, discrimination against lift-off signals on the basis of the phase change in the input impedance. The latter feature occurs only when the probe is operated simultaneously in two or more modes of resonance of the ferromagnetic sphere.

A portable instrument that operates in this manner has been constructed and is being used to study the behavior of fatigue cracks in various materials under different loading conditions. The object is to identify crack dimensions through a better understanding of the "signatures" obtained with this type of probe. Of particular significance is a study in conjunction with the Thrust Program of closure stress and crack opening under load.

(2) Quantitative Modeling of Flaw Responses in Eddy Current Testing

Graduate Student: C. P. Warren

The general objective of this project is to develop the theory of eddy current flaw testing in metallic structures, using the reciprocity relation approach, and to apply this theory to the interpretation of results obtained by testing experimental models of flaws. The theoretical effort will be quite general, but experimental work is focused primarily on the denting problem in PWR steam generators. Determination of signature information suitable for application to adaptive learning methods is the main objective. A secondary objective will be to study new probe geometries suitable for improving the chances of detecting the initial stages of denting in the PWR problem.

The general approach being followed in this project is a theoretical electromagnetic formulation of the impedance change δZ at the

terminals of an eddy current probe due to the presence of a flaw in the test piece. The objective is to explore in this way the relationship between the flaw signal (or signature) and the actual shape and size of the flaw, with the purpose of trying to improve the flaw characterization capabilities of eddy current testing. Another topic to be addressed is the use of test probe field shaping in order to optimize performance for specific test piece configurations and test flaw geometries, following a spatial Fourier transform analysis. Experiments are being performed with the aim of verifying theoretical predictions, especially in the case of the denting problem geometry.

The denting problem arises from a buildup of a magnetite corrosion layer between the support plate structures and the heat exchanger tubes in a PWR steam generator. This continuing buildup eventually produces mechanical damage of the tubes and requires the development of methods for detection and treatment before this point is reached. Eddy current signals from magnetite layers are being studied both theoretically and experimentally, and special coils are being designed to optimize these signals.

(3) Processing of Optical Images With Optically Controlled Acoustic Transducers

Graduate Student: D. Pettibone

The research is directed to the study of a new technique for performing coherent Fourier processing of picture information (filtering, compression, correlation and pattern recognition) that offers promise of eventually realizing compact lightweight picture processing devices suitable for air-borne and space applications. The basic approach is to convert the optical image information into the form of a coherent very high frequency acoustic image, where both phase and amplitude information are directly accessible but where the parallel processing techniques of coherent optics are still applicable. General objectives of the project are to verify the principles of the proposed technique by constructing an experimental system and to explore both refinements and additions to the proposed system, as well as to evaluate in general terms its basic performance characteristics and limitations.

This project was concluded during the present reporting period with a demonstration of the feasibility of a hybrid MOS-RAM acoustic device for performing two-dimensional Fourier transforms. Details are given in the reference publications. An important feature of this device is that it also has the potential for performing two-dimensional correlations without the intermediate step of Fourier transformation.

(4) Interactions of Acoustic Waves With Domains in Ferroic Materials

Graduate Student: M. M. Fejer

The goal of this project is to study the nonlinear interaction of acoustic waves with domain walls in ferroic (ferromagnetic, ferroelectric and ferroelastic materials) with a few, first of all, of achieving a better understanding of the basic physics involved and of evaluating the potential of such applications for new device applications. Any domain wall, whatever its nature, exhibits a relatively abrupt change in material properties from one side to another, resulting from a rearrangement of the microscopic structure from one domain to the next. Such a discontinuity in material properties constitutes, in a sense, the fundamental element in all boundary value problems involving wave propagation and is therefore the basic "building block" for the analysis of a large variety of wave interaction devices. Discontinuities arising from domain walls have the particularity of being mobile - that is, they can be displaced by an applied magnetic field in a magnetic material, by an electric field in a ferroelectric material, and by an elastic field in a ferroelastic material - and, for this reason, they offer possibilities of realizing wave interaction devices whose structure can be changed electronically at a more or less rapid rate. In some cases, also, a "latching" feature exists. The domain structure remains in its new configuration after removal of the switching field. Possible device applications involving arrays of material discontinuities realized by various domain wall structures include diffraction and phase matching gratings, directional couplers, filters and memory stores.

In this project we are concerned especially with nonlinear interactions between acoustic waves and ferroelastic domain walls, i.e., (1) the effect of a domain wall on the nonlinear properties of the medium,

(2) the influence of domain wall structures on acoustic (and optical) harmonic generation, and (3) the displacement of a domain wall or walls under the action of static forces generated by "rectification" of an acoustic wave. Initially, work focused on gadolinium molybdate (GMO) but more recently we have also begun to consider another ferroelastic, neodymium ultraphosphate (NUP). A source of supply of the second material is available to us externally. In the case of GMO we are having crystals grown for us in the CMR crystal facility. Our current experiments are concerned with measuring some of the third-order elastic constants by second harmonic generation in resonant and traveling wave systems.

(5) Variational Analysis of Resonant Scattering of Acoustic Waves From Cracks and Slots in Plates

Graduate Student: M. Tan

This project is concerned with the application of variational and moment method techniques to the analysis of acoustic wave scattering from slots and discontinuities in plates, with particular emphasis on resonant scattering. The materials relationship of this program is through the potential interest of the results for nondestructive evaluation technology applied to ultrasonic flaw detection in plates. A general variational method has been developed for the intramode scattering from two- and three-dimensional cracks or slots in plates. This lends itself to the evaluation of complicated scattering problems, involving strong boundary interactions, in terms of approximate field solutions. A study is being made of removal of the singularity of the variational expression kernel in order to improve convergence of the calculation. The basis of the analysis is normal mode expansion in terms of elastic plate modes.

(6) Acoustic Wave Scattering From Surface Cracks

Graduate Student: S. Ayter

The purpose of this project is to develop theoretical criteria for the detection and characterization of surface cracks and flaws in materials by means of Rayleigh wave scattering. From a materials point of view it may therefore be classified in the area of Materials Testing

Techniques. Emphasis is being placed on the use of mechanical resonance of a crack as a means for determining the dimensions of the crack. When an incident Rayleigh wave impinges on an open crack, it launches Rayleigh waves on the crack faces. These are multiply reflected at the crack edges and the surface corners, producing standing wave resonances whose natural frequencies are characteristic of the crack dimensions (depth and width). A theory of these resonances was developed in the previous reporting period and experiments with near field transducers are now being set up for the purpose of measuring the resonances directly, rather than by scattering. A theory of rough and nonplanar cracks, covering both scattering and resonance effects, is under development.

(f) Elastic Domain Wall Waves in Ferroelectric Ceramics and Single Crystals

Graduate Student: H. Kunkel

The purpose of this research is to investigate the use of new types of elastic waves as probes for examining the material properties of piezoelectric and electrostrictive types of ferroelectric ceramics and single crystals. The elastic waves to be considered have the character of being guided as interface waves along the domain walls in the ceramic (boundaries between regions of different electrical poling orientation) or of being trapped between pairs of domain walls. A general numerical integration method has been developed for calculating elastic wave guidance along a "duct" of mechanical and piezoelectric material properties change in an infinite medium, and the problem of ducting in finite bodies is to be considered. Experiments have been started on plates of PZT piezoelectrics and lead magnesium niobate electrostrictives.

Reference Publications:

1. B. A. Auld, D. W. Pettibone, J. D. Plummer, and R. G. Swartz, "An Electronically Addressed Bulk Acoustic Wave Fourier Transform Device," in 1979 IEEE Ultrasonics Symposium Proceedings, J. deKlerk and B. R. McAvoy, eds. (Piscataway, N.J.: IEEE, 1979), pp. 184-188.

2. B. A. Auld and D. K. Winslow, "Microwave Eddy Current Experiments With Ferromagnetic Resonance Probes," in Symposium on Eddy Current Characterization of Materials and Structures (to be published).
3. B. A. Auld, "Theoretical Characterization and Comparison of Resonant Probe Microwave Eddy Current Testing With Conventional Low Frequency Eddy Current Methods," in Symposium on Eddy Current Characterization of Materials and Structures (to be published).

2. MATERIALS SYNTHESIS USING VAPOR DEPOSITION TECHNIQUES

T. W. Barbee, Jr., Senior Research Associate, Center for Materials Research

Professional Associates:

M. R. Beasley
T. H. Geballe
W. H. Holmes
D. L. Keith

R. H. Pantell
M. A. Piestrup
D. A. Stevenson
W. A. Tiller

Graduate Students:

R. T. Barclay
W. L. Carter
A. N. Chu
W. P. Low

S. T. Ruggiero
K. L. Seaward
R. G. Walmsley

Agency Support:

NSF-MRL through CMR Thrust Program on Metastable Materials
NSF-MRL through CMR Vapor Phase Synthesis Facility Support
AF F49620-78-C-0009
DARPA MDA903-79-C-0484
LLL 5303809

Technical Objective:

Development of new or optimized materials by structural control through use of vapor deposition processes in a manner ensuring that deposition process parameters rather than thermally activated bulk mechanisms determine the material structure.

Approach:

An experimental study of synthesis process parameter effects on the structure and properties of materials synthesized using vapor deposition techniques. Sputter deposition has been emphasized using magnetron techniques with reactive and inert atmospheres.

(1) Layered Synthetic Microstructures (LSM)

Professional Associates: M. R. Beasley, T. H. Geballe, D. L. Keith

Graduate Students: W. P. Low and S. T. Ruggiero

Techniques have been developed for synthesis, by vapor deposition, of layered structures of elemental materials having experimentally determined layer thicknesses varying from one atomic layer to 500 atomic layers. Niobium-germanium layered samples have been synthesized in our laboratory and structurally characterized. The superconducting properties of these samples are currently being studied by Mr. Steve Ruggiero, a student of Professor M. R. Beasley. Other materials of superconducting interest are also being synthesized and studied. A technical article reporting these results has been submitted for publication.

Also a series of LSMs of niobium/lanthanum, niobium/zirconium, niobium/titanium, molybdenum/zirconium, and molybdenum/titanium have been synthesized and studied. Transport properties and structural analyses are being carried out by Mr. W. P. Low, a student of Professor T. H. Geballe.

High electron contrast LSM structures have been prepared and their potential as dispersion elements for x-rays investigated using CuK_{α} radiation. Evaluation of LSM formed using this process has been carried out for tungsten/carbon structures. Multiple beam dynamic calculations that include absorption corrections have been performed. These calculations indicated that the peak diffracted intensity in first order for the sample having 61 D spacings and a D of $20 \text{ \AA}$ should be 70%. Measurements yielded approximately 40% showing that high peak reflectivity is attainable. Resolution ($E/\Delta E$) was experimentally observed to be approximately 42 in agreement with theory which predicted 40.

The difference between the calculated reflectivity (~70%) and the observed reflectivity (~40%) for the sample have 61 diffracting planes and a D spacing of $20 \text{ \AA}$ has been shown to be associated with interface roughness.

(2) Vapor Quench Stabilized Noncrystalline Cu/Zr, Cu/Ti, and CuHf Alloys (Metastable Materials Thrust Research)

Professional Associate: D. A. Stevenson

Graduate Student: R. G. Walmsley

Phase separation is observed in many glass systems, particularly in silicate base alloys. It is also found in many of the chalcogenide glasses. In addition, it has been inferred in noncrystalline metal alloys from subtle changes in radial distribution functions and deterioration of mechanical properties, particularly ductility. We have observed phase separation in Cu/Zr and Ti/Zr sputter deposition synthesized alloys. Alloys having a phase separated structure are brittle and exhibit poor corrosion resistance. Therefore, this observation of phase separation behavior is of both scientific and technological importance. In contrast, sputter deposited 304 SS/carbon noncrystalline alloys showed no evidence of phase separation (x-ray and TEM analysis) and exhibited marked ductility and corrosion resistance.

A systematic investigation of the relationship between synthesis parameters and resulting structure has been undertaken by Mr. R. G. Walmsley, a student of Professor D. A. Stevenson. Results to date demonstrate that synthesis process parameters have a large effect on the resulting amorphous structure which is clearly reflected in property measurements, particularly anodic polarization measurements.

(3) Transition Radiation as a Source of X-ray Radiation

Professional Associates: R. H. Pantell, M. A. Piestrup

Graduate Student: A. N. Chu

We report the first observation of x-rays produced from medium energy electrons (100MeV) penetrating two periodic structures: (1) a solid layered structure of carbon and germanium synthesized by sputter deposition techniques ($t_c = 2.16\mu$, $t_{Ge} = 1.66\mu$) consisting of six carbon/germanium layer pairs, and (2) a foil stack of forty 6μ thick mylar sheets separated by 500μ s in vacuum. 4.96 keV ($2.5 \text{ \AA}$) x-radiation was produced with a 60% band width. In the past such x-ray energies were obtained only with electron beams having energies greater than 1 GeV.

(4) Reactive Sputtering

Professional Associates: W. A. Tiller, D. L. Keith
Graduate Students: R. T. Barclay

Reactive sputtering of insulating oxides has been undertaken during this past year. Particular emphasis has been placed on SiO_x . Techniques for synthesis of insulating and conducting silicon/oxygen alloys have been developed allowing formation of films of controlled stoichiometry on room temperature substrates at rates of approximately $35 \text{ \AA}/\text{sec}$. The properties of this material are being measured and their relationship to synthesis process conditions determined.

This process has also been applied to the synthesis of zinc oxide for use as a piezoelectric transducer. High deposition rates of approximately 10μ an hour are easily obtained. Material of high quality than heretofore possible using sputtering techniques is reproducibly synthesized using this process. It is clear that this technique may be extended to other systems amenable to reactive sputtering.

(5) Noncrystalline Superconducting Alloys

(Metastable Metals Thrust Research Program)

Professional Associate: T. H. Geballe
Graduate Student: W. L. Carter

Noncrystalline Mo-Ge, Mo-Si, Mo-B, and Mo-C alloys have been synthesized by sputter deposition from separate sources in both a fixed composition and phase spread mode. Superconducting properties including critical temperature and critical field are being measured. In addition, TEM studies are underway to verify the noncrystalline state structure and to study the crystallization behavior.

Reference Publications:

1. T. W. Barbee, Jr., B. E. Jacobson, D. L. Keith, "Microstructure of Amorphous 304 Stainless Steel-Carbon Alloys Synthesized by Magnetron Sputter Deposition," *Thin Solid Films*, **63**, 143 (1979).
2. T. W. Barbee, Jr. and D. L. Keith, "Layered Synthetic Microstructures: Application as X-ray Dispersion Elements," *Lithography/Microscopy Beam Line Design Workshop*, Feb. 1979, Ed. by C. R. Dannemiller, SSRL Rept. # 79/02, 185.

Reference Publications (continued):

3. A. N. Chu, M. A. Piestrup, T. W. Barbee, Jr., and R. H. Pantell, "Observation of Soft X-ray Transition Radiation from Medium Energy Electrons," Rev. Sci. Instrum. 51(5), 597 (1980).
4. A. N. Chu, M. A. Piestrup, T. W. Barbee, Jr., and R. H. Pantell, "Transition Radiation as a Source of X-rays," J. Appl. Phys. 51(3), 1290 (1980).
5. J. H. Underwood, T. W. Barbee, Jr., and D. L. Keith, "Layered Synthetic Microstructures: Properties and Applications in X-ray Astronomy," Space Optics - Imaging X-ray Optics Workshop SPIE, 184, 123 (1979).

3. DEFORMATION IN SOLIDS

D. M. Barnett, Professor, Materials Science and Engineering and
Division of Applied Mechanics (Mechanical Engineering)

Graduate Students:

W. F. J. Deeg (Ph.D. received 6/80)
L. A. Gore (Ph.D. expected 9/80)
M. P. Scott (Ph.D. expected 10/80)

Agency Support:

EPRI RP 609-1
AFOSR 2-DJA-786
NSF-MRL through CMR - Thrust Research Program on
Plasticity and Metal Working

Technical Objectives:

(1) To quantitatively determine the state of residual stress in hydrostatically extruded aluminum billets for comparison with the same stress states predicted by finite element simulation and measured by more conventional x-ray techniques.

(2) To develop analytical and computational machinery for performing stress analyses of piezoelectric solids containing cracks, inclusions, and dislocations.

(3) To determine via computer simulation the equilibrium shapes of dislocation loops in stressed anisotropic crystals.

Research Report:

1. Non-Destructive Acoustic Determination of Residual Stresses

Graduate Student: M. P. Scott (Ph.D. to be completed 10/80)

The complete pointwise state of stress in aluminum billets hydrostatically extruded to area reductions of about 25% have been obtained by measuring relative longitudinal acoustic wave velocity shifts across extruded samples. This technique for residual stress determination is non-destructive in nature and is fully automated and extremely rapid. In the past year we have obtained extremely good correlation between the acoustically determined residual stresses and those measured by x-ray

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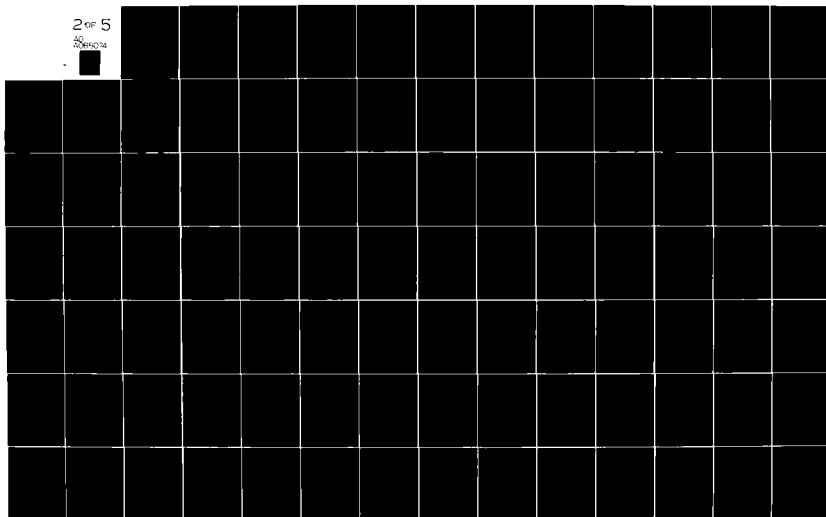
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techniques and predicted by finite element computer simulation. This study will be extended in the future by using acoustic shear waves to study non-axi-symmetric residual stress states, such as those about welds or those produced during rolling. A portion of this work has been conducted as part of a "Thrust" program on Metal Working and Plasticity.

2. Stress Analysis of Defects in Piezoelectric Solids

Graduate Student: W. F. J. Deeg (Ph.D. received 6/80)

A rather complete framework for performing stress analysis of piezoelectric (and, hence, necessarily anisotropic) solids containing cracks, dislocations, and misfitting inclusions has been developed. The fracture mechanics of slit cracks in piezoelectrics was studied in detail, and we have shown that reasonable values of applied electric fields in many piezoelectrics are capable of arresting cracks which would otherwise propagate catastrophically.

3. Equilibrium Shapes of Dislocation Loops

Graduate Student: L. A. Gore (Ph.D. to be completed 9/80)

Equilibrium shapes of dislocation shear loops have been computed for more than a dozen crystals of cubic symmetry under a series of applied stresses. The algorithm for determining equilibrium shapes is based upon a rigorous energy minimization principle using the proper dislocation self-force expression. A novel feature of the algorithm is its use of tension splines to effect accurate relaxation to the equilibrium shape. Cases in which the dislocation "line tension" becomes negative over certain orientations have been examined; the algorithm treats these "unstable" orientations easily and produces equilibrium loops with corners.

Reference Publications:

1. M. P. Scott, D. M. Barnett, and D. B. Ilic, The Non-Destructive Determination of Residual Stress in Extruded Billets from Acousto-elastic Measurements, 1979 Ultrasonics Symposium Proceedings, New Orleans, La. (Sept. 1979).
2. W. F. J. Deeg and D. M. Barnett, The Fracture Mechanics of Slit Cracks in Piezoelectric Solids (submitted to International Journal of Solids and Structures, June, 1980).

4. PHOTOELECTRONIC MATERIALS PHYSICS

Clayton W. Bates, Jr., Professor, Materials Science and Engineering
and Electrical Engineering

Professional Associates:

C. D. Robbins*
G. K. Wertheim**
D. N. E. Buchanan**
H. R. Greenstein-Visiting Scholar
J. B. Mooney†
D. D. Cubicciotti†
Z. Maczenski-Visiting Scholar††

*With Diagnostic Information, Inc.

**With Bell Laboratories,
Murray Hill, New Jersey

†With SRI International

††From The Technical University
of Warsaw

Graduate Students:

L. Galan*
S. J. Yang*
A. Raza

*Received Ph.D. during report period.

Agency Support

NASA NSG 2346
NSF-MRL through CMR
NSF-ECS-7909453
SERI Subcontract XS-9-8104-4

Technical Objectives:

The objectives here are to investigate the structural, electronic and optical properties of crystalline and amorphous materials and to correlate these properties with their photoelectronic behavior. Recent studies have been concerned with low work function surface layers sensitive to visible and infrared radiation (photoemitters) and semiconducting compounds for use in solar cells.

Approach:

The photoelectric yield over a wide electron energy range is studied and related to such properties as the bandgap and other material parameters for the photoemissive surfaces. X-ray photoelectron spectroscopy (XPS) is currently being used to explore valence bands, charge states of elements in complex systems, and stoichiometry.

Optical absorption, Hall Effect, and resistivity measurements complement the XPS studies on the solar cell materials.

Research Report:

(1) XPS Studies of $\text{Na}_2\text{KSb}(\text{Cs})$ Photoemitters

Graduate Student: L. Galan

Professional Associate: C. D. Robbins

Alkali antimonide photocathodes Na_3Sb , K_3Sb , Cs_3Sb , Na_2KSb and particularly $\text{Na}_2\text{KSb}(\text{Cs})$ (S-20) were studied under ultrahigh vacuum conditions using x-ray photoemission spectroscopy (XPS). Core-electron binding energies determined by XPS can be understood by essentially the same ionic model that has been applied successfully to study other ionic solids. Large extraatomic relaxation energies, due to electronic polarizability, were estimated by correlating the energy shifts of photoelectrons and Auger electrons. From the good agreement between experimental and calculated binding energies it was concluded:

a) Alkali-saturated antimonides are ionic solids with a valence charge transfer of about 0.8 electrons from each alkali to antimony.

b) The binding energy of the top of the valence band or intrinsic photoemission threshold is about 3 eV. The exceptionally low photoemission thresholds of cubic compounds were explained by surface band bending.

c) A difference in Madelung energy of about 1.5 eV between the two cation sites in cubic alkali antimonides, predicted from their perfect crystal structures, is not present in XPS spectra. This was explained by the highly disordered lattices of these compounds.

The ionicity of alkali antimonides is demonstrated also by XPS

spectra of the valence band, in agreement with previous ultraviolet photoemission studies. These spectra show the valence band as the $\text{Sb}5p^6$ atom-like levels with essentially no admixture of alkali levels.

The hypothesis of a predominantly ionic bond in alkali antimonides proved to be very successful in explaining and correlating many properties of these materials that remained not well understood. The large charge transfer to Sb screens the nucleus potential producing very small binding energies. The special situation of the valence electrons in these solids, with very small binding energies and highly polarizable yet strongly localized on the anions, explains their unique properties, particularly their small intrinsic photoemission thresholds and band gaps. An ionic model also explains their crystal structures, the relative stability of hexagonal and cubic phases and its relation to lattice disorder and type of electric conduction.

Recent developments have shown that XPS can be used efficiently as a quantitative surface analysis technique. Our XPS intensity measurements were studied together with results of previous investigations, and it was concluded that:

i) The bulk of Na_2KSb and $\text{Na}_2\text{KSb}(\text{Cs})$ photocathodes is formed mainly by Na_2KSb phase with high concentration of alkali vacancies and, thus, strongly p-type.

ii) Over this material, a surface layer, from 20 to 50 Å thick, of NaK_2Sb and also K_2CsSb in S-20 photocathodes, is formed during the last stages of photocathode formation.

iii) Our XPS measurements show that Na is present in the surface layer of S-20 photocathodes, probably in the form of NaK_2Sb .

iv) The role of the surface layer in obtaining an efficient photocathode is multiple. The different nature of bulk and surface layer with regard to lattice disorder and non-stoichiometry allows the production of an excellent heterojunction configuration resulting in strong surface band bending, low effective photoemission threshold and high quantum efficiency.

(2) XPS Study of the S-1 (Ag-O-Cs) Photocathode

Graduate Student: S. J. Yang

Although the silver-oxygen-cesium photocathode (Ag-O-Cs) has been known for over 50 years and has been the subject of a large number of publications, nevertheless no satisfactory explanation of its properties had been given. This photocathode, called the S-1, because it was the first one used in practical devices, is prepared through the interaction of cesium vapor with a preoxidized silver film (formed by a glow discharge of silver in oxygen), followed by the deposition of a small amount of silver. We have studied the fabrication of this surface using the techniques of X-ray Photoelectron Spectroscopy and photoyield measurements in three distinct stages: (1) The formation of Ag_2O and studies of oxygen adsorbed on freshly evaporated Ag surfaces, (2) the cesiation of Ag_2O with additional studies of Cs and O on pure Ag, (3) further Ag deposition and completion of the S-1 photocathode.

In (1) we have verified the existence of Ag_2O being formed by glow discharge of silver in oxygen with the $\text{O}1s$ core level at a binding energy of 529.5 eV. In Ag_2O two oxygen atoms with covalent radii are located at the tetrahedral sites $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$ with each oxygen surrounded by four silver atoms. The interatomic distance between two adjacent silver atoms is larger than in metallic silver ($3.35 \text{ \AA}$ in Ag_2O vs. $2.88 \text{ \AA}$ in metallic silver). This lattice expansion causes localization of the $\text{Ag}5s$ electrons which appear separated from the $\text{Ag}4d$ by 2.5 eV. Oxygen heavily adsorbed on Ag goes into the octahedral sites at $(1/2, 1/2, 1/2)$, $(1/2, 0, 0)$, $(0, 1/2, 0)$ and $(0, 0, 1/2)$ just under the silver surface. These oxygen atoms with covalent radii cause no expansion of the silver lattice and all of the Ag core levels and Auger peaks are the same (peak position and shape) as for metallic silver. Oxygen atoms in the octahedral sites are quite stable and the $\text{O}1s$ core level intensity remains unchanged after baking in ultrahigh vacuum up to 450°C . Oxygen atoms in the tetrahedral sites are unstable being easily reduced by cesium vapor.

During the cesiation of Ag_2O (2), two oxygen states with $\text{O}1s$ bind-

ing energies of 527.5 eV and 531.5 eV were observed in good photocathodes. The 527.5 eV peak was assigned to oxygen in Cs_2O and that at 531.5 eV to oxygen in Cs_{11}O_3 . The Auger parameter (defined as the kinetic energy difference between Auger line and related core level) was used in verifying the presence of the cesium suboxide. This parameter varied from 810.5 eV for pure Cs to 806.5 eV for Cs_2O_4 . Values of 808.5 eV and larger were always associated with the suboxide of Cs or free Cs. The peak position of the O1s in Cs_{11}O_3 is in agreement with previous studies of this system. Cs_2O was produced in a separate experiment with the O1s at 527.5 eV.

A model of the S-1 photocathode (3) has been proposed in this work. The matrix of an S-1 is Cs_2O with Ag particles dispersed in it. The cesium suboxide clusters are mixed with silver atoms on the grain boundaries and photosurface. Silver acts as a catalyst and stabilizer on the S-1 surface.

The photoemission mechanism in a S-1 photocathode is explained as follows: High quantum efficiency at photon energies higher than 4 eV is due to inter-band electronic transitions in the Cs_2O matrix. The peak response between 3 eV and 4 eV is caused by emission from the dispersed Ag particles. The visible and near IR response is explained by electron excitation from the conduction band of silver and tunnelling through the barriers between silver particles and Cs_2O .

(3) Electronic Structure of CsSn

Professional Associates: G. K. Wertheim
D. N. E. Buchanan

Cesium has the unusual property of forming ionic compounds with electronegative metals, e.g. CsAu , a semiconductor with 2.5 eV band gap. Another interesting material is Cs_3Sb which has found application as a photoemitter. The group IVA metals are also known to form intermetallic compounds with the alkali metals, e.g. NaPb . We have studied CsSn to investigate the charge transfer and to test its utility as a photoemitter.

Thin films of Cs-Sn intermetallic compounds formed by the reaction

of evaporated Sn layers with Cs vapors were studied by X-ray photoelectron spectroscopy. The stable end product was identified as equiatomic CsSn. It was produced as a p-type semiconductor. Core electron binding energies give evidence of substantial charge transfer from Cs to Sn. The Mössbauer effect isomer shift shows a 5s-electron concentration between those of grey and white tin, indicating that the transferred charge dominantly enters 5p states. Oxidation of CsSn yields a surface covered with cesium suboxide which has good photoemissive properties. A new compound tentatively identified as CsSn_4 was found.

(4) Structural, Thermodynamic, and Electronic Studies of CuInS_2 and CuInSe_2 films for Solar Cell Applications prepared by Spray Pyrolysis

Graduate Student: A. Raza

Professional Associates: J. B. Mooney
D. D. Cubicciotti

This program was initiated on 1 September 1979 with the major objective of the preparation of a solar cell using spray pyrolysis for the deposition of all but the contact metalization, and having the structure glass/Au grid/p-CuInSe₂/n-CdS/Al.

The major variables studied were spray rate, total volume of solution sprayed, and the ratios of copper to indium and sulfur/selenium in the spray solutions. These are being correlated with the stoichiometry in the surface and bulk, optical absorption, Hall Effect, and resistivity of the films produced.

Studies to date have consisted mainly of X-ray fluorescence, XPS, and some thermodynamical calculations. The main finding of these studies is that under a wide variation in the concentration of the elements in the starting spray solution stoichiometry is approximately achieved in the bulk but is not on the surface.

List of Materials-Related Publications Since Last Report

1. G. K. Wertheim, C. W. Bates, Jr., and D. N. E. Buchanan, "Electronic Structure of CsAu", Solid State Communications 30, 473 (1979).

2. C. W. Bates, Jr., G. K. Wertheim, and D. N. E. Buchanan, "Nature of the 318 eV Plasmon in X-ray Photoemission from Silver", Physics Letters 72A, 178 (1979).
3. C. W. Bates, Jr., et al., "XPS Studies of Cesium Antimonide Photoemitters", Thin Solid Films, Vol. 69, 175 (1980).
4. C. K. Wertheim, C. W. Bates, Jr., J. Wernick, and D. N. E. Buchanan, "Pseudoalloy Behavior at Interfaces", Appl. Phys. Lett. 35, 403 (1979).
5. S. J. Yang and C. W. Bates, Jr., "The Role of Cesium Suboxides in Low Work-Function Surface Layers Studied by X-Ray Photoelectron Spectroscopy: Ag-O-Cs", Appl. Phys. Lett. 36, 675 (1980).
6. C. W. Bates, Jr., et al, "Electronic Structure of CsSn", Phys. Rev. B15 (1980).

5. STRUCTURES OF AMORPHOUS MATERIALS AND SYNCHROTRON RADIATION

A. I. Bienenstock, Professor, Materials Science & Engineering
and Applied Physics

Professional Associates:

J. Stöhr
S. C. Rowland
W. K. Warburton

Graduate Students:

S. M. Brennan
S. Laderman
G. B. Stephenson

Agency Support:

NSF-DMR 73-07692 (SSLR)
NSF-DMR 79-08554
NSF-INT 77-06310
EXXON unrestricted grant

Technical Objectives:

To investigate atomic arrangements in amorphous materials in an effort to understand thermal, crystallization, electronic and vibrational properties. To determine atomic arrangements at the surfaces of materials. To develop synchrotron radiation techniques and instrumentation.

Approach:

The methods used during the past year were x-ray diffraction and extended x-ray absorption fine structure analysis.

Research Report:

- (1) Dynamic Small Angle X-ray Scattering

Professional Associate: W. K. Warburton

Graduate Students: S. Laderman
G. B. Stephenson

A high-count rate system is being developed which will be able to quickly collect many consecutive small-angle x-ray scattering (SAXS) patterns. This will allow the in situ study of samples undergoing processes such as crystallization, phase separation, precipitation or glass transition. Dynamic SAXS studies of the kinetics of these processes will provide definitive experimental data which has not been obtainable previously.

During the past year, a study of the detector system alternatives has led to significant modification of the design of the dynamic SAXS system. A position-sensitive X-ray detector system is being built which employs a linear photodiode array. When fully operational (anticipated this autumn), complete SAXS patterns will be collectable every 10 to 0.1 seconds, depending on sample scattering efficiency. In order to take advantage of the high count rate capability of the detector, a focussed beam line is being used to provide the necessary flux.

During the next year, we plan to use the system to study phase separation kinetics in amorphous materials. A preliminary study of the scattering efficiency of phase-separated sodium-borosilicate glasses has indicated that a more intensely scattering system would be preferable for the study of early-stage phase separation kinetics. Several other oxide glass systems are under consideration.

In collaboration with a group at EXXON Research and Engineering Company, we have also begun studies of the sizes of asphaltenes in several heavy crude oils. Here, it is intended to study the kinetics of asphaltene precipitation using the dynamics SAXS system.

(2) Structural Studies of Amorphous Materials

Professional Associate: S. C. Rowland
Graduate Student: S. Laderman

The bulk of our structural studies on amorphous materials are reported in the section devoted to the Thrust Program on Metastable Materials. In addition, fluorescent EXAFS studies have recently been performed on As_2Se_3 glasses containing low concentrations of Cu. The goal of this work is to determine whether the Cu is tetrahedrally coordinated, as we found it to be in more concentrated glassy Cu- As_2Se_3 alloys, or if some other coordination is prevalent.

We have also continued radial distribution studies of germanium-chalcogen glasses containing noble metals.

(3) EXAFS Studies of Low-Z Adsorbates and Surface Structure ¹⁻⁷

Professional Associate: J. Stöhr

Graduate Student: S. Brennan

During the past year, the research was focussed on the development of the electron yield EXAFS technique for the study of low-Z adsorbates on surfaces. In particular, we intended to develop surface EXAFS to the point where submonolayer coverages could be investigated. Experiments of this kind are particularly interesting as they complement experiments by means of other techniques such as photoemission, Low Energy Electron Diffraction (LEED) or Electron Energy Loss Spectroscopy (EELS).

Considerable progress has been made in the development of the experimental technique as well as elucidating the potential and reliability of low-Z EXAFS measurements. The data quality has been greatly improved by using a reference intensity monitor which allows to normalize out any structure in the monochromator transmission function and intensity modulations due to electron beam instabilities of the storage ring. With the novel reference monitor low-Z adsorbate coverages on surfaces down to 1/3 monolayer can now be investigated as shown in

Ref. 6. As discussed in Refs. 3 and 4 we have for the first time exploited the polarization dependence of the EXAFS signal to obtain the complete structure of oxygen on Al(111). Besides the O-Al distance we were able to also study the lateral separation of the O atoms in the chemisorbed overlayer. The polarization dependence is a unique feature of surface EXAFS measurements and will have many future applications.

Reference Publications:

1. J. Stöhr, R. S. Bauer, J. C. Menamin, L. Johansson, and S. Brennan, "SURFACE EXAFS INVESTIGATION OF OXYGEN CHEMISORPTION ON GaAs(110)," *J. Vac. Sci. Technol.* 16, 1195 (1979).
2. J. Stöhr, L. Johansson, I. Lindau, and P. Pianetta, "EXAFS STUDIES OF THE BONDING GEOMETRY OF OXYGEN ON Si(111) USING ELECTRON YIELD DETECTION," *J. Vac. Sci. Technol.* 16, 1221 (1979).
3. L. I. Johansson and J. Stöhr, "BONDING OF OXYGEN ON Al(111): A SURFACE EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDY," *Phys. Rev. Lett.* 43, 1882 (1979).
4. J. Stöhr, L. I. Johansson, S. Brennan, M. Hecht and J. N. Miller, "A SURFACE EXTENDED-X-RAY-ABSORPTION-FINE-STRUCTURE STUDY OF OXYGEN INTERACTION WITH Al(111) SURFACES," *Phys. Rev. B* (to be published).
5. J. Stöhr, R. Jaeger, J. Feldhaus, S. Brennan, D. Norman and G. Apai, "EXAFS STUDIES ABOVE THE C, N, O AND F K ABSORPTION EDGES," *Applied Optics* (to be published).
6. S. Brennan, R. Jaeger, J. Stöhr and D. Norman, "SURFACE EXAFS OF OXYGEN ON Al(111) AT SUBMONOLAYER COVERAGE," *Proceedings, VI Intern. Conf. on Vacuum Ultraviolet Radiation Physics, Charlottesville* (June 1980).
7. L. I. Johansson, J. Stöhr, S. Brennan, M. Hecht and J. N. Miller, "OXYGEN INTERACTION WITH Al(111): A SURFACE EXAFS STUDY," *Proceedings, Intern. Conf. Solid-Vacuum Interface VI, Delft, Holland* (May 1980).
8. A. Bienenstock, "Applications of Synchrotron Radiation," *IEEE Trans. Nucl. Sci.* NS-26, 3781 (1979).

9. A. Bienenstock, "An Overview of the Stanford Synchrotron Radiation Laboratory, " in Proceedings of the National Conference on Synchrotron Radiation Instrumentation, National Bureau of Standards, Gaithersburg, Maryland, June 1979, to be published in Nucl. Instr. and Methods.
10. A. Bienenstock, "Materials Research at Stanford Synchrotron Radiation Laboratory," Materials Research Society Annual Meeting, Cambridge, Mass., Nov. 27, 1979, to be published in Proceedings of Symposium on EXAFS and Synchrotron Radiation, edited by B. K. Teo.
11. A. Bienenstock, "Relation of Roles of In-Laboratory and Synchrotron Radiation EXAFS Facilities, "to be published in the Proceedings of the Workshop on Laboratory EXAFS Facilities and their Relation to Synchrotron Radiation Sources, Seattle, April 1980. Edited by E. Stern.

6. PROPERTIES OF ADSORBENTS AND CATALYSTS

M. Boudart, Professor, Chemical Engineering and Chemistry

Professional Associates:

J. E. Benson
P. Bruylants
R.A. Dalla Betta
T. Yoneda
C. Yuan

Graduate Students:

W. G. Borghard
W. Cheng
W. Holstein
S. Ichikawa
E. Iglesia
M. McDonald
G. Meitzner
T. Oyama
J. Sanchez *
L. Volpe
R. Weber
G. Zhang

* Received M.S. during report
period

Agency Support:

NSF DMR 77-24222	NSF DAR 79-10071
NSF ChE 77-22722	DE AS03-76 SF 00326
NSF ChE 77-15385	
NSF ENG 79-09141	
NASA NCA20R-745-908	
Exxon Research and Engineering Company	
NSF-MRL through CMR - Thrust Program on Alloy Catalytic Materials	

Technical Objective:

To prepare and characterize finely divided materials and understand their chemical surface reactivity and catalytic activity in selected reactions.

Approach:

For the rational synthesis of catalytic materials, the physical chemistry of their preparation and of what follows it, namely the genesis of the catalyst, is studied by means of Infra-Red Absorption Spectroscopy (IRS), electron spin resonance (ESR), Mössbauer spectroscopy (MES), Auger electron spectroscopy (AES), X-ray diffraction (XRD), X-ray scattering (XRS), X-ray absorption (XRA), extended X-ray absorption fine structure (EXAFS), magnetic susceptibility measurements as well as conventional methods of physisorption, chemisorption and chemical reactivity including catalytic tests. The same methodology is applied to the structural and electronic characterization of the new materials, the final aim being an understanding of their catalytic activity and selectivity in a number of reactions.

Research Activity

Gold particles stabilized on Y zeolites have been synthesized in a size range small enough that the metal agglomerates appear amorphous to X-ray diffraction (particle diameter less than 1.5nm). This novel state of gold was prepared by procedures similar to those which, for platinum, yield clusters of platinum atoms (size less than 1nm) located within the supercages of Y zeolites. In the case of platinum, replacing Na^+ counterions in the zeolite support with protons or multivalent cations like Ca^{3+} reduces the average electron density per platinum atom as measured by XRA. This electron deficiency correlates with increased catalytic activity by the platinum clusters for hydrogenation and isomerization reactions and with a decreased affinity of the clusters for dioxygen. Work is underway to determine if changes of zeolite cations and of metal particle size modify the behavior of gold clusters.

A second project has dealt with gasification of carbon by water vapor and hydrogen, reactions that are used effectively in coal conversion. Kinetic studies have been made of the uncatalyzed and platinum catalyzed gasification of a high surface area carbon under

differential conditions to determine reaction rate expression, activation energy, product selectivity, effect of product inhibition, and kinetic isotope effects. Samples were characterized by physical adsorption of nitrogen and hydrogen titration of preadsorbed oxygen to determine total and platinum surface areas. Results from the catalyzed carbon-hydrogen reaction have permitted significant progress in understanding the reaction mechanism.

In the case of the catalyzed carbon-steam reaction hydrogen inhibition has been found to limit the overall rate of carbon gasification.

Reference Publications:

1. L. Leclercq, K. Imura, S. Yoshida, T. Barbee and M. Boudart, "Synthesis of New Catalytic Materials: Metal Carbides of the Group VI B Elements," in Preparation of Catalysts II (1979), 627-639.
2. E. L. Kugler and M. Boudart, "Ligand and Ensemble Effects in the Adsorption of Carbon Monoxide on Supported Palladium-Gold Alloys," J. of Catal. 59, 201-210 (1979).
3. K. Fujimoto and M. Boudart, "Preparation of Supported Iron Clusters and Their Mossbauer Effect Spectra," J. de Physique, C2-81 - C2-84 (1979).
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7. PRIMARY PHOTOCHEMISTRY OF PHOTOSYNTHESIS

S. G. Boxer, Assistant Professor, Chemistry

Graduate Students:

R. R. Bucks
C. A. Chidsey
A. Kuki
E. F. McCord
R. Moog
M. G. Roelofs
K. A. Wright

Agency Support:

ACS PRF 9963-64
Research Corporation
NSF-MRL through CMR
USDA #5901-0410-8-0147-0
DOE SERI - #139

Technical Objective:

To obtain an understanding of the mechanism of the primary photochemical events of photosynthesis. Specific objectives include elucidation of the origin of the efficiency of the forward reaction (nearly 100%), the mechanism of stabilization of separated charge for times up to tens of nanoseconds, the generation of triplet excited states by anion-cation annihilation and the fabrication of artificial molecular systems which simulate these properties.

Approach:

This problem is approached along several convergent paths. (1) The synthesis of molecular aggregates which contain the molecules known or suspected to participate in the primary photochemistry. (2) Examination of the structure of real reaction centers using high-resolution magneto-photoselection technique. (3) Investigation of the fundamental spectroscopic properties of the chlorophylls and the nature of chlorophyll-protein interactions using chlorophyll-apomyoglobin complexes. (4) The use of large magnetic fields to selectively perturb spin-dependent reactions as a means to provide detailed kinetic and magnetic information about reaction centers.

Research Report:

(1) R. R. Bucks - A large series of molecules has been synthesized which brings together the molecular constituents which participate in the primary photochemistry of photosynthesis. These include singly linked dimers and trimers, prepared from metal containing and metal free chlorophylls, and doubly linked cofacial analoges. Variables include redox potential, distance and solvent dielectric. The photo-physical properties of singly linked arrays have been extensively investigated on the 3-5000 ps time scale in a search for charge transfer. Evidence for charge transfer is found when the potential of electron donor excited state is more than 300 mV above the acceptor.

(2) M. Roelofs - The electron spin resonance spectrum of the triplet excited state of Rhodospseudomonas spheroides R-26 reaction centers has been studied after excitation with the polarized narrow-bandwidth output of a tunable dye laser from 520-670 nm. A theory is developed relating experimental observables to the angles between the electronic transition dipole moment of the excited chromophore and the principle magnetic axis system of the triplet state of the dimeric trap. Data is presented which demonstrates that the treatment is correct and useful, and angles are obtained for the Q_x transitions of bacteriopheophytin. High-resolution magnetophotoselection data in the region of the bacteriochlorophyll Q_x transitions can be combined with polarized photobleaching experiments to provide direct information on the structure of dimeric trap.

(3) K. Wright, A. Kuki, and R. Moog - The first well-defined 1:1 complex between chlorophyll and a protein has been prepared by replacing heme in myoglobin and hemoglobin with a series of chlorophylls. We call these green proteins the chloroglobins. These complexes have been studied in detail as a model for chlorophyll-protein interactions. Well-formed crystals of these complexes have been prepared which provide a defined orientation of chlorophylls. The orientations of transition dipole moments and long-range exciton interactions have been examined using a microspectrophotometer. These protein crystals offer a new type

of material in which the chromophores can be viewed as constituting an oriented gas with unique site-substitution in a lattice, ideal for studying energy transport.

(4) C. Chidsey and M. Roelofs - We have discovered that the triplet yield in reduced photosynthetic reaction centers can be perturbed in a well-defined way by application of large magnetic fields. The field lifts the degeneracy between singlet and triplet radical pair energy levels at low field, and enhances the frequency of coherent singlet-to-triplet conversion, by increasing the difference in resonance frequency of the radicals, at high field. This result is interpreted as direct evidence for a difference in the g-factors of the primary radical ions in photosynthesis. The data can be fit to an appropriate theory for the field dependence. This analysis yields the g-factor difference and the rate-constants for radical-ion recombination to the singlet ground and excited triplet states.

(5) F. M. McCord - The 360 MHz nmr spectrometer at the Stanford Magnetic Resonance Laboratory has been modified to permit laser irradiation of the sample during the nmr experiment. The reaction between photoexcited flavins and tryptophan has been studied in great detail and analyzed using the technique of Chemically Induced Dynamic Polarization. From this analysis one unambiguously assigns the nmr spectrum of tryptophan, determines that the reaction can proceed by electron transfer or hydrogen abstraction and can specify the hyperfine interaction in short-lived tryptophan radical intermediates. The latter can be used to examine the electronic structure of tryptophan.

Reference Publications:

1. S. G. Boxer and M. G. Roelofs, "Chromophore Organization in Photosynthetic Reaction Centers: High-Resolution Magneto-Photoselection," *Proc. Natl. Acad. Sci., U.S.A.* 76, 5636 (1979).
2. S. G. Boxer and K. A. Wright, "Preparation and Properties of a Chlorophyllide-apoMyoglobin Complex," *J. Amer. Chem. Soc.*, 101, 6791 (1979).
3. C. Chidsey, M. G. Roelofs and S. G. Boxer, "The Effect of Large

Magnetic Fields and the G-factor Difference on the Triplet Population in Photosynthetic Reaction Centers," Chem. Phys. Letters, XXX (1980).

4. E. McCord, R. R. Bucks and S. G. Boxer, "360 MHz Laser CIDNP Study of Tryptophan Derivatives and Tryptophan in Small Peptides," Biochem. Biophys. Res. Comm., XXX (1980).
5. T. Netzel, R. R. Bucks, S. G. Boxer and I. Fujita, " P_{sec} Studies of Models for the Primary Photochemistry of Photosynthesis," in Picosecond Phenomena, XXX (1980).

8. INTRINSIC CHEMICAL REACTIVITY

John I. Brauman, Professor, Chemistry

Professional Associates:

P. C. Hiberty
F. K. Meyer

Graduate Students:

P. S. Drzaic
R. L. Jackson
B. K. Janousek*
J. M. Jasinski
C. R. Moylan

M. J. Pellerite
R. N. Rosenfeld*
C. M. Rynard
S. C. Shatas

*Received Ph.D. during report
period

Agency Support:

NSF CHE 78-21064
PRF 10848-AC5,6

Technical Objective:

To obtain an understanding and separation of intrinsic (molecular) factors and solvation phenomena which affect the chemical reactivity and spectroscopy of ions and neutral molecules.

Approach:

We study a variety of chemical and photochemical reactions both ionic and molecular in both the gas and condensed phase. Comparison of results allows us to understand intrinsic effects (from the gas-phase) and intrinsic plus solvation effects (from condensed phases).

Research Report:

(1) Gas-Phase Ionic Reactions

Professional Associates:

P. C. Hiberty
F. K. Meyer

Graduate Students:

J. M. Jasinski	M. J. Pellerite
C. R. Moylan	R. N. Rosenfeld

We have studied reactions of nucleophiles with carbonyl compounds, demonstrating a number of unusual features of the potential energy surface. We have also studied proton transfer and isotope effects in hindered acids, and extended our studies of nucleophilic displacement reactions.

(2) Electron Affinities, Photochemistry of Ions

Professional Associates: P. C. Hiberty
F. K. Meyer

Graduate Students: P. S. Drzaic B. K. Janousek
R. L. Jackson C. M. Rynard

We have determined the electron affinity of the ethynyl radical and accompanied this with a rather elaborate quantum mechanical calculation. We have written an extensive review on molecular electron affinities. We have determined the electron affinity of CH_3S and CD_3S and the spin-orbit splitting and vibrational frequencies in these radicals. Finally, we have obtained strong evidence for the existence of dipole supported states of negative ions which are found near the threshold for electron photodetachment.

(3) Laser Induced Chemistry

Professional Associates: F. K. Meyer

Graduate Students: P. S. Drzaic R. N. Rosenfeld
J. M. Jasinski C. M. Rynard
C. R. Moylan S. C. Shatas

We have studied infrared multiphoton induced dissociation of ions, exploring a variety of features of the photophysics of multiphoton absorption. We have also induced electron photodetachment from a number of negative ions.

Reference Publications:

1. O. I. Asubiojo and J. I. Brauman, "Gas Phase Nucleophilic Displacement Reactions of Negative Ions with Carbonyl Compounds," J. Am. Chem. Soc. 101, 3715 (1979).
2. R. N. Rosenfeld, J. M. Jasinski, and J. I. Brauman, "The Infra-red Photodissociation of CH_3OH^- ," J. Am. Chem. Soc. 101, 3999 (1979).
3. R. N. Rosenfeld, J. M. Jasinski, and J. I. Brauman, "Infrared Multiphoton Electron Detachment from the Benzyl Anion," J. Chem. Phys. 71, 1030 (1979).
4. B. K. Janousek and J. I. Brauman, "Electron Affinities," in Gas Phase Ion Chemistry, M. T. Bowers ed., Vol. 2, Academic Press New York, N. Y., 1979, pp. 53-86.
5. B. K. Janousek, J. I. Brauman, and J. Simons, "An Experimental and Theoretical Determination of the Electron Affinity of the Ethynyl Radical, HC_2 ," J. Chem. Phys. 71, 2057 (1979).
6. R. L. Jackson, A. H. Zimmerman, and J. I. Brauman, "Resonant States at Threshold Observed in Electron Photodetachment Cross Sections of Polyatomic Negative Ions," J. Chem. Phys. 71, 2088 (1979).
7. S. Datta, J. I. Brauman, and R. N. Zare, "Isotope Enrichment and Stereochemistry of the Products from the Reaction of Electronically Excited Iodine Monochloride with cis- and trans-1,2-Dibromoethylene," J. Am. Chem. Soc. 101, 7173 (1979).
8. J. P. Collman, J. I. Brauman, and K. M. Doxsee, "Carbon Monoxide Binding to Iron Porphyrins," Proc. Natl. Acad. Sci. USA, 76, 6035 (1979).
9. B. K. Janousek and J. I. Brauman, "Electron Photodetachment of Thiomethoxyl and Deuterothiomethoxyl Anions: Electron Affinities, Vibrational Frequencies, and Spin-orbit Splitting in CH_3S and CD_3S ," J. Chem. Phys. 72, 694 (1980).

9. GEOCHEMICAL STUDIES OF AMORPHOUS AND CRYSTALLINE SILICATES AND
SILICATE MELTS

Gordon E. Brown, Jr., Associate Professor, Geology

Professional Associates:

B.H.W.S. de Jong, Occidental Research Corp.
C. M. Taylor, Research Associate, School of Earth Sciences
G. A. Waychunas, Research Associate, CMR

Graduate Students:

A. Hessenbruch
M. F. Hochella, Jr.
K. D. Keefer
J. E. Shigley

Agency Support:

NSF-MRL through CMR
Memorex
Standard Oil of California

Technical Objectives:

(1) To study the structure and physical properties of chemically homogeneous silicate glasses and melts as functions of composition and temperature in order to formulate structure-property-composition relationships for geologically relevant silicate melts. (2) To study the complexing of base metal ions and the polymeric structure of silicate and aluminate tetrahedra in hydrothermal solutions in order to understand the processes resulting in the concentration of base metals in ore deposits. (3) To determine the crystal structures of various silicate and sulfide minerals. (4) To investigate the paragenesis of various silicate and phosphate minerals, particularly those from granite pegmatites.

Approach:

The short-range and micro-structures of silicate glasses and melts are studied by a combination of methods including (1) x-ray radial distribution analysis; (2) small angle x-ray scattering; (3) x-ray emission, absorption, and photoelectron spectroscopy; and (4) viscosity-conductivity measurements. The speciation of silicate and aluminate tetrahedra in aqueous solutions is studied by NMR spectroscopy. Crystal structure determination is carried out in the usual manner using precision x-ray intensity measurements. Our studies of mineral paragenesis involve field mapping, electron microprobe analysis, and x-ray diffraction.

Research Report:

(1) Structural Studies of Silicate Glasses and Melts

Graduate Students: M.F. Hochella, Jr.
K.D. Keefer

Professional Associates: B.H.W.S. de Jong
C. M. Taylor
C. A. Waychunas

During the past year we have continued structure-property studies of binary alkali and alkaline-earth silicate glasses and melts, concentrating mainly on the relationship between melt structure and internal nucleation of crystals. We have interpreted $\text{SiK}\beta$ x-ray emission, O 1s photoelectron, and Raman spectra of these glasses in terms of degree of polymerization of silicate tetrahedra and have correlated these interpretations with ease of nucleation as well as with a spate of other melt properties. We conclude that binary alkali and alkaline earth silicate melts with the highest concentrations of monomeric silica species exhibit the greatest ease of crystal nucleation.

In a test of the Bockris "iceberg" model for silicate melts and glasses, we carried out combined heating experiments and small angle x-ray scattering studies of $\text{CaMgSi}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$ glasses.

In spite of the fact that Raman spectra suggest the presence of monomeric silica polymers as well as chains and higher polymers - a necessary distribution of polymeric units for the presence of highly polymerized "icebergs" separated by regions with less polymerized species - SAXS and TEM experiments showed no direct evidence of micro-phase separation. Instead, small (~ 1200 Å) nuclei were detected which appear to increase in radius of gyration with heat treatment.

We have continued our modelling studies of polymerization-depolymerization reactions in alumino-silicate melts and in aqueous solutions containing silica, using molecular orbital calculations. In this work we have calculated ΔG of reactions between various molecular silicate units and a variety of the geologically common network modifying species in melts including the alkali metal cations, H_2O , CO_2 , F^- , and Cl^- . The results of these calculations permit us to test various proposed reactions and to rationalize a variety of geochemical phenomena including the mechanism by which certain aluminosilicates dissolve in aqueous solutions.

We have also begun a major effort to structurally characterize chemically simple alumino-silicate melts and glasses using high temperature x-ray scattering methods, EXAFS spectroscopy, and computer simulation of melt-glass structure. As discussed in the last report, our efforts to perform high temperature x-ray scattering studies on melts using conventional diffractometry have been thwarted by difficulties in containerizing the melt sample. We are currently exploring the use of a fixed sample, energy dispersive x-ray system which eliminates the problem of changes in sample shape during the experiment. During the last report period we obtained Fe K-edge EXAFS data for several silicate glasses containing iron and for one crystalline model compound, $Na^{VI}FeSi_2O_6$. The objective of this work was to determine if iron oxidation state is controlled in part by composition rather than extrinsic oxygen fugacity and to compare the EXAFS data on oxidation state and coordination number with that from Mossbauer and optical absorption spectroscopy on the same glass samples. Our work showed

that EXAFS-derived coordination numbers and oxidation states for the chemically simple glasses examined are in good agreement with the results of other more established methods. During the present report period we have obtained additional Fe K-edge EXAFS data on other crystalline model compounds including Fe_2SiO_4 , magnesio-wustite, hercynite, and Fe-doped LiAl_2O_4 . Preliminary analysis of these new data suggests that useful information can be obtained for single site, single oxidation state iron oxides but that multi-site, multi-oxidation state oxides of iron will be difficult to characterize using EXAFS techniques. We are currently awaiting additional beam time at SSRL for EXAFS study of other transition-metal containing silicate glasses and crystalline model compounds. We have obtained and are currently debugging computer programs for molecular dynamics and Monte Carlo simulations of silicate melt structure. A variety of simulations are planned to test current hypotheses concerning Al-coordination changes at high pressure in silicate melts and the coordination numbers of alkali and alkaline earth cations in silicate melts.

In collaboration with Drs. A. Piwinskii and H. Weed of Lawrence Livermore Labs, we are carrying out simultaneous viscosity-conductivity measurements on silicate melts in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. We are particularly interested in changes in viscosity and conductivity in melts with constant $\text{Na}_2\text{O}:\text{SiO}_2$ ratio but varying Al_2O_3 content. The rotating cup viscometer for these measurements has been put in working order and data collection is well underway. A series of parallel high pressure viscosity measurements on volatile-containing melts are being carried out in our labs at Stanford using an internally heated pressure vessel and the falling Pt-sphere method. Our objective here is to understand the effects of H_2O and CO_2 on viscous flow in silicate melts, the hypothesis being that H_2O causes depolymerization, and therefore a decrease in viscosity, whereas CO_2 has the opposite effect. The apparatus has been constructed and tested during this report period and we are now obtaining data.

(2) Molecular Speciation in Hydrothermal Solutions

Professional Associates: B.H.W.S. de Jong
G. A. Waychunas

During the past report period, deJong, in collaboration with W. Dibble of the Geology Department, has carried out a series of ^{27}Al and ^{29}Si NMR experiments on aqueous solutions containing various alkali and alkaline earth cations in varying amounts. Changes in Al coordination number were monitored as a function of pH and ionic strength. Changes in silica polymerization were monitored as functions of alkali content, pH, and temperature (32° - 94°C) of the solution. Increases in alkali content and temperature were found to favor depolymerization of silicate polymeric units. Changes in polymer distribution were found to be dependent on alkali content but not on type of alkali.

In collaboration with M. Apted of the Geology Department, we have begun design work on a high pressure (up to 2 kbar) high temperature (up to 500°C) cell for the EXAFS work on hydrothermal solutions containing base metal cations such as Cu. Construction and testing of this cell will be carried out during the summer and fall. The objective of this project is to study the types of complexes formed by base metal ions in chloride and sulfide bearing aqueous solutions at pressures and temperatures typical of those experienced by hydrothermal solutions in the earth's crust.

(3) Structural Study of Crystalline Silicates, Sulfides and Sulfates

Professional Associates: J. R. Clark, U.S. Geological Survey
B.H.W.S. de Jong
G. E. Harlow, American Museum of
Natural History

Graduate Students: M.F. Hochella, Jr.
K.D. Keefer

During this report period, we have solved the structures of several new minerals including rasvumite, KFe_2S_3 , and magnesium hydroxysulfate hydrate, $\text{MgSO}_4 \cdot \frac{1}{3} \text{Mg}(\text{OH})_2 \cdot \frac{1}{3} \text{H}_2\text{O}$, using the Patterson method. The former structure consists of double, edge-sharing chains of Fe-S tetrahedra parallel to $\underline{c}$ and face-sharing pairs of K-S polyhedra also forming double chains parallel to $\underline{c}$. The iron is high spin and has a valence state near + 2.5.

The hydroxysulfate structure is made up of isolated SO_4 tetrahedra cross-linked by chains of face-sharing octahedra, $\frac{2}{3}$ of which are occupied by Mg. This is the first reported structure with face-sharing Mg octahedra. This particular phase has been tentatively identified as a precipitate from sea water (at pH near 2.5) where hot (350°C) hydrothermal solution is emitted from submarine hot springs.

In addition to these structure solutions, we have completed analysis of x-ray and neutron diffraction data for $\text{NaAlSi}_3\text{O}_8$. The objective of this study was to directly refine the Al-Si distribution among the four non-equivalent tetrahedral sites using the neutron data. This objective was accomplished and refined coordinates from the independent x-ray and neutron experiments agree within the standard errors of these measurements.

(4) Paragenesis of Silicate and Phosphate Minerals

Graduate Students: A. Hessenbruch
J. E. Shigley

We are continuing our combined field-laboratory studies of two well-known California mineral localities. Our work on the paragenesis of phosphate phases at the Stewart pegmatite in San Diego County is progressing smoothly. Since the last report period, we have chemically characterized a suite of primary and secondary phosphates using optical microscopy, electron microprobe, atomic absorption analysis and x-ray diffraction. Unlike phosphate paragenesis in some granitic pegmatites, the Stewart phosphates appear to have undergone little alkali-alkaline earth metasomatism. We have devised a preliminary alteration model for the Stewart phosphates which involves Li-leaching, Fe-Mn oxidation, and hydration of the primary lithiophilite $\text{Li}(\text{Mn,Fe})\text{PO}_4$ to a variety of secondary phosphates. At least one new secondary phosphate phase has been found and we are currently characterizing it further. Several preliminary synthesis experiments involving melt growth of LiMnPO_4 have been carried out starting with a representative mix of the phases found at the Stewart Pegmatite.

Our work on a suite of Ba-Ti silicate phases from the New Idria District in San Benito County is also well underway. During the last report period detailed field mapping and sample collecting were completed and we have begun chemical and structural characterization of the rare suite of silicate phases associated with the serpentinites in this famous mineral locality.

Reference Publications:

1. B.H.W.S. de Jong and G.E. Brown, Jr., "Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions: I. Electronic structures of $H_6Si_2O_7$, H_6SiAlO_7 , and $H_6Al_2O_7$." *Geochim. Cosmochim. Acta* 44, 491-511 (1980).
2. B.H.W.S. de Jong and G.E. Brown, Jr., "Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions: II. The network modifying effects of Mg^{2+} , K^+ , Na^+ , Li^+ , H^+ , OH^- , F^- , Cl^- , H_2O , CO_2 , and H_3O^+ on silicate polymers." *Geochim. Cosmochim. Acta* 44, (in press).
3. B.H.W.S. de Jong, K.D. Keefer, G.E. Brown, Jr. and C.M. Taylor, "Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions: III. $SiK\beta$ x-ray emission spectroscopic characterization of local Si environments in alkali-alkaline earth silicate glasses and its relation to internal nucleation." *Geochim. Cosmochim. Acta* (submitted).
4. J.R. Clark and G.E. Brown, Jr., "The crystal structure of rasvumite, KFe_2S_3 ." *Amer. Mineral.* 65 (in press).
5. G.E. Harlow and G.E. Brown, Jr., "Low albite: an x-ray and neutron diffraction study." *Amer. Mineral.* 65 (in press).
6. G.E. Brown, Jr., "X-ray scattering and spectroscopic studies of silicate glasses and melts." *Prog. Geol. Soc. Amer. Ann. Mtg.* 11, 426 (1979).
7. K.D. Keefer, "A small angle x-ray scattering study of diopside and diopside70quartz30 glass." *Prog. Geol. Soc. Amer. Ann. Mtg.* 11, 455 (1979).
8. B.H.W.S. de Jong, W.E. Dibble, Jr., and L.W. Cary, " ^{11}An ^{27}Al and ^{29}Si pulsed NMR study on the molecular speciation of Al and Si in aqueous solutions. EOS, Trans. Amer. Geophys. Union 60, 974 (1979).
9. K.D. Keefer, M.F. Hochella, Jr., and B.H.W.S. de Jong, "The crystal structure of the magnesium hydroxysulfate hydrate $MgSO_4 \cdot 1/3 Mg(OH)_2 \cdot 1/3 H_2O$." *Acta Crystallogr.* (in press).

10. PHOTOELECTRONIC PROPERTIES OF SOLIDS

R. H. Bube, Professor and Chairman, Materials Science and Engineering
Professor, Electrical Engineering

Professional Associates:

A. L. Fahrenbruch	M. Kasuga
M. D. Golmayo	W. Kot
F. Guastavino	T. Suda

Graduate Students:

T. Anthony	J. Nielsen
J. Aranovich	C. Y. Ng
M. S. Casey	F. A. Ponce
F. G. Courreges*	M. J. Tsai*
C. Eberspacher	F. C. Wang
Z. S. C. Jan*	J. Werthen
	C. C. Wong

* Received PhD during report period

Agency Support:

SERI XJ-9-8031-1
SERI XR-9-8087-1
DOE DE-AS03-76ER70047
Rockwell F98X-550040-650
NSF INT 79-06574

Technical Objectives:

To investigate the photoelectronic properties of solids, both crystalline and non-crystalline, in order to understand the underlying phenomena and to improve the properties and performance of electronically active materials and devices, particularly those involved in the photovoltaic conversion of solar energy.

Approach:

To couple a materials synthesis and device fabrication program closely to develop an understanding of transport and junction properties for film-on-crystal and all-film heterojunctions, heteroface junctions and Schottky barriers, particularly in materials systems potentially suitable for large-area thin-film solar cells for terrestrial applications.

Research Report:

(1) Photoelectronic Properties of II-VI Heterojunctions

Graduate Students: T. Anthony F. A. Ponce
 J. Aranovich J. Werthen
 F. G. Courreges

This year has seen the completion of phases of our program with manuscripts written and accepted for publication in the areas of (1) mechanism of the transport currents in $\text{Cu}_2\text{S}/\text{CdS}$ junctions, (2) preparation and properties of ITO/CdTe junctions by rf sputtering of ITO onto single crystal p-type CdTe, and (3) preparation and properties of ZnO/CdTe junctions by spray pyrolysis of ZnO onto single crystal p-type CdTe.

In the investigation of $\text{Cu}_2\text{S}/\text{CdS}$ junctions prepared by the "dry" method, it was found that the behavior of the short-circuit current and the open-circuit voltage are describable in terms of a deep, donor-like level in the CdS region adjacent to the metallurgical interface, which controls tunneling into the Cu_2S of electrons from the CdS. The ionization energy of this donor level is determined to be 0.45 eV and its density at the interface to be 10^{19} cm^{-3} . This donor level acts as a recombination center to decrease the short-circuit current, and as a tunneling center to reduce the open-circuit voltage.

Solar efficiencies up to 8% with $V_{oc} = 0.82 \text{ V}$ and $J_{sc} = 14.5 \text{ mA/cm}^2$ were produced by rf sputtering of ITO films onto single crystal p-type CdTe substrates. A careful system of investigation reveals that the ITO/CdTe junctions formed by this process consist actually of $n^+-\text{ITO}/n\text{-CdTe}/p\text{-CdTe}$ buried homojunctions with about a 1 micrometer thick layer of n-CdTe formed by heating of the surface of the CdTe during sputtering. The chief degradation mechanism involves a decrease in V_{oc} with a transformation of the buried homojunction structure to an actual ITO/CdTe heterojunction.

Solar efficiencies up to 8.8% with $V_{oc} = 0.54 \text{ V}$ and $J_{sc} = 19.5 \text{ mA/cm}^2$ were produced with ZnO/CdTe junctions prepared by spray pyrolysis deposition of ZnO films on single crystal p-type CdTe substrates. This is the highest value of efficiency reported to date for an authentic

heterojunction cell based on CdTe. Principal experimental variables in cell preparation were substrate temperature and post-deposition heat treatment temperature for annealing in hydrogen. The forward transport current is describable in terms of a tunneling model in which bulk and interface deep traps control the forward characteristics.

Work currently in progress concerns four principal areas: (1) high resolution transmission electron microscopy of CdTe bulk and defects, (2) photovoltaic heterojunction preparation and properties on CdTe, (3) low resistance ohmic contacts to p-CdTe, and (4) electro-deposition of CdTe thin films.

In the application of high resolution TEM techniques in collaboration with Prof. R. Sinclair, a specimen preparation technique has been developed for bulk and thin film specimens, imaging of atomic structure in CdTe has been achieved with resolutions of less than 2Å, and various defects have been observed and analyzed in bulk CdTe. These results constitute a first for application to semiconductor materials and interfaces with imaging of individual atoms and atomic planes.

The effect of pre-deposition etchant and surface treatment of CdTe on the final junction formed with a large bandgap window material has been investigated. The effect of pre-deposition heat treatment of p-type CdTe in hydrogen is quite dramatic: open-circuit voltages on subsequently formed CdS/CdTe junctions are as large as 0.92 V, suggesting the formation of a buried homojunction. Other effects of hydrogen treatment of the surface of p-type CdTe are being investigated using surface photovoltage, luminescence, and Schottky barrier properties. Especially promising results were obtained in initial attempts to deposit ITO/CdTe junctions by electron-beam evaporation of ITO; solar efficiency of 9.0% has been achieved.

The most promising low-resistance contacts to p-CdTe developed to date consist of evaporated Cu on a surface etched with $K_2Cr_2O_7$: $H_2SO_4:H_2O$.

(2) Photovoltaic Heterodiodes Based on Indium Phosphide

Graduate Students:	M. S. Casey	M. J. Tsai
	C. Eberspacher	C. C. Wong

The reason that sputtered ITO/InP solar cell junctions with large lattice mismatch have the same efficiency as CdS/InP junctions with good lattice match is shown to be that sputtered ITO/InP junctions actually consist of n^+ -ITO/n-InP/p-InP buried homojunctions. To demonstrate this and to show that the homojunction formation is caused by thermal damage to the InP surface during sputtering deposition rather than from impurity diffusion from the oxide, a series of five different metal oxide/InP junctions have been formed by sputtering of the oxide, all with high solar efficiency ($\sim 10\%$). Junctions have been prepared both from single-crystal InP:Cd and from epitaxial crystal films of InP:Zn. The effects of sputter deposition of the oxide have been simulated by sputter etching of the InP surface, and the effects analyzed through measurements of the properties of Au/InP junctions, and of the Hall effect and photoluminescence of InP surfaces. Some heat treatment of the sputtered cells is required to achieve maximum efficiency, but excessive heat treatment causes degradation and often transformation from homojunctionlike to heterojunctionlike solar cell behavior. An actual In_2O_3 /InP heterojunction solar cell was prepared by thermal oxidation of the InP.

The major approaches currently being pursued are the following: (1) basic evaluation of the changes in InP surface induced by oxidation (in air, O_2 , or H_2O), heat treatment in a neutral atmosphere (N_2 , He or Ar), heat treatment in vacuum, or heat treatment in a reducing atmosphere (H_2); (2) evaluation of phenomena involved in the preparation of ZnO/InP or ITO/InP junctions by spray pyrolysis deposition of the oxide on single crystal p-type InP; (3) evaluation of phenomena involved in the preparation of CdS/InP junctions, in which the CdS is deposited on the InP single crystal substrate by vacuum evaporation, spray pyrolysis or chemical vapor deposition.

We have also been engaged in the preparation of CdS/InP cells

prepared by vacuum evaporation of CdS onto InP epitaxial layers deposited on p^+ -InP single crystal substrates, and onto polycrystalline InP layers deposited on p^+ -GaAs layers on Mo or glass substrates by the metalorganic chemical vapor deposition method by investigators at Rockwell International.

(3) Photoelectronic Properties of Zinc Phosphide Crystals, Films and Junctions

Graduate Students: J. Nielsen F. C. Wang
C. Y. Ng

The closed tube horizontal growth method has been pursued for the growth of single crystals of Zn_3P_2 . This material is p-type and with a bandgap optimum for photovoltaic cells. The as-grown resistivity of this single crystal material is about 50 ohm-cm, which can be reduced to 10 ohm-cm by subsequent annealing in hydrogen at 410°C. Such crystals have been doped with Ag impurity by diffusion after growth to yield samples with apparent resistivity in the 1 ohm-cm range. Initial Hall effect measurements on a 200 ohm-cm sample indicated $p = 6.2 \times 10^{15} \text{ cm}^{-3}$ and hole mobility = 5.2 $\text{cm}^2/\text{V-sec}$. Good ohmic contacts were made with Ag.

Whereas heat treatment of Zn_3P_2 crystals reduces the resistivity if carried out in H_2 or Ar, a marked increase in resistivity is observed if heat treated in vacuum, and a conducting surface ($ZnO?$) is produced by heat treatment in oxygen. Good rectifying diodes were prepared by vacuum evaporation of Mg onto etched surfaces of Zn_3P_2 . A barrier height of 0.75 eV was measured from capacitance data in good agreement with the published value of 0.80 eV. Layers of Mg with controllable properties have been achieved for such Mg/ Zn_3P_2 diodes.

Zn_3P_2 films deposited on glass by a close-spaced vapor transport (CSV) method were amorphous, whereas those deposited on single crystal CdS were polycrystalline. The resistivity of these films deposited by CSV in Ar is about 1500 ohm-cm. Microprobe analyses of these films consistently give the result of 69 atomic % Zn and 31 atomic % P. Laser annealing of the films does not appreciably change the resistivity but

does aid in crystallization. Thick films of Zn_3P_2 deposited by CSVT with a range of source temperatures between 615° and 695°C showed an activation energy for film growth rate (1.3 micrometers/min to 4.0 micrometers/min) of about 1 eV. Because of these promising initial results on Zn_3P_2 films major improvements are being made in the CSVT process to increase control and reproducibility.

(4) Heterostructures, Homojunctions and Schottky Barrier Solar Photovoltaic Convertors Based on CdTe Prepared by Hot-Wall Flash Evaporation

This program has been initiated with National Science Foundation International Division support in collaboration with the personnel of C.I.E.A. del I.P.N. in Mexico City. Workers in Mexico City have developed a new hot-wall flash evaporation method for the production of n- and p-type CdTe films; we are characterizing these films, preparing junction structures involving the films, and analyzing the properties of these junctions for solar energy conversion.

Reference Publications:

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2. R. H. Bube, F. G. Courreges, A. L. Fahrenbruch, and M. J. Tsai, "Oxide/Semiconductor Photovoltaic Heterojunctions Based on CdTe or InP," in 2nd E.C. Photovoltaic Solar Energy Conference, eds. R. Van Overstraeten and W. Palz, D. Reidel Publishing Co., Dordrecht: Holland (1979), p. 432
3. J. Aranovich, A. Ortiz and R. H. Bube, "Optical and Electrical Properties of ZnO Films Prepared by Spray Pyrolysis for Solar Cell Applications," J. Vac. Sci. Technol. 16, 994 (1979)
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6. F. G. Courreges, A. L. Fahrenbruch and R. H. Bube, "Sputtered Indium-Tin Oxide/Cadmium Telluride Junctions and Cadmium Telluride Surfaces," J. Appl. Phys. 51, 2175 (1980)

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8. W. G. Haines and R. H. Bube, "Tunneling Currents in the Copper Sulfide/Cadmium Sulfide Heterojunction," 14th IEEE Photovoltaic Specialists Conference (1980), p. 718
9. M. J. Tsai, A. L. Fahrenbruch and R. H. Bube, "Sputtered Oxide/Indium Phosphide Junctions and Indium Phosphide Surfaces," J. Appl. Phys. 51, 2696 (1980)

11. IMPROVED NONLINEAR MATERIALS

R. L. Byer, Professor, Applied Physics

Professional Associates:

I. Bass, Sonoma State College
G. Giuliani, University of Rome, Italy
P. Oesterlin, Freiburg University, Germany
J. Unternahrer, Swiss Nuclear Institute, Switzerland

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*Received PhD during report period.

Agency Support:

AFOSR-80-0144
ARO-DAAG29-77-G-0221
NSF-CHE-791-12673
NASA-NSF-2289 and NSG-2372
DOE-LLL-3488009
NSF-MRL through CMR

Technical Objective:

To improve nonlinear, electro-optic and laser materials and to apply new and improved materials to tunable laser devices for problems in laser spectroscopy, analytical measurements, and remote monitoring of air pollution and combustion processes.

Approach:

During the past year we have extended our work on LiNbO_3 for use in parametric oscillator tunable devices. We have grown, fabricated, and tested a number of boules oriented in the 01.3 direction. These crystals have enabled us to successfully operate the tunable source under full computer control for extended times and thus to make significant new measurements in Raman spectroscopy and remote air pollution. We have

also worked closely with local industry to test and evaluate LiNbO_3 material for tunable source applications.

We extended and successfully completed a growth and evaluation program for "hot phasematching" LiNbO_3 , which is suitable for frequency doubling a Nd:YAG laser source. We demonstrated doubling efficiencies of greater than 40 percent. This material is potentially very important for providing high average power in the visible by second harmonic generation of a Nd:YAG laser source.

We have initiated crystal growth of urea which has been shown to be useful for high peak and average power second harmonic generation. This crystal will play an important role in future laser measurement efforts.

12. STUDIES IN CATALYSIS

J.P. Collman, Professor, Chemistry

Professional Associates:

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† Left during report period.

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A.M. Madonik	

* Received Ph.D. during report period.

** Received M.S. during report period.

Agency Support:

NIH GM17880
NSF CHE78-09443
NSF CHE77-22722

Technical Objective:

The long range goals of this research are to model metalloenzymes, to develop homogeneous, multimetallic catalysts, and to invent electrode catalysts for multielectron reductions.

Approach:

We are preparing transition metal porphyrin complexes which mimic the active sites in certain hemoproteins--hemoglobin, myoglobin, and the cytochrome P₄₅₀ oxygenase family. We are also preparing binary "face-to-face" porphyrins which are intended to serve as catalysts

for the oxygen cathode in a fuel cell. We are also developing organo-transition metal reagents for stoichiometric organic synthesis and exploring their reaction mechanisms.

Models for Myoglobin and Hemoglobin

Using our synthetic analogues for the oxygen binding hemoproteins, we have measured the relative equilibrium binding affinities for carbon monoxide and oxygen, thus obtaining the so-called M values for these synthetic analogues. A new "capped" porphyrin shows the M value of myoglobin. This substantiates our earlier hypothesis concerning the role of the distal residues in distorting carbon monoxide and thus lowering its affinity.

Models for Mixed-Function Oxygenases

During the past year we have continued our work attempting to synthesize the synthetic analogues for the active site in the various stages of the cytochrome P₄₅₀ catalytic cycle. This work is still in progress. We are carrying out XAFS studies of model compounds in conjunction with studies of P₄₅₀ to determine the nature of sulfur ligation in the enzymatic system (collaboration with Hodgson).

The Preparation of Catalytic Electrodes

We have completed the syntheses of approximately 20 "face-to-face" binary porphyrins. Several of these compounds have been discovered to catalyze the four-electron reduction of oxygen to water at +0.7 volts (versus SHE) without forming significant hydrogen peroxide. We estimate the turnover number of this reaction at 90 seconds⁻¹. This work is vigorously being pursued as a possible new approach to the oxygen cathode for fuel cell applications.

Transition Metal Clusters and Fischer-Tropsch Catalysis

We have constructed (in collaboration with Michel Boudart) a cyclic reactor and have begun a kinetic analysis of homogeneously catalyzed Fischer-Tropsch reactions recently reported by Muetterties. We have

also constructed an infrared cell capable of withstanding the very corrosive aluminum chloride-sodium chloride melts required for this work. Mechanistic studies of this reaction are still in progress. This work is nearing completion.

Site Isolated Homogeneous Catalysts

We have prepared a silica-bonded bidentate phosphine ligand. Immobilized rhodium catalysts prepared from this ligand have been examined in the context of catalytic olefin hydrogenation and the oxo reaction. These studies are directed towards understanding steps in the reaction mechanisms which might involve more than a single metal center.

Reference Publications:

1. J.P. Collman, M. Marrocco, P. Denisevich, C. Koval, and F. Anson, "Potent Catalysis of the Electroreduction of Oxygen to Water by Dicobalt Porphyrin Dimers Adsorbed on Graphite Electrodes," *J. Electroanal. Chem.* 101, 117 (1979).
2. R.E. Ginsburg, J.M. Berg, R.K. Rothrock, J.P. Collman, K.O. Hodgson, and L.F. Dahl, "The Geometrical Influence of Solid-State Ion-Pair Interactions of Alkali Metal Ions with a Binuclear Iron Acyl Monoanion, $[\text{Fe}_2(\text{CO})_5(\text{C}(\text{O})\text{R})(\mu_2\text{-PPh}_2)_2]^-$ (where R = Ph, Me): Structural Analyses of the $[\text{Li}(\text{THF})_3]$, $[\text{Na}(\text{THF})_2]^+$, and $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Salts," *J. Am. Chem. Soc.* 101, 7218 (1979).
3. J.P. Collman, T. Kent, K. Spartalian, G. Lang, T. Yonetani, and C. Reed, "High Magnetic Field Mossbauer Studies of Deoxymyoglobin, Deoxyhemoglobin, and Synthetic Analogues," *Biochim. et Biophys. Acta* 580, 245 (1979).
4. R.E. Ginsburg, R.K. Rothrock, R.G. Finke, J.P. Collman, and L.F. Dahl, "The (Metal-Metal)-Nonbonding $[\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)_2]^{2-}$ Dianion: Synthesis, Structural Analysis of its Unusual Dimeric Geometry, and Stereochemical-Bonding Implications," *J. Am. Chem. Soc.* 101, 6550 (1979).
5. J.P. Collman, J.I. Brauman, and K.M. Doxsee, "Carbon Monoxide Binding to Iron Porphyrins," *Proc. Natl. Acad. Sci. USA* 76, 6035 (1979).
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7. J.P. Collman, G.B. Jameson, F.S. Molinaro, J.A. Ibers, K.S. Suslick, and J.I. Brauman, "Models for the Active Site of Oxygen-Binding Hemoproteins: The Structures and Dioxygen Properties of (2-Methylimidazole)meso-tetra(, , , -o-pivalimidophenyl)-porphyrinatoiron(II)· Ethanol and its Dioxygen Adduct," J. Am. Chem. Soc. 102, 3224 (1980).
8. J.P. Collman, T.R. Halbert, and K.S. Suslick, "Oxygen Binding to Heme Proteins and their Synthetic Analogs," Chapter 1 in Metal Ion Activation of Dioxygen, T. Spiro, Ed., Wiley, New York (1980).
9. J.P. Collman, J.I. Brauman, K.M. Doxsee, T.R. Halbert, E. Bunnenberg, R.E. Linder, C.N. LaMar, J. Del Gaudio, G. Lang, and K. Spartalian, "Synthesis and Characterization of 'Tailed Picket Fence' Porphyrins," J. Am. Chem. Soc. 102, 4182 (1980).

13. THEORETICAL PHYSICS OF CONDENSED MATTER

S. Doniach, Professor, Applied Physics

Professional Associates:

B. A. Huberman
I. Lindau

Graduate Students:

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S. A. Trugman*
Se-Jung Oh

*Received MS during report period.

Agency Support

NSF DMR79-13102 (I. Lindau, Principal Investigator)
NSF-MRL through CMR

Research Report:

(1) Motion of Vortices in Two-Dimensional Granular Superconductors

For thin films in which the superconducting grains (about $100 \text{ \AA}$ in diameter) are weakly coupled by insulating Josephson junctions, the phase disordering temperature T_{2D} is expected to occur at a small fraction of the BCS transition temperature T_{BCS} of the bulk superconductor. At intermediate temperatures $T_{2D} < T < T_{BCS}$ work with S. Trugman leads to the conclusion that free thermally excited vortices will tend to be localized by the random effective potential resulting from a random distribution of Josephson couplings. Fluctuations in phase due to electric coupling to normal currents lead to an inelastic dephasing time $\tau \sim e^{T/T_{BCS}}$. As τ becomes very long it is expected that the decay of superflow leading to electrical resistivity due to vortex migration will become dependent on the size of the sample. For intermediate values of τ we show that the vortices undergo a diffusive motion in the random potential leading to a resistivity which depends slowly on temperature. This may explain the "foot" seen in resistance-temperature curves for systems of this type.

(2) Extension of Kosterlitz Scaling Theory to the Vortex Plasma
Regime of Thin Film Superconductors

The theory of Kosterlitz and Thouless of vortex depairing in thin (2-dimensional) superfluids is being extended into the regime (finite applied magnetic field or $T > T_{2D}$) where an appreciable fraction of vortex-antivortex pairs are unbound. Work with S. Trugman to extend the Kosterlitz renormalization group to a system of vortices interacting through a screened potential $K_0(kr)$ (the 2-D analog of the Yukawa potential) has shown that in the low density regime, the form of the potential is reproduced when the effect of short range pairs is integrated out, but with a modified screening length. For $T < T_{2D}$ the screening length κ^{-1} decreases very slowly upon scaling, while for $T > T_{2D}$ it increases very rapidly. The resulting scaling equations for κ , vortex charge and chemical potential should enable an interpolation between the Kosterlitz behaviour and the high temperature Debye-Huckel limit. If this proves to be the case, the theory will allow a systematic formulation of the Doniach-Huberman calculation of the effect of weak magnetic fields on the resistivity of thin film superconductors.

(3) Effects of Pinning on Superflow of Thin Films

Work with D. Browne on the kinetics of vortex motion in the presence both of pinning centers and vortex-antivortex depairing has led to the formulation of a set of kinetic equations in which the effects of "creep" leading to a decay of superflow proportional to the logarithm of the time and of depairing leading to a power law in t have been combined. Fits to data of Hallock on decay of superflow in thin He^4 films lead to the conclusion that pinning effects play an important role in the observed decay, even though the density of pinning sites in the film is relatively small. A preliminary account of these results has been published.

(4) Nonlinear Effects in Vortex Depairing

Work with D. Browne on the dynamics of vortex-antivortex unbinding in the presence of an oscillating supercurrent has led to a nonlinear dependence of the depairing rate on superfluid velocity which is an extension of work of Ambegaokar and Teitel on the Fokker-Planck equation for vortex motion. The calculations should lead to an understanding of nonlinear response of thin superfluid films to the oscillations of the substrate observed by Reppy and his students at Cornell University. Similar calculations would apply to the measurement of the dynamic diamagnetism of thin superconducting films observed by Hebbard and Fiory at Bell Labs if these measurements are extended to the nonlinear regime.

(5) Relaxation Effects in Resonant Photoemission

Work with Se-Jung Oh has led to a calculation of the expected line shape of photoemission lines in the case where the incoming photon excites an intermediate resonant state. Relaxation effects in which the solid being irradiated reacts to the primary photoexcitation by the formation of plasmons and electron-hole pairs have been considered. We show that the satellite structure (in the case of plasmons) has an intensity which in general will be expected to exhibit at least two resonant peaks as the photon energy is tuned through the resonance, corresponding to excitation of the fully or partially relaxed intermediate state. The theory is being applied to resonant photoemission observations in Ce metal conducted by I. Lindau and collaborators. The general approach will also be applicable to a variety of other spectroscopies such as Raman scattering and Auger emission, and may be useful in studying the nature of the electronic coupling for chemisorbed atoms on metallic substrates.

Publications:

B.A. Huberman and S. Doniach, "Melting of Two Dimensional Vortex Lattices," to appear in Phys. Rev. Letters.

R. Jullieu, P. Pfeuty, J.N. Fields, and S. Doniach, "Theoretical Study of the Kondo Lattice," J. de Physique 40, C5-20 (1979).

Publications: (cont'd)

D.A. Browne and S. Doniach, "Effects of Pinning on the Decay of Superflow in Thin Superfluid Films," Proc. Conference on Inhomogeneous Superconductors. AIP Conference Series, 1980.

B. Huberman and S. Doniach, "Topological Excitations in Thin Superfluid Films: A Review," Proc. Conference on Inhomogeneous Superconductors. AIP Conference Series, 1980.

14. THEORETICAL AND EXPERIMENTAL BIOPHYSICS

S. Doniach, Professor, Applied Physics

Professional Associates:

K. O. Hodgson
C. R. Natoli
R. Fairclough

Graduate Students:

D. K. Misemer
F. W. Kutzler
R. C. Lye

Research Report:

(1) Quantum Chemistry of X-ray Absorption Edge Structure

An extensive series of computations of the one-electron photo-absorption cross section of molecular clusters is now coming to fruition. Calculations showing gross chemical effects — the change in K-edge absorption spectrum of Ge on going from GeH_4 to GeCl_4 are being published in Phys. Rev. A. An extensive study of K-absorption in transition metal complexes MoO_4^{2-} , MoS_4^{2-} and CrO_4^{2-} has been completed and shows rather satisfactory agreement with experiment. In particular the enabling of $1s \rightarrow 3d$ transitions by the symmetry breaking tetragonal field of the ligand shows up very clearly. The position of the continuum edge and the appearance of continuum "shape resonances" provides the first systematic explanation of a number of spectral features previously interpreted (and sometimes misinterpreted) using only atomic level assignments. We now have a quantitative understanding of the role of the ligand 'cage' in controlling the position and width of the continuum resonances. This work is to appear in J. Chem. Phys.

Current research is directed to understanding the very prominent spectral features, so-called "white lines", which appear at L_{II} and L_{III} edges of a number of elements, including the rare-earths. We are also calculating the expected dependence of absorption spectra of anisotropic molecules on X-ray polarization, observed at SSRL by K. O. Hodgson and his group.

(2) Anomalous Small Angle X-ray Scattering from Biological Molecules

The structure of many important biological molecules — proteins and membrane systems — is hard to elucidate using conventional X-ray crystallographic techniques owing to the fact that they do not readily form single crystals. Small angle X-ray scattering has been used for a number of years to gain structural information for noncrystalline systems, but the information is hard to extract owing to the angular averaging (as in "powder patterns") of the diffracted rays.

Anomalous X-ray scattering has been used in crystallography to help solve the phase problem of inverting the diffracted intensity to obtain the electron density of the scattering molecule. We are currently applying similar techniques to help sort out the structure of noncrystalline materials. In particular by chemically labelling with one or more rare earth atoms, and tuning the X-ray wavelength through the X-ray L-absorption edge we have demonstrated very large anomalous scattering effects in small angle scattering from Tb-doped parvalbumin and Tb-doped acetylcholine receptor membranes from electric fish. The latter are of particular biophysical interest as they contain molecular assemblies about $100 \text{ \AA}$ across which function as a kind of "biological transistor", switching about 10^4 sodium ions in 1 msec in response to the arrival of one acetylcholine molecule.

To further these studies, R. C. Lye has constructed a small angle X-ray camera for use at SSRL in conjunction with a linear electronic position sensitive proportional counter functioning at up to 50 kHz. The resulting diffraction patterns may be taken in 80 minutes at SSRL compared to about 24 hours using a conventional X-ray tube.

Publications:

R.C. Lye, J.C. Phillips, D. Kaplan, S. Doniach, and K.O. Hodgson, "White Lines in L-edge X-Ray Absorption Spectra and Their Implications for Anomalous Diffraction Studies of Biological Molecules," Proc. Nat. Acad. Sci. USA, in press.

C.R. Natoli, F.W. Kutzler, D.K. Misemer, and S. Doniach, "First Principles Calculation of X-Ray Absorption Edge Structure in Molecular Clusters," Phys. Rev. A, in press.

Publications: (continued)

F.W. Kutzler, C.R. Natoli, D.K. Misemer, S. Doniach, and K.O. Hodgson, "Use of One Electron Theory for the Interpretation of Near Edge Structure in K Shell X-ray Absorption Spectra of Transition Metal Complexes," J. Chem. Phys., in press.

15. COAL SLAG PHENOMENA IN OPEN CYCLE MHD GENERATORS

R. H. Eustis, Professor, Mechanical Engineering and Director, High
Temperature Gasdynamics Laboratory

Professional Associates:

C. H. Kruger, Professor, Mechanical Engineering
J. K. Koester, Senior Research Associate

Graduate Students:

P. C. Ariessohn
R. M. Nelson

Agency Support:

EPRI RP468-1

Technical Objective:

The technical objective of this research program is to provide an understanding of the effect of coal slag deposits on the performance of magnetohydrodynamic (MHD) generators. These deposits are expected to influence the fluid mechanics, electrical performance, and materials selections for MHD generators.

Approach:

The program involves studies of the fluid mechanics of slag layers including the mechanism of deposition, the effect of slag droplets and mineral vapor on plasma conductivity, and the effect of slag layers on the electrical performance of MHD generators. A special effort is made to incorporate extensive diagnostics into the experimental program for direct measurement of as many parameters as possible. The laboratory program is accompanied by a modeling effort which is useful both in understanding the physical processes which occur and in extrapolating results to other conditions or to larger scale systems.

Research Report:

(1) Ash Droplet Size and Concentration

A two-wavelength laser transmissometer has been used to make in-situ measurements of ash droplet size and concentration in a coal combustion plasma. Combustor parameters were varied to achieve various ash loadings, fuel/air equivalence ratios, flame temperatures and residence times. The measurements were performed utilizing both Illinois #6 and Montana Rosebud coals. Ash droplet mean diameters of 1.4 to 2.8 μm have been observed with Illinois #6 coal and mean diameters of 1.3 to 2.2 μm have been observed with Montana Rosebud coal. Ash droplet size appears to be a decreasing function of temperature and to be relatively independent of stoichiometry, residence time and ash loading.

(2) High Temperature Slagging Electrodes

A high-temperature (1700-1900°K) platinum alloy capped magnesia electrode was developed and successfully tested for diffuse operation at current densities up to 3 amps/cm². The transition current density for arcing was determined as a function of electrode temperature. The electrical characteristics (including electrode voltage drops) of a high-temperature electrode section and a cold electrode section were measured at three levels of magnetic field and compared. Hall voltage and interelectrode AC resistance distributions were measured and correlated with the plasma core behavior inferred from voltage probe measurements. A diffuse mode, two-dimensional model for current density and potential distributions was developed which includes the effects of slag layer hydrodynamics, slag layer energy transport, and assumed plasma boundary layers. Numerical solutions for this model are presented as a function of wall temperature and magnetic field.

Reference Publications:

1. J. K. Koester and R. A. Perkins, "Discharge and Corrosion Characteristics of Slagging Metal Electrodes for MHD Power Generators," J. Materials for Energy Systems, 1, 2 (Sept. 1979), 41-54

2. P. C. Ariessohn, R. H. Eustis, and S. A. Self, "Measurements of the Size and Concentration of Ash Droplets in Coal-Fired MHD Plasmas," 7th International Conference on MHD Electrical Power Generation, Boston, Mass., June, 1980.
3. R. M. Nelson and J. K. Koester, "Diffuse Mode Current Transport in a Slagging MHD Generator," *ibid.*

16. EXPERIMENTS AT LIQUID HELIUM TEMPERATURES ON MACROSCOPIC QUANTUM EFFECTS,
MATERIAL PROPERTIES, GENERAL RELATIVITY, AND SUPERCONDUCTING ACCELERATORS

W. M. Fairbank, Professor of Physics
C. W. F. Everitt, Adjunct Professor
R. P. Giffard, Assistant Professor of Physics
H. A. Schwettman, Professor of Physics

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G. S. LaRue	M. A. Taber
J. A. Lipa	R. C. Taber
	J. P. Turneure

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P. F. Michelson*	G. A. Westenskow

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Agency Support:

NSF PHY76-23559	AFOSR 80-0067
NSF MPS73-08748-A04	AFOSR 80-0026
NSF PHY76-80105	AFOSR F49620-77-C-058
NSF PHY73-08870	NASA NCA2-OR745-708
NSF PHY76-80168	NASA NGR-05-020-019
ONR N00014-76-C-0848	ERDA EY-76-S-03-0326, PA48
ARMY DASG60-77-C-0083	ERDA EY-76-S-03-0326, PA49

Technical Objective:

This research is directed toward the study of the basic problems of physics using low temperature techniques. In addition to experiments studying the special properties of superconductors and helium for their sake, we exploit their unique properties to perform experiments in other fields of physics such as gravitation and relativity, biophysics and medicine, particle accelerators and the search for fractionally charged particles.

Research Report:

(1) Positron Source and Photon Counting Detector

Research Associates: J. M. Madey

Graduate Student: G. A. Westenskow

A source of magnetic ground state positrons at energies below 10^{-7} eV is required for operation of the positron free fall experiment. Positrons in this energy range cannot be obtained from natural β^+ emitters.

The approach we have adopted is to capture a small number of relatively low energy (~ 100 eV) positrons and to trap them within a solenoidal magnetic field between electrostatic mirrors. Provided that the trap proves to be stable, the positrons can readily be thermalized to energies of the order of 10^{-4} eV. Adiabatic expansion can be used to lower the energy to the required 10^{-7} eV.

The availability of low energy ground state electrons from a thermalization process of this type makes possible the development of a photo-electric effect detector for use at millimeter wavelengths. The detector is based on excitation of the $n = 1$ cyclotron level of magnetic ground state electrons trapped in a high Q cavity resonant at the cyclotron frequency. Theoretical estimates of the performance predict a noise temperature less than 1°K and quantum efficiencies of the order of 10%. Such a detector would have immediate application in millimeter wave radio astronomy.

We are now testing a prototype thermalizer which can function as a photon counting detector. Trapping and partial thermalization have been achieved; improvements in progress should help realize complete thermalization.

(2) Force of Gravity on Elementary Charged Particles and Surface Shielding Effect

Graduate Student: J. Henderson

Low energy electron beam techniques have been developed which permit the measurement of the force of gravity on slow electrons and positrons, thus allowing a direct test of the gravitational equivalence of matter and anti-matter. The electron experiment has already been performed, yielding results which seem clear, but which also seem to indicate the presence of an unexplained shielding effect in the metallic drift tubes used in this experiment. Recent work has been directed toward exploring the nature of this shielding effect and the conditions under which it exists. There appears to be strong evidence for the presence of a large temperature dependence in the magnitude of the shielding. Experiments are now in progress to determine the detailed behavior of this temperature dependence. Measurements on the positron await the completion of a source of ultra-low energy positrons; a prototype of this source is now being tested.

Other techniques are now being employed to study the surface properties of oxidized copper in an effort to understand the physical basis for the surface shielding effect. These techniques include microwave surface impedance studies, sensitive contact potential measurements with a vibrating plane capacitor, and high resolution magnetic susceptibility measurements.

(3) Search for a Quark

Postdoctoral Student: George LaRue

Graduate Student: Jim Phillips

The purpose of this experiment is to search for fractionally charged particles (quarks) on superconducting niobium spheres supported by a magnetic field. The experiment measures the net electric charge on a niobium ball of mass approximately 5×10^{-5} gm. Fractionally charged particles, if they are contained on a niobium ball, would be observable as a non-integral net charge on the ball. Measurements have been made on nine niobium balls with a sensitivity of approximately $\pm 0.02 e$, where e is the electron charge. Forces simulating non-integral residual charges have been observed on some of these balls. The central issue in this experiment is to determine unambiguously whether or not these forces are due to fractional charges or are caused by spurious dipole forces. The spurious forces have been accounted for and the results indicate that there are fractional charges on matter. Four balls were heat-treated on a tungsten plate and the residual charges were $(+.337 \pm .009)e$, $(-.001 \pm .026)e$ and $(-.331 \pm .070)e$ and $(+.345 \pm .035)e$. On five balls heat-treated on a niobium plate the residual charges were close to zero.

(4) Development of a Sensitive Cryogenic Gravitational Wave Detector

Research Associates: M. S. McAshen

C. Chun

R. C. Taber

P. F. Michelson

Using cryogenic techniques it is possible to make extremely sensitive gravitational radiation detectors. We are presently developing a low temperature detector which, in its present configuration, will be more than 10^3 times more sensitive than the room temperature antennas which have been used until now. The main concept of the detector is a 4800 kg aluminum antenna which will be maintained at a temperature between 1.5 and 4 K. The amplitude of vibration in the fundamental mode of the antenna is converted to an electrical signal by a superconducting resonant transducer, and amplified by a Josephson effect parametric

device operating at 9 GHz. During the past year various components were finally tested, and assembly of the detector completed. A preliminary test of the cryostat without the antenna was successful, and the complete detector was cooled to liquid helium temperature for the first time. Preliminary measurements show that the detector is capable of a noise temperature for pulse detection of 3 mK. Potential for at least another order of magnitude in sensitivity exists without substantial modification of the detector or cryostat.

In the next year we intend to use the detector in measurements of the background flux of gravitational radiation at a sensitivity level between three and four orders of magnitude better than previous experiments. The level of sensitivity attained will be sufficient to detect the radiation of less than $10^{-2} M_0 c^2$ into gravitational waves of bandwidth 10^3 Hz at the galactic center. We also plan to pursue vigorously a program to improve the sensitivity of the detector with particular emphasis on the transducer.

(5) Interfacial Surface Energy Between Superfluid Helium-3A & B Phases

Graduate Student: B. J. Neuhauser

I will measure the surface energy between the superfluid A & B phases of helium-3 by observing the motion of the AB phase boundary when it encounters a grid while the helium-3 sample is being slowly cooled. A pickup coil senses the flux produced by magnetization of the superfluid phases and couples it into a SQUID via a superconducting transformer. Because $X_A > X_B$, changes in the distribution of A & B phases cause changes in flux which are readily detected by the SQUID system.

Cooling to millidegree temperatures is accomplished by demagnetizing a CMN salt pill which is in intimate contact with the helium-3. Thermometry is done by measuring the susceptibility of lanthanum-diluted CMN. Precise temperature and pressure control systems have been developed for this experiment.

(6) Experiments in Very Low Magnetic Fields

Research Associate: B. Cabrera

We have obtained magnetic fields smaller than 10^{-8} gauss in a cylindrical superconducting lead shield that is four inches in diameter and thirty inches long. This magnetic field level, an order of magnitude smaller than we had previously obtained, corresponds to at most a few flux quanta trapped in the superconducting shield. We are using a superconducting double point-contact magnetometer with a resolution of 10^{-9} gauss to measure the very small magnetic fields. We have constructed an apparatus to measure the magnetic flux trapped in a superconducting cylinder 1/2 inch in diameter by 4 inches long. We have the sensitivity to see individual flux quanta penetrating the walls of this cylinder, and thus study the pinning of flux in superconductors. One of these shields has been used in conjunction with a detection coil coupled to a SQUID as a magnetic monopole detector. Our present sensitivity is 1/50 of a Dirac monopole. Our data to date is consistent with zero magnetic charge.

(7) Nuclear Polarization of He^3

Graduate Student: M. A. Taber

We have used He^3 optical pumping techniques to produce dilute polarized He^3 and He^4 gas mixtures. Such mixtures have been successfully condensed into a low magnetic field region and the precession of the He^3 magnetization has been observed in an applied transverse field of 10^{-4} gauss by use of a SQUID magnetometer. Initial magnetization has been greater than 10^{-5} gauss with a signal to noise of 1000 to 1. We have completed a series of experiments to measure the spin-lattice relaxation time (T_1) of the liquid He^4 -polarized He^3 mixture under various conditions and as a function of applied field. The relaxation times vary from approximately 4 hours at 55 μ gauss to 35 hours at 1.8 mgauss for a bare Pyrex sample bulb. Using a solid H_2 wall coating of ~40 molecular layers thick has yielded a relaxation time of 130 hours at 2.9 mgauss. At lower fields the relaxation times approached those of the bare bulb.

These experiments are a continuation of an effort devoted to development of a He^3 nuclear gyroscope.

(8) Magnetocardiology (Joint Project with Stanford Hospital)

Graduate Student: M. C. Leifer

We are developing two new magnetic techniques for non-invasive clinical observation of human cardiac function. The first measures magnetic susceptibility changes associated with the motion of blood within the heart. The second technique involves the use of a superconducting gradient magnetometer to measure the magnetocardiogram, the magnetic field generated by the electrical activity of the heart. We have built a large magnetic shield and a computer signal-processing system. The clinical value of the magnetic field measurements will be determined by studying normal patients and patients with various cardiac diseases.

(9) Josephson Effect and Superconducting Magnetometers

Assistant Professor: R. P. Giffard

Research Associate: P. F. Michelson

The general features of the Josephson effect are now well known, and superconducting weak links are widely used in sensitive magnetometers and amplifiers (SQUIDS). We are studying in detail the sources of noise in existing magnetometers and attempting to measure typical noise temperatures in the frequency range 1-10 kHz. In order to understand the high frequency limitations of weak links, we are using microwave impedance measurements at X-band to compare details of their behavior with theory. An outstandingly sensitive SQUID magnetometer has been developed and tested at 9.1 GHz.

(10) Equivalence Principle Accelerometer

Adjunct Professor: C. W. F. Everitt

Research Associate: P. W. Worden, Jr.

The experiment is intended to test the application of cryogenic technology to a measurement of the uniqueness of free fall, particularly

with regard to investigating the ultimate limitations to sensitivity and a possible earth-orbiting equivalence principle experiment. A pair of superconducting test masses of different materials are suspended in essentially frictionless linear magnetic bearings. The masses are cylindrical with dimensions optimized to minimize gravity gradient effects, and are free to move along the cylinder axis. An electronic control mechanism keeps each mass centered with respect to the casing by tilting the support plane provided by the magnetic bearing. The control efforts required to keep the masses centered are appropriately scaled and subtracted to one part in 10^5 , providing a signal proportional to any differential acceleration which may exist. The difference signal may then be recorded and Fourier analyzed to determine the relative amplitudes of the various frequency components.

The limiting sensitivity of the experiment on earth is set by seismic noise and the accuracy of the subtraction process. A difference of one part in 10^{12} in the ratio of inertial to gravitational mass is estimated to be the limit of sensitivity on earth. In low earth orbit the sensitivity is limited by tidal sloshing of the liquid helium refrigerant and is probably one part in 10^{17} .

(11) Relativity Gyroscope Experiment

Adjunct Professor: C. W. F. Everitt
Senior Research J. A. Lipa
Associates: B. Cabrera
J. T. Anderson
Research Associate: G. M. Keiser

In 1960 Professor Leonard Schiff of Stanford University suggested a new test of general relativity based on observing the precessions of very accurate gyroscopes in an earth-orbiting satellite. Since 1962, a group of physicists and engineers from the Hansen Laboratories and the Department of Aeronautics and Astronautics have been designing and developing the experiment using cryogenic techniques. A model of the flight gyroscope and liquid helium dewar has now been operating at Stanford for a number of years. The experiment is expected to be flown in 1985.

(12) Superconducting Meson Channel

Professor: H. A. Schwettman

Research Associate: R. C. Taber

A superconducting pion channel has been developed and constructed. It consists of two 10 ft. diameter torroidal superconducting magnets, each having 60 pancake forms. Cooling is achieved by conduction from liquid helium tubing placed on the edge of the coil forms. This novel application of large scale superconducting technology results in a large solid angle exceeding 1 steradian for the collection of pions. The purpose of the magnet is to collect and deliver pions for use in cancer therapy in a proposed hospital facility.

The present research program is devoted primarily to dosimetry and radiobiology measurements. These measurements are intended to provide the basis for designing and operating the proposed facility.

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17. MOLECULAR EXCITED STATE DYNAMICS IN THE CONDENSED PHASE

M. D. Fayer, Associate Professor, Chemistry

Graduate Students:

D. E. Cooper*	L. Madison
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Research Report:

A. Intermolecular Interaction Dynamics and Optical Dephasing: Pico-second Photon Echo Measurements in Mixed Molecular Crystals¹

Picosecond optical coherence techniques are employed to study dynamical intermolecular interactions in low concentration mixed molecular crystals, i.e. pentacene in naphthalene at 1.4 K. A concentration-dependent broadening of the optical homogeneous line is observed. Stimulated photon echo measurements rule out excited state transport as the broadening mechanism. The photon echo results exhibit a linear concentration dependence and a theory is proposed that accounts for the broadening in terms of phonon-induced fluctuations in guest-guest dipole-dipole interactions. Detailed considerations indicate that the system is best described in terms of localized excitations rather than delocalized impurity band states. In the low concentration limit, there is additional broadening of the homogeneous line beyond that produced by the lifetime. A model is presented describing this broadening in terms of phonon-induced modulation of the guest-host van der Waals interactions, i.e. in terms of a fluctuating crystal shift.

B. Laser Induced Phonons: A Probe of Intermolecular Interactions in Molecular Solids²

A new type of density dependent spectroscopy is developed and applied to the study of acoustic phonons and excited state-phonon interactions in molecular crystals. It is shown that intermolecular separations in solids can be varied in a controlled manner along a selected crystalline direction and that the consequences of the molecular displacements can be observed optically in time resolved transient grating, absorption and fluorescence experiments. The technique involves the generation of specific acoustic waves (phonon modes of definite wave vector) by transient grating optical excitation of the sample. The resulting time-dependent density changes cause time-varying spectral shifts, the magnitude of which are dependent on the detailed nature of the anisotropic intermolecular interactions in the crystal, e.g. anisotropic van der Waals interactions in molecular crystals can be directly investigated. First a formalism is presented which permits the determination of the nature of the phonons produced (longitudinal, quasi-longitudinal, or quasi-transverse) by transient grating excitation in anisotropic crystals. Next, the effect of the transient grating generated phonons on experimental observables (absorption, fluorescence and transient grating) due to anisotropic spectral shifts is obtained. Model calculations illustrate the results. Finally experimental data for the perylene pure crystal excimer system are presented. The various types of phonons predicted by theory are observed and phonon dispersions are obtained for several crystal directions. Direction dependent excimer spectral shifts are also observed.

C. Exciton Scattering and the Dephasing of ESR and Optical Absorption Lines: The 1,2,4,5-Tetrachlorobenzene Triplet Exciton Problem³

The relationship between exciton scattering induced dephasing of the ESR and the optical transitions of triplet exciton bands is examined by properly including exchange in the lineshape formalism. First, a simple heuristic model demonstrates that while the optical dephasing time can be associated with the exciton scattering rate, the

ESR dephasing time is more closely associated with the distribution of final states in the scattering process. The full exchange problem is then examined and a formal solution is obtained for the low power steady state ESR spectrum. Application to the 1,2,4,5-tetrachlorobenzene triplet exciton system shows that the exciton ESR spectrum with its associated 1 μ sec dephasing time can be reproduced using a 20 psec exciton scattering rate obtained from the optical dephasing time. Exciton scattering occurs to a small region of k space (~5% of the band) surrounding the initial k state. These results resolve the apparent conflict between the optical and ESR spectra in this system and indicate that exciton transport, while not strictly coherent, is nonetheless predominantly wavelike in character.

D. Site-Dependent Vibronic Linewidths and Relaxation in the Mixed Molecular Crystal Pentacene in p-Terphenyl⁴

The different linewidths and shapes observed in absorption spectra of the first vibronic transition of the four sites of pentacene in p-terphenyl are examined. A model involving vibrationally-induced line narrowing and lattice coupling is suggested to explain the differences. The importance of local environment in vibrational relaxation is discussed.

Reference Publications:

1. D. E. Cooper, R. W. Olson and M. D. Fayer, "Intermolecular Interaction Dynamics and Optical Dephasing: Picosecond Photon Echo Measurements in Mixed Molecular Crystals," J. Chem. Phys. 72, 2332 (1980).
2. K. A. Nelson and M. D. Fayer, "Laser Induced Phonons: A Probe of Intermolecular Interactions in Molecular Solids," J. Chem. Phys., May (1980).
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18. CRYSTAL GROWTH

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D. Elwell, Associate Director, Crystal Synthesis, Center for Materials Research

R. K. Route, Senior Research Associate, Center for Materials Research

Professional Associates:

A. Borshchevsky (no longer at Stanford)	R. A. Huggins
	W. L. Kway
R. L. Byer	G. M. Rao
R. C. De Mattei	W. A. Tiller
T. H. Geballe	

Technical Assistants:

S. M. Cain
R. A. Carranza
R. J. Raymakers
M. M. Simkins

Graduate Students:

K. S. Ahn
F.-C. Wang
S. Westphal

Agency Support:

DOE through CMR
NAVAIR through CMR
NASA through CMR
ONR through CMR

Rockwell International Science
Center through CMR
Hughes Research Laboratories
through CMR

Technical Objective:

To develop sufficient understanding of crystal growth processes to enable the preparation of a wide variety of materials with closely controlled properties.

Approach:

Through careful evaluation of thermodynamic and kinetic factors combined with detailed analysis of experimental parameters, optimized

growth conditions can be achieved for most materials. Studies of phase equilibria, nucleation, growth anisotropy, interface morphology and thermal and mechanical stresses are particularly important parameters in crystal growth.

Research Report:

(1) Electrodeposition of Silicon for Solar Cells

D. Elwell, R. S. Feigelson, S. Cain, R. C. De Mattei, R. A. Huggins, and G. M. Rao

Silicon is the material most likely to meet the challenge of low production cost which is the most difficult requirement for terrestrial solar cells. The aim of this investigation is to develop techniques for the economic production of polycrystalline silicon by electrocrystallization of molten salts.

Inclusion-free deposits of silicon have been made on silver and graphite substrates at 750°C using a solution of K_2SiF_6 in the LiF/NaF/KF eutectic. The highest purity layers contain only 10 ppm of total impurities, so this process shows great promise for the production of large area solar cells.

The alternative approach which is being pursued is to deposit bulk silicon by a method analogous to the Hall process for aluminum production. This method relies on electrodeposition of silicon above its melting point, so that very rapid deposition rates can be achieved. A furnace has been designed and constructed for electrodeposition at temperatures in the range 1420°-1500°C and the first electrodeposition of silicon in the liquid state was achieved using a $BaO/SiO_2/BaF_2$ melt. The deposit is in the form of roughly spherical particles up to 5 mm in diameter and 99.98% purity without any pre-electrolysis. Studies are in hand to improve the purity and to develop a process for efficient removal of the silicon from the melt.

(2) Electrodeposition of Silicon Carbide

D. Elwell, R. S. Feigelson, S. Cain, R. C. De Mattei, and
M. M. Simkins

Silicon carbide is potentially of great importance as a high-temperature semiconductor. No method presently available has given bulk crystals of semiconductor quality and this is the first attempt to use electrodeposition for this purpose.

The synthesis of SiC by molten salt electrolysis has been achieved using three melts: $K_2SiF_6/Li_2CO_3/LiF/KF$ at approximately 750°C, $SiO_2/Na_2CO_3/NaBO_2/LiF$ at approximately 750°C, and Li_2CO_3/SiO_2 at approximately 1000°C. The synthesis of SiC below 1000°C does not seem to have been reported previously. Best results were obtained, however, using the Li_2CO_3/SiO_2 melt. The deposits often contain an excess of carbon in the form of graphite and current studies are centered upon the production of single phase deposits and on improving grain size so that epitaxial layers may eventually be deposited on single crystal SiC substrates.

(3) Crystal Growth of Gallium Nitride

D. Elwell, R. S. Feigelson, W. A. Tiller, M. M. Simkins, and
S. Westphal

GaN is a wide-band semiconductor which can be used for LED's and lasers operating in the blue and blue-green wavelength regions. Although it has been deposited as fairly pure epitaxial layers on sapphire, bulk crystals are not yet available. The aim of this investigation is to prepare crystals from solution in gallium.

Best results have been obtained by flowing ammonia with hydrogen over drops of gallium each weighing about 0.1 g. The GaN is produced by a surface reaction and crystals up to 1.5 mm in size have been grown. The crystals are amber in color and translucent. Multinucleation makes it difficult to grow large crystals and the present phase of the program is concerned with studies of crystal growth and nucleation as a function of supersaturation and temperature.

(4) Stability of Crystal Growth from the Melt

D. Elwell, R. S. Feigelson, K. S. Ahn, R. A. Carranza, and
W. A. Tiller

The problem of stability of growth of a plane interface is one of the most important in crystal growth. The aim of this investigation is to obtain a comprehensive set of data on maximum stable growth rates and material parameters for a model system, for comparison with theories of morphological stability.

Cesium cadmium chloride CsCdCl_3 has been chosen as the material for this investigation and has been found particularly suitable for direct observational studies at temperatures below $600\text{--}650^\circ\text{C}$ where thermal radiation becomes troublesome. Cobalt has been found to be the most suitable dopant and attempts will be made to measure the Co profile in the region of the solid-liquid interface using a laser absorption method.

The study includes Co segregation measurements using crystals grown by the pulling from doped melts. The equilibrium segregation coefficient for growth in the (0001) direction has been found to be 0.16 and segregation measurements in various crystallographic directions as a function of growth rate and crystal rotation rate are in progress.

(5) Growth of $\text{GdDy}(\text{MoO}_4)_3$ Single Crystals

W. L. Kway and R. S. Feigelson

The rare earth molybdate $\text{GdDy}(\text{MoO}_4)_3$ belongs to a class of materials recently found to be of great importance. These materials exhibit not only ferroelectric, piezoelectric, and pyroelectric properties, but also ferroelastic properties. When these materials are used in electro-optic or acousto-optic devices, the ferroelastic properties can be utilized to modulate electromagnetic or acoustic energy through the movement of domain walls when an electric field is properly applied.

The choice of $\text{GdDy}(\text{MoO}_4)_3$ for the present study was made based on two factors: (1) great device potential, and (2) ease in single crystal growth. As indicated by previous studies, single crystals may be grown with reasonable success by the Czochralski technique. However, since impurity inclusions are an inherent problem with rare earth oxides, together with the problem of volatility of MoO_3 , further study and technique development are needed in its material preparation in order to

improve the compositional quality. Also, since there are several phase transitions which may occur during slow cooling of the crystal from growth to room temperature, special techniques for annealing and quenching of the crystal must be developed in order to obtain crack free boules of reasonable size.

(6) Growth of CdTe Crystals

R. S. Feigelson and R. J. Raymakers

Cadmium telluride crystals have been grown in the CMR Crystal Laboratory over the past few years for use as substrates for heterojunction photovoltaic cells. Boules were grown by the vertical Bridgman method in sealed quartz ampoules and were typically polycrystalline with the number of grains per boule varying from as few as three to greater than twenty. Attempts to correlate polycrystallinity with various growth conditions such as growth rate, temperature gradient and composition gave only tenuous results, but decanting experiments did show that the growth interface shape was concave with respect to the crystal, a condition which favors multigrain structures. It was found difficult experimentally to create a planar or slightly convex interface shape.

A few studies, particularly in the Russian literature, suggested that the introduction of low frequency acoustic vibration into the growth system improved grain size in certain castings and crystal growth experiments. Also, it has been thought that crucible rotation in Bridgman growth leads to improved quality.

A modification of our CdTe growth apparatus was made to permit both crucible rotation and the application of mechanical vibrations to the growth ampoule. Preliminary experiments were recently carried out with (1) no rotation or vibration (control sample), (2) rotation alone, and (3) vibration alone (100 Hz). The control crystal was, as usual, polycrystalline. The boule which was subjected to rotation alone was also still polycrystalline but the boule orientation did change so that the plane of easy cleavage was perpendicular to the boule axis rather than its normal 30° inclination.

The application of mechanical vibrations to the growth ampoule during growth produced dramatic results. The boule was virtually single, free of grains except at the top. It was clearly the best crystal produced in our laboratory in terms of its macroscopic structure. The exact mechanism or mechanisms responsible for the dramatic improvement in crystal quality is not understood. As has been demonstrated in our laboratory mechanical vibrations can accelerate mixing. The effectiveness depends on the frequency and amplitude of the acoustic signal, the aspect ratio of the system and the fluid properties. Future work will center on reproducing this result, identifying the mechanisms involved in improved crystal quality, and optimizing the process.

(7) Growth of Urea Crystals

R. S. Feigelson, R. K. Route, R. L. Byer, and R. J. Raymakers

It has recently been shown by a number of investigators that crystals of urea have great potential for nonlinear optical applications, in particular, ultraviolet generation.

A program was started recently to develop both melt and solution growth techniques for the preparation of large urea single crystal samples of high optical quality. Melt decomposition, which currently makes crystal growth from molten urea difficult, is being studied. It is hoped that a technique for stabilizing urea melts can be developed thereby permitting growth by the Bridgman-Stockbarger or zone leveling method of crystal growth.

The growth of urea crystals from methanol and methanol-water solutions has begun and at present seed crystals are being prepared. Growth parameters, such as temperature, cooling rate, bath composition, etc. are being studied and optimized.

(8) Growth of Single Crystal Optical Fibers

W. L. Kway and R. S. Feigelson

An extensive single-crystal fiber-research program was started last year to (1) develop equipment and techniques for the growth of single crystal fibers, (2) to study the growth and properties of fibers of var-

ious high melting, ferroic and laser materials (Nd:YAG, LiNbO₃, and YIG) for fiber optic device research and (3) to investigate growth mechanisms involved in fiber growth.

The pedestal growth technique which will be used for single crystal fiber growth is similar to a modified float zone method. It will employ a CO₂ laser heat source and a special differential pulling system which will permit pulling the fibers from the hot zone at a rate which will be greater than that with which the source material is fed into the hot zone. Pull rates will be on the order of 5-20 mm/min. Since small diameter fibers (25-200 μ m) and steep temperature gradients are involved, the maximum allowable growth rates for these fibers will be much higher than for bulk crystals of the same composition.

The growth apparatus must be of high precision and operate under conditions of very low vibration. The fiber pulling apparatus is now completed and a special laboratory has been set up for the growth operation. The CO₂ laser and vibration dampening table are installed and the last of the system construction, coupling the laser beam to the pulling apparatus, is currently underway.

(9) Growth of YbPd₂Ge₂ from Germanium-Rich Solutions

R. K. Route, T. H. Geballe, and R. S. Feigelson

A new family of rare earth-rhodium-tin intermetallic compounds with the representative formula (RE)Rh_xSn_y have recently been synthesized in single crystal form. Those compounds containing the heavier rare earth ions are superconducting with a range of transition temperatures. Those with the lighter rare earths are generally magnetic. The study of analogous compounds is currently of great interest today in order to further the understanding of superconductivity and long range magnetic order, and the effects of mixed valency on transition temperature and critical field. One mixed valency compound which may have potential for a high superconducting transition temperature is YbPd₂Ge₂. High quality crystals of this composition have not yet been prepared: hence, its properties are currently unknown. While direct fusion has so far failed to produce a single

phase product, growth from germanium-rich solutions appears to be a worthwhile avenue for investigation.

The objective of this program will be first to determine the nature of the germanium-rich section of the Yb-Pd-Ge ternary phase equilibrium diagram. Once the desired YbPd_2Ge_2 phase can be synthesized from solution, preliminary solution growth experiments will be carried out to obtain single crystals for property evaluation.

(10) Optical Imaging of Growth Defects in Infrared Crystals

R. S. Feigelson and R. K. Route

This project involved the use of two recently developed and commercially available infrared optical imaging systems for studying growth defects in several important semiconductor crystals such as CdGeAs_2 and Ti_3AsSe_3 . These compounds are not transparent to the typical IR image converter whose range extends to only 1.2 μm . The two new systems which were originally designed to image black body radiation were used in a mode where transmitted illumination was imaged instead. One type of system utilizing an IR-sensitive vidicon is sensitive to 2.0 μm . The other, using either an InSn or a HgCdTe photodetector is sensitive in the 2-5.6 μm and the 8-14 μm range. With standard macro lens systems, both were capable of resolving millimeter and submillimeter growth defects such as internal cracks, voids, and precipitates. These defects, except for surface cracks, cannot otherwise be observed without cutting the crystals and preparing them for metallographic examination.

(11) Growth of Zn_3P_2 Single Crystals

R. K. Route, R. S. Feigelson, and F.-C. Wang

This project is part of an overall program to study potential uses of binary compounds for large scale terrestrial photovoltaic applications. Zn_3P_2 was chosen because it is a direct gap material with a bandgap (1.25 eV) near to the optimum 1.4 eV value. It has variable resistivity depending on heat treatment and tends to grow p-type. It has been grown by vapor transport techniques and from zinc solutions, and thin films can be

deposited by physical vapor deposition. The objective of this project is to grow high quality single crystals of Zn_3P_2 for electrical and optical characterization and for possible application in Zn_3P_2 -CdS heterostructure devices.

Zn_3P_2 melts congruently at 1193°C but transforms polymorphically at 880°C . Hence crystal growth must be carried out below the 880°C transformation temperature. Fortunately the material sublimes congruently and exhibits moderate equilibrium sublimation pressures below this temperature ($p = 60$ torr at 850°C). High quality, large grain, poly and single crystal boules in cm-dimensions are being grown by the closed tube vapor transport technique. These crystals display optimum low resistivity p-type behavior in contrast to crystals grown elsewhere by the effusion hole method which are typically high resistivity and less suitable for heterostructure devices.

(12) Growth of Infrared Crystals for Acousto-Optic and Electro-Optic Applications

A. S. Borshchevsky, R. K. Route, R. S. Feigelson, and R. J. Raymakers

Over the last decade the Center for Materials Research has maintained a continuous, strong interest in the growth and characterization of a wide variety of ternary semiconductor compounds. By their nature these materials tend to be infrared (IR) transmitting and consequently find application in a wide range of IR optical applications such as mixers, modulators and tunable filters.

During the past year our main emphasis has been on the prediction, growth, and characterization of new semiconductor compounds for acousto-optic (AO) and electro-optic (EO) applications. By starting with known AO and EO materials and considering the factors such as index of refraction, etc., which affect the relative figures of merit, it is possible to generate potentially more active analogs by substitution of iso-electronic elements. Going one step farther, having identified a potentially interesting candidate such as $\text{A}_x\text{B}_y\text{C}_z$ one can search for other compounds which may exist in the A-B-C ternary system. Using this approach, two

totally new IR compounds were synthesized and grown as single crystals, and are being characterized: AgTlSe and Tl_9BeTe_6 . In addition, CdInTe_2 , a peritectically decomposing compound was grown in single crystal form from In-rich solutions for the first time. The CdSe-TlSe binary join was also established for the first time and was found, contrary to published data, to consist of a classical degenerative eutectic and to contain no intermediate compounds.

(13) Growth of High Phase Match Temperature LiNbO_3 Single Crystals for High Power Device Applications

W. L. Kway, R. L. Byer, and R. S. Feigelson

Among its numerous applications, LiNbO_3 is an important material for second harmonic generation (SHG). New high power laser applications, however, require LiNbO_3 crystals with high optical quality and low optical index damage. For this reason it was desirable to produce crystals which 90° phasematch at a high temperature since it has been established that LiNbO_3 self-anneals at temperatures $\geq 170^\circ\text{C}$. To achieve this goal, a program was initiated to grow LiNbO_3 crystals with elevated phasematch temperatures and high optical quality.

Standard LiNbO_3 crystals having high optical quality are grown from a congruent melt and phasematch at 0°C (as pumped by a Nd:YAG laser at $1.06\text{ }\mu\text{m}$). It has been found that, by increasing the Li_2O content in the melt and doping with MgO , the phasematch temperature can be raised significantly. During the course of this program, we were able to grow LiNbO_3 crystals with large homogeneous regions which phasematched at 180°C (and as high as 200°C). The homogeneity of the crystals was evident from the small ΔT shown in the SHG power vs. temperature curve. However, the SHG conversion efficiency was impaired due to the difficulty encountered in poling these crystals, because the Curie temperature of the material is raised to very near its melting point with increasing Li_2O content.

To overcome the efficiency problems, some other approaches were examined. It was found that the LiNbO_3 crystals grown recently have self-annealing temperatures much below the previously established value

of 170°C, falling on the average to about 130°C. A lower self-annealing temperature allows a reduction in the Li_2O content in the melt and therefore the crystal. As a result, the degree of poling can be greatly improved, yielding a much higher SHG efficiency. When the Li_2O content in the melt was lowered, a crystal with a phasematch temperature of 145°C, high optical quality, and an SHG conversion efficiency of 29%, approaching the theoretical value of 35% was produced.

Reference Publications:

1. D. Elwell, R. S. Feigelson, and M. Simkins, "Electrodeposition of InP," submitted for publication to J. Electrochem. Soc.
2. A. S. Borshchevsky and R. S. Feigelson, "The Existence of Semiconductor Compounds of the Type CdTlX_2 (X - S, Se, Te)," submitted for publication to Mat. Res. Bull.
3. G. Rao, D. Elwell, and R. S. Feigelson, "Electrowinning of Silicon from K_2SiF_6 - Molten Fluoride Systems," J. Electrochem. Soc. (accepted for publication).
4. R. S. Feigelson and R. K. Route, "New Materials for Acousto-Optic Devices," SPIE, 214, 76, (1980).
5. R. S. Feigelson and R. K. Route, "Optical Imaging of Growth Defects in Improved Crystals, J. Cryst. Growth, 49, 399 (1980).
6. A. S. Borshchevsky, R. K. Route, and R. S. Feigelson, "Effects of Heat Pretreatment of Starting Materials on the Optical Transparency of CdGeAs_2 Crystals," Mat. Res. Bull, 15, 409, (1980).
7. R. S. Feigelson and R. K. Route, "Vertical Bridgman Growth of CdGeAs_2 with Control of Interface Shape and Orientation," J. Crystal Growth, 49, 261 (1980).

19. MACROMOLECULAR RESEARCH

P. J. Flory, J. G. Jackson-C. J. Wood Emeritus Professor of Chemistry

Professional Associates:

K. Dill	R. Matheson*
B. Erman*	Wu Da-Cheng
P. Irvine	

Graduate Students:

L. DeBolt*

* Left during report period

Agency Support:

AFOSR 77-3293-A,B,C
NSF DMR 76-20638-A01, A02
NSF DMR 80-06624

Technical Objective:

To develop a better basis for understanding macromolecules and for interpreting their behavior.

Approach:

Currently investigations are under way in the following areas:

1. Rubber elasticity and the effect of dilation on the stored elastic free energy. Theory of rubber elasticity.
2. Statistical mechanics of stiff-chain molecules.
3. Liquid crystals: theory and experiment.
4. Investigations on the optical anisotropies of polymers and oligomers, including polystyrene, polyacrylates and poly (methyl methacrylate).
5. Electric birefringence of oligomers and polymers.
6. Theory of interphases of chain molecules in semicrystalline polymers, in monolayers and in membrane bilayers.

Reference Publications:

1. H. Pak and P. J. Flory, "Relationship of Stress to Uniaxial Strain in Crosslinked Poly(Dimethylsiloxane) Over the Full Range from Large Compressions to High Elongations," J. Polym. Sci.: Polym. Phys. Ed., 17, 1845 (1979).

2. P. J. Flory, "Molecular Theory of Rubber Elasticity," *Polymer*, 20, 1317 (1979).
3. P. J. Flory and G. Ronca, "Theory of Systems of Rodlike Particles. I. Athermal Systems," *Mol. Cryst. Liq. Cryst.*, 54, 289 (1979).
4. P. J. Flory and G. Ronca, "Theory of Systems of Rodlike Particles. II. Thermotropic Systems with Orientation-dependent Interactions," *Mol. Cryst. Liq. Cryst.*, 54, 311 (1979).
5. P. J. Flory, "Molecular Structure, Conformation and Properties of Macromolecules," *Pure & Appl. Chem.*, 52, 241 (1980).
6. B. Erman, P. J. Flory and J. P. Hummel, "Moments of the End-to-End Vectors for Para-Phenylene Polyamides and Polyesters," *Macromolecules*, in press.
7. J. P. Hummel and P. J. Flory, "Structural Geometry and Torsional Potentials in Para-Phenylene Polyamides and Polyesters," *Macromolecules*, in press.
8. B. Erman, W. Wagner, and P. J. Flory, "Elastic Modulus and Degree of Cross-Linking of Poly(Ethyl Acrylate) Networks," submitted to *Macromolecules*.
9. K. A. Dill and P. J. Flory, "Interphases of Chain Molecules: Monolayers and Lipid Bilayer Membranes, *Proc. Nat. Acad. Sci.*, in press.
10. P. J. Flory, "Introductory Lecture: Levels of Order in Amorphous Polymers" *Faraday Disc. (Cambridge)*, in press.
11. D. Y. Yoon and P. J. Flory, "Molecular Morphology in Semi-crystalline Polymers," *Faraday Disc. (Cambridge)*, in press.

20. PHOTOPHYSICS OF AMORPHOUS SOLID STATE POLYMER BLENDS:
COMPATIBILITY AND RELAXATION BEHAVIOR

Curtis W. Frank, Associate Professor, Chemical Engineering

Graduate Students:

M. A. Gashgari
R. G. Gelles
S. N. Semerak

Agency Support:

Army Research Office
National Science Foundation
Research Corporation - Cottrell Science Grant
NSF-MRL through CMR

Technical Objective:

The objective of this research is to provide a molecular basis for the analysis of the thermodynamics of polymer-polymer interactions and molecular mobility in amorphous solid state polymer blends. Of particular interest is the effect of sample thermal and mechanical processing history on chain conformational rearrangement associated with the glass transition and the sub-glass beta relaxation.

Approach:

Excimer fluorescence is employed as a molecular probe of inter-molecular aggregation and intramolecular segmental rotation. The experimental program encompasses the thermodynamics of both compatible and incompatible blends and the kinetics of transformation from one state to the other. For any given blend, the first stage of investigation is the consideration of the degree of dispersion of the guest aromatic vinyl polymer in the host polymer matrix. Dissimilar polymer chains will be intimately entangled for compatible blends whereas local domains of concentration higher than the bulk average will exist for incompatible blends. In the former case, the local concentration of aromatic rings will be reduced with a corresponding reduction in the number of intermolecular excimer forming sites. Of

course, the intramolecular excimer sites will be unaffected. As thermodynamic interactions between guest and host polymers become less favorable, clustering of like species will result in an increase in the local density of aromatic rings. Hence, the number of intermolecular excimer sites will increase.

Once the molecular morphology has been established for a sample with a given processing history, molecular rearrangement associated with sub glass and glass transition phenomena may be studied by heating the solid sample. The application of the excimer probe to detection of segmental mobility is identical in concept to the investigation of rotational diffusion in dilute solution described elsewhere, albeit with considerably different time scales. If the blend is compatible, information on intramolecular segmental motion may be inferred from the observed changes in excimer fluorescence during heating. If the blend is incompatible or undergoes phase separation, information on the increase in local aggregation or chain clustering may be obtained.

Research Report:

Several studies on the compatibility of blends of aromatic vinyl polymers with a series of poly(alkylmethacrylates) and with polystyrene are nearing completion. These studies have focussed on a number of variables which are known to affect the degree of compatibility including the nature of chemical interactions between guest and host polymers, the concentration of guest polymer, the molecular weights of both guest and host polymers, and the temperature at which the film is solvent cast.

The effect of enthalpic interactions between guest and host polymers has been examined for blends of poly(2-vinylnaphthalene), poly(acenaphthalene) or poly(4-vinylbiphenyl) with host polymers selected from an homologous series of poly(alkylmethacrylates). Low concentration blends (.2% guest aromatic vinyl polymer by weight) were prepared by solvent casting at 22°C. In each case, the ratio of excimer to monomer emission intensities, I_D/I_M is at a minimum when the

solubility parameters of the guest and host polymers are equal. At very high dilution for concentrations of 0.003% by weight or less, the observed I_D/I_M is independent of the host matrix. Between .003% and 0.1% there is an abrupt rise in I_D/I_M followed by a linear increase for all higher concentrations. These host and concentration effects are analyzed in terms of a phenomenological clustering model which is able to predict the nominal bulk concentration at which the local concentration within a phase separated domain is rich in guest polymer.

In a study of the effect of casting temperature, the I_D/I_M fluorescence results have been used to generate an experimental phase diagram which indicates that the blends exhibit lower critical solution temperatures. Furthermore, for blends in which thermodynamic equilibrium is ensured by the appropriate solvent casting conditions, the experimentally determined binodal curve agrees very well with the binodal calculated using Flory-Huggins solution theory.

Research in the relaxation area has focused on instrumentation development in two areas. First, a new sample holder with a small thermal mass has been built which will be used for heating/cooling experiments. It can be mounted on translational and rotational stages for precise optical alignment for either backface or frontface illumination. Second, two new detection channels have been added to the polychromator.

Publications:

1. C.W. Frank, M.A. Gashgari, P. Chutikamontham and V. Haverly. "Excimer Fluorescence as a Molecular Probe of Polymer Blend Compatibility II. The Effect of Concentration on Blends of Aromatic Vinyl Polymers with Poly(alkylmethacrylates)." Second Cleveland Symposium on Macromolecules: Structure and Properties of Amorphous Polymers, Elsevier, in press.
2. C.W. Frank and M.A. Gashgari, "Excimer Fluorescence as a Molecular Probe of Polymer-Polymer Interactions in the Amorphous Solid State." Proceedings of the Katzir Conference: Luminescence from Macromolecules--Biological and Synthetic, June 1980, New York Academic Press.

This work was supported partially by the NSF-MRL program through the Macromolecular Research at Stanford.

21. PHOTOPHYSICS OF POLYMERS IN SOLUTION: ENERGY TRANSFER AND INTRA-MOLECULAR ROTATIONAL DIFFUSION

Curtis W. Frank, Associate Professor Chemical Engineering

Graduate Student:

P. D. Fitzgibbon

Agency Support:

Stanford Institute for Energy Studies
Petroleum Research Fund of the American Chemical Society

Technical Objective:

The objective of this research is to develop a model for electronic energy migration in aromatic vinyl polymers which are free to undergo intramolecular rotational diffusion.

Approach:

A major element of the photophysical behavior of the aromatic vinyl polymers is the formation of excimers, which are electronically excited states formed between coplanar aromatic rings one of which is in a singlet excited state, the second in the ground state. There are two possible means by which excitation energy may be localized at such a geometrical structure. In the first, referred to as migrational sampling, absorption of radiation by a pendent aromatic ring is followed by a random hopping of the singlet exciton until competitive trapping occurs at an excimer forming site. Although the population of suitable excimer forming polymer chain conformations is small due to the steric repulsive forces in the opposed aromatic rings, the exciton trapping efficiency at a preformed excimer site is quite high. In addition, the remainder of the polymer chain acts as an "antenna" composed of many isolated aromatic rings each of which is capable of becoming excited and subsequently transferring the excitation energy along the chain by a non-radiative process. Thus, the overall sensitivity to energy transfer is quite high. Finally, the excimer is an intrinsic trap as opposed to an extrinsic trap such as an added dopant which makes

it possible to detect coupling between exciton hopping and chain vibrational modes, if such coupling exists.

In the second sampling mechanism, termed rotational sampling, the residence time of the excitation on any given aromatic ring is long with respect to the time required for Brownian rotational motion around backbone bonds. Thus, it is possible that the appropriate excimer forming geometry between aromatic rings on adjacent repeat units could be reached within the residence time. Since interconversion of excimer and non-excimer dyads involves short chain segmental motion around backbone bonds, excimer fluorescence is the ideal tool to study the contribution of internal potential energy barriers and bulk solvent viscosity to rotational diffusion processes.

Research Report:

Research during the past year has concentrated on the study of the rotational sampling process through use of hydrostatic pressures to 430 megapascals in order to achieve a continuous variation in bulk solvent viscosity. Both low molecular weight model compounds and high polymers have been examined. The model/polymer systems studied include: 1,3 bis (1-naphthyl) propane/poly(1-vinylnaphthalene), 1,3 bis (2-naphthyl) propane/poly(2-vinylnaphthalene) and 1,3 bis (4-biphenyl) propane/poly(4-vinylbiphenyl). The rotational diffusion process has been analyzed using Kramers theory for Brownian motion in a hindered potential. In the viscosity range between one and five centipoise, the friction constant is best fit using a Gierer-Wirtz microviscosity approach which emphasizes the influence of free volume in the solvent. At higher viscosities, Stokes-Einstein behavior appears to prevail. The most interesting result is that the rotational barrier height and the volume required for the rotational process to occur are very similar in the model compound and high polymer. This is consistent with the conclusion that "crankshaft" motions do not occur in the chain backbone, in contrast to what has been previously proposed. Further work is continuing on stereospecific model compounds and polymers.

22. METAL FATIGUE

Henry O. Fuchs, Professor Emeritus, Mechanical Engineering
A. K. Miller, Associate Professor, Materials Science & Engineering
Drew V. Nelson, Assistant Professor, Mechanical Engineering

Support:

Electric Power Research Institute

Graduate Students:

V. G. Baghdasarian	S-B. Lee
Y. S. Garud	V. Pannaganti

Approach:

Many plausible theories on the effect of complex multiaxial stresses (strains) on fatigue behavior have been proposed. The greater or lesser validity of hypotheses can be checked using discriminating specimens. The location of failure on such specimens tells which of the several hypotheses being checked is superior for a given type of loading (e.g., out-of-phase, combined bending and torsion).

All existing theories tend to be quite restricted in their applicability (i.e., treating only constant amplitude, proportional straining), whereas actual service loadings are generally non-proportional and non-uniform. A new, more generally applicable criterion for multiaxial fatigue is being developed.

Research Report:

- A. Specimens for out-of-phase bending and torsion have shown that currently accepted theories based on shear stress amplitude underestimate the damage of 90 degree out-of-phase bending and torsion.
- B. Garud has developed the hypothesis that plastic work per cycle is the key variable which correlates with multiaxial fatigue life. He has

developed computer programs which calculate plastic work with data from the uni-axial cyclic stress-strain curve and the loading cycle. To do this he had to devise a new hardening rule for non-proportional cyclic straining. Life predictions based on this method correlate well with existing data. However, results of pure torsion tests show significantly longer life than predicted. This difference may be caused by an effect of normal stresses on crack initiation or by much longer crack propagation life.

The plastic work approach holds great promise for easier and better methods of checking the adequacy of proposed designs. A better understanding of the secondary effect of normal (or hydrostatic) stress on multiaxial fatigue behavior is needed.

- C. Lee has developed a three-parameter description for smooth specimen fatigue under out-of-phase torsion and bending. The three parameters are the bending fatigue strength, the torsion fatigue strength, and a factor which, together with the phase angle, determines an exponent in the description. The parameters depend on material and possibly on the number of cycles to failure. For generally used structural materials, the three parameters can be determined fairly easily. Lee's method then becomes the simplest way of calculating the effects of out-of-phase, mono-frequency torsion and bending.

Publications:

1. Garud, Y. S., "A New Approach to the Evaluation of Fatigue under Multiaxial Loadings," Symposium on Fatigue of Metals and Composites, ASME, New York, (1979).
2. Fuchs, H. O., "Fatigue Research with Discriminating Specimens," Fatigue of Engineering Materials and Structures, Vol. 2 pp. 207-215 (1980).
3. Fuchs, H. O. and Stephens, R. J., Metal Fatigue in Engineering, Wiley, (1980).

23. ION IMPLANTATION AND LASER ANNEALING OF SEMICONDUCTORS

J. F. Gibbons, Professor, Electrical Engineering

Graduate Students:

L. Christel
K. Conway
K. F. Lee
R. B. Gold

A. Lietoila
Y. I. Nissim
F. C. Wu

Agency Support:

ARPA MDA 903-80-C-0238
ARPA MDA 903-78-C-0128
ARPA MDA 903-78-C-0290
AROD DAAG29-78-G-0119
NSF DMR 78-19970

Technical Objective:

The general objective of the research performed in this group is to study the physics of ion implantation and beam annealing processes in semiconductors. Efforts during this past year have been directed toward improvements in the predictions of range distributions in ion implanted targets and the development of laser and electron beam techniques for annealing implantation-produced damage in ion-implanted materials and recrystallizing polysilicon films.

Research Report:

(1) Range and Damage Distributions in Ion Implantation

Graduate Student: L. A. Christel

The purpose of this project is to formulate the range and damage distribution problem in terms of the Boltzmann transport equation, thus permitting direct computation of channeling phenomena, knock-on range distributions and damage in multilayered targets. In the past year, the following progress has been made on this problem:

- Refinement of a computer program based on the Boltzmann formalism to include damage distributions and recoil (knock-on) range distributions in multilayered targets.

- Considerable increase in execution speed of the above program by simplification and better efficiency.
- Very good agreement with experimental results for recoil and damage distributions calculated with the above program.
- Preliminary investigation of channeling effects.

In the coming year our work will be directed toward the following objectives:

- Implementation of the Boltzmann program or results obtained thereby into the general process modeling program SUPREM III.
- Further investigation of channeling phenomena.
- Experimental investigation of more common multilayer systems, e.g, aluminum on Si or SiO₂.
- A simplified theory of recoil range distributions.

Discussion of objectives for FY 1981

(a) Although an increase in speed of the Boltzmann program was obtained, the added complexity of including recoil and damage effects still results in a computation of considerable complexity. Calculations now require between 5 and 30 minutes of CPU time on a DEC system 20. In the coming year we hope to implement a simple version of the program (no recoil or damage) in the general process modeling program SUPREM III. This version would be capable of calculating primary ion range distributions in multilayered targets in a few minutes. Since some runs of SUPREM now require 15 - 20 minutes of CPU, this objective seems quite feasible at the present time.

(b) During FY 1980 another program was written in an attempt to simulate the channeling/dechanneling of ions in crystalline solids. For example, the [110] channel of silicon was modelled as 6 string potentials arranged in a next near hexagonal configuration. The trajectories of individual ions were then studied as a function of energy and point of impact. By assuming that ions entered the channel at each point of its cross section with uniform probability, concentration profiles could be built up. This investigation was only marginally successful in illuminating possible mechanisms involved in the occurrence of experimentally

observed exponential tails in range distributions. The work on the recoil problem took priority so the channeling problem was not investigated further.

In the coming year however, we hope to return to this problem. It is hoped that a successful model could also be incorporated in the Boltzmann program.

(c) Up to this point in time we have been comparing the results of Boltzmann calculations to published experimental data of others and agreement has been very good. Unfortunately, experimental data does not exist for many multilayer systems of interest. In the coming year, we hope to pursue our own experiments in order to investigate concentration discontinuities and recoil range distributions in some of these systems. The Al on Si and Al on SiO₂/Si systems are probably of greatest interest at this time.

(d) In our calculations of recoil range distributions, a few common characteristics have been observed. In particular, we have found that most recoil range distributions are characterized by exponentially decaying concentration profiles. We have found that for a particular system (e.g. SiO₂/Si) the characteristic decay length in the exponential region is a function only of the maximum energy obtainable by the recoiling species, and is independent of incident ion and film thickness. In the coming year we hope to investigate further such common characteristics in the hope that a simple set of relations might be found which predict (at least approximately) recoil range distributions in the general case. This aspect of our work will require a great deal of study and tremendous progress over the next year is not expected. It is hoped however that we can take the first steps toward this goal and at least obtain some empirical relations which might be used to estimate recoil range distributions in common structures.

Reference Publications:

- [1] Application of the Boltzmann Transport Equation to Ion Range and Damage Distributions in Multi-Layered Targets, L. A. Christel, J. F. Gibbons and S. Hylroie, submitted to Journal of Applied Physics.

(2) Crystallization Mechanisms in Laser-Annealed Semiconductors

Graduate Student: R. B. Gold

Objective: To study the crystallization and reaction mechanisms characteristic of laser-induced process, and compare them to their conventional thermal counterparts.

Results: During the study of laser-annealed Ge-GaAs heterostructures, reported in last year's report, it was found that deposited amorphous Ge (and, in certain cases, Si) thin films exhibited anomalous crystallization behavior when irradiated by a scanning cw laser. This "explosive" crystallization is characterized by rapid, self-sustaining radial growth from a central nucleus; growth rates above 100 cm/sec have been observed. A model was developed which attributed this effect to the heat of crystallization; since slow heating (as in a furnace) causes such films to relax to fine-grain polycrystalline structures, and use up the heat of crystallization in the process. The effect is only observed when the heating rate is very rapid, as with a laser. Quantitative agreement was achieved between observed characteristics and those predicted by the model [1]. This has led to an improved understanding of the kinetics and thermodynamics of laser-induced crystallization.

A model was also developed for the response of a thermally-activated process, such as diffusion or regrowth, to irradiation by a scanned cw laser [2]. It was found that the effect could be interpreted in terms of a conventional furnace anneal at an "effective temperature", for an "effective time". Quantitative expressions were derived for these effective values in terms of material constants and experimental parameters. This model has since been successfully applied to analyses of the kinetics regrowth of ion-implanted Si, formation of metal-silicides, and diffusion of As in Si.

Reference Publications:

- [1] Laser-Induced Explosive Radial Crystallization of Deposited Ge and Si Thin Films, R. B. Gold, J. F. Gibbons, T. J. Magee, J. Peng, and R. Ormond, presented at the Materials Research Society Symposium on Laser-Solid Interactions and Laser Processing, Cambridge, MA, November, 1979. To be published in Proceedings.

- [2] Modelling of Solid-Phase Thin-Film Reactions Induced by a Scanning cw Laser, R. B. Gold and J. F. Gibbons, presented at Materials Research Symposium, Cambridge, MA, November 1979. To be published in Proceedings.

(3) Properties of Laser-Recrystallized Polycrystalline Silicon as Device Material

Graduate Student: K. F. Lee

Objective: The goal of this project is to study of the properties of laser-recrystallized polycrystalline silicon films as a device material.

Results: Following the successful fabrication of MOSFETs in laser-recrystallized polysilicon described in the last report, the properties of laser-recrystallized polysilicon has been further characterized. Thermal oxidation of the material has been studied [1]. The orientation of the crystallites has been shown by x-ray to exhibit a weak $\langle 111 \rangle$ orientation, in contrast to a strong $\langle 110 \rangle$ texture in fine-grain polysilicon [1]. Interface charges, both between the laser-recrystallized polysilicon and the underlying dielectric [2], as well as between the dielectric and the single crystal substrate [3], have been characterized. In both cases, with the dielectric being oxide, the interface charges were found to resemble, but were inferior to, those of thermally grown oxide. With the dielectric being silicon nitride, the interface properties are poor, as in conventionally fabricated material. Minority carrier lifetime in the material has been measured by a transient capacitance method and from diode characteristics, and gave a value of $\sim 10^{-9}$ sec. [4]. Aluminum Schottky-barrier field-effect transistors have also been fabricated in the material [5]. A novel CMOS structure using a single gate for both n and p channel devices has been fabricated [6]. Bulk silicon was used for the p channel device while laser-recrystallized polysilicon was used for the n channel device.

Reference Publications:

- [1] Crystal Structure and Thermal Oxidation of Laser-Recrystallized Polysilicon, T. I. Kamins, K. F. Lee, J. F. Gibbons, Appl. Phys. Lett. 36 (7), 550 (1980).

- [2] Charges at a Laser-Recrystallized-Polysilicon-Silicon/Insulator Interface, T. I. Kamins, K. F. Lee, J. F. Gibbons, IEEE Elec. Dev. Lett. 1 (1), 5 (198).
- [3] Interface Charges Beneath Laser-Annealed Insulators on Silicon, T. I. Kamins, K. F. Lee, J. F. Gibbons, to be published in Solid State Electronics.
- [4] Properties of MOSFETs Fabricated in Laser-Annealed Polysilicon Films, K. F. Lee, J. F. Gibbons, K. C. Saraswat, T. I. Kamins, H. W. Lam, A. F. Tasch, Jr., T. C. Holloway, presented at Materials Research Society Symposium on Laser-Solid Interactions and Laser Processing, Cambridge, MA, November 1979, to be published in Proceedings.
- [5] One-Gate-Wide CMOS Inverter on Laser-Recrystallized Polysilicon, J. F. Gibbons, K. F. Lee, to be published in IEEE Elec. Dev. Lett.

(4) Solid Solubility and Metastable Concentrations of As in Si

Graduate Student: Arto Lietoila

Objective: To measure the solubility of As in Si; to study properties of concentrations exceeding the solubility.

Results: Cw laser annealing is capable of completely activating As in Si to a concentration of about 10^{21} cm^{-3} . Concentrations above $3 \times 10^{20} \text{ cm}^{-3}$ are, however, thermally unstable and relax to $3 \times 10^{20} \text{ cm}^{-3}$ or less during thermal equilibrium annealing. Deactivation is quick even at 400°C . The solubility of As in Si as an electrically active dopant has been determined by ion implanting and laser annealing a metastable (10^{21} cm^{-3}) concentration and subjecting it to thermal equilibrium annealing. The solubility is $9 \times 10^{19} \text{ cm}^{-3}$ at 700°C and $3.2 \times 10^{20} \text{ cm}^{-3}$ at 1000°C .

When deactivation from the metastable state takes place at 400 - 500°C , MeV ion channeling measurements show that As goes to nonsubstitutional lattice sites. However, at 900°C the amount of nonsubstitutional As increases only slightly even though electrical activation decreases dramatically. It is suggested that at this temperature some complexes

are formed where the displacement of As-atoms from the lattice sites is small.

(5) CW Laser Assisted Diffusion of Sn in GaAs From SnO₂/SiO₂ Source.

Graduate Student: Y. I. Nissim

Objective: To study the laser-assisted diffusion of tin in GaAs from deposited oxide films.

Results: An original way of doping GaAs with tin has been studied. The doping source for Sn diffusion consists of a SnO₂/SiO₂ solution spin-on, a semi-insulating Cr-doped GaAs substrate, and encapsulated with a 0.5 μm layer of CVD silicon dioxide. The in-diffusion of Sn from this double layer "source cap" is initiated with a slow thermal ramp. Subsequent laser scans from a cw argon ion laser can assist both the diffusion and the activation of the Sn impurity which began during the ramping cycle. This new technique has allowed us to produce thin n⁺ layers ($n \approx 10^{19}/\text{cm}^3$) on insulating substrates.

The evaporation of Ti-Pt-Au or Al on these diffused layers produces low resistance ohmic contacts without requiring a subsequent alloy. This process is of particular interest for GaAs MESFETs since these metallizations are also suitable to Schottky barrier gates on lightly doped material. The effect of the laser irradiation to values of specific control resistance is drastic. A reduction of two orders of magnitude is obtained after scanning a thermally ramped sample (10^{-4} to $10^{-6} \Omega\text{-cm}^2$ after scanning). The value of contact resistance in the low $10^{-6} \Omega\text{-cm}^2$ is obtained for a large window of laser powers, making the process very reproducible. The resistance of the resulting planar contacts is roughly 0.1Ω for 1 mm contact width. These contacts appear to be thermally stable, 1000 hours at 320°C produces an increase in resistance of less than 50%.

(6) Comparison of Laser Annealing and Thermal Annealing as a Solar Cell Processing Step

Graduate Student: F. Wu

Objective: To investigate processing techniques for improving the conversion efficiencies of solar cells.

Results: Previous studies have indicated that cw laser annealing can be used to recrystallize ion-implanted damage silicon to almost defect-free conditions as determined by TEM [1]. Experiments have been performed to compare the effects of cw laser annealing and thermal annealing on similarly processed ion-implanted concentrator silicon solar cells. It is found that laser annealing alone is not enough to replace the use of a furnace annealing cycle in producing high efficiency solar cells [2]. Studies of the open circuit voltages seem to indicate that thermally annealed cells show a factor of five better minority carrier lifetimes in the crystal. This may be attributed to residue point defects that remain even after the laser processing. Moreover, solar cells that received a subsequent thermal treatment following the laser anneal show similar efficiencies as the ones that received the thermal annealing only. Currently, using integrated circuit compatible techniques, conversion efficiencies of better than 16.5% are being repeatedly produced.

Reference Publications:

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- [2] Application of cw Beam Processing to Semiconductor Device Fabrication, J. F. Gibbons, A. Lietoila, Y. Nissim and F. C. Wu, presented at Materials Research Symposium, Cambridge, MA, November 27-30, 1979. To be published in Proceedings.

24. MÖSSBAUER EFFECT AND RELATED PHENOMENA

S. S. Hanna, Professor, Physics
D. L. Clark, Assistant Professor, Physics[†]
H. T. King, Assistant Professor, Physics

[†] Departed 12/31/79

Professional Associates:

D. Ramsay
G. von Eynatten*

* Visiting scholar from
Universität Konstanz, W. Germany
Departed 3/31/80

Graduate Students:

N. S. Dixon
L. S. Fritz
J. R. Hall

Agency Support

NSF PHYS 77 24631

Our research is directed toward combining the fields of nuclear physics and low temperature physics in order to study both fundamental and applied physics phenomena. Many of our studies are done at low temperatures (in a ^3He - ^4He dilution refrigerator) and provide information which cannot be obtained with conventional NMR or NQR techniques.

Research Report:

- (1) Mössbauer Spectroscopy of Thulium Hyperfine Interactions and Electronic Relaxation with a ^3He - ^4He Dilution Refrigerator

Graduate Students: N. S. Dixon
L. S. Fritz

Many important phenomena in solid state physics may be investigated by using the nuclear system as a probe of the electronic system through hyperfine interactions. The Mössbauer effect is a particularly precise and elegant method for extracting such information from the nuclear system.

The Mössbauer effect of ^{169}Tm was used to investigate electronic phenomena in Tm ions such as crystal field effects, electronic relaxation among crystal field states, non-integral valence states, magnetic

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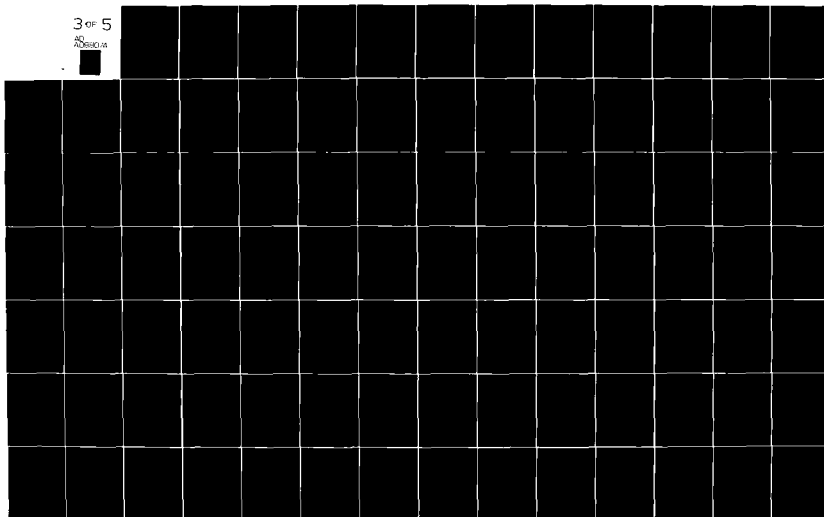
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order, and Jahn-Teller distortions. The low temperatures necessary for these studies were obtained with a ^3He - ^4He dilution refrigerator.

The temperature dependence of the quadrupole interaction from 0.040 K to 1100 K was used in conjunction with optical data to extract crystal field parameters and wavefunctions for the zircon structure compounds TmVO_4 , TmAsO_4 , and TmPO_4 . The compounds TmVO_4 and TmAsO_4 undergo a Jahn-Teller distortion at low temperatures, and crystal field parameters for the distorted phase were also determined. The asymmetry of the quadrupole doublets observed for these compounds is indicative of electronic relaxation.

Mössbauer spectra of thulium metal taken at temperatures from 0.065 K to 300 K showed similar asymmetric quadrupole doublets above the magnetic ordering temperature, $T_N = 56$ K, and complex hyperfine structure below T_N . A previous multiple-site interpretation of such spectra, which failed to account for the asymmetric doublets above T_N , was shown to also be inadequate at lower temperatures. By including the effects of electronic relaxation, the Mössbauer spectra of thulium metal were fully characterized throughout the entire temperature range of these experiments with a single one-site model.

The chalcogenide compounds TmS , TmTe , and TmSe also appear to show electronic relaxation effects in their Mössbauer spectra, but only the electronic ground state properties and the non-integral valence character of TmSe were of major concern for the present work. In TmS the Tm ion is nearly pure Tm^{3+} , and its low temperature spectra were seen to be well described by the expected $^3\text{H}_6$ electronic configuration in the ground state, together with a small distribution of exchange fields consistent with recent neutron diffraction results. In TmTe the Tm ion is nearly Tm^{2+} , and its spectra were seen to be well characterized by the expected $^2\text{F}_{7/2}$ configuration. On the other hand, in TmSe the Tm ion has shown non-integral valence character, and the spectra were seen here to be well accounted for by a Tm^{2+} - Tm^{3+} mixed valence configuration, although the precise nature of the valence mixing is still uncertain.

(2) Mössbauer Effect Investigation of Mixed Valency in YbBe₁₃

Graduate Students: N. S. Dixon

L. S. Fritz

Visiting Scholar: G. von Eynatten

Contrary to previous reports^{1,2} of intermediate valency in YbBe₁₃, a recent investigation³ of the cubic intermetallic compound found EPR and magnetization measurements to be consistent with the Γ_7 ground state of Yb³⁺ for $x = 0.45(5)$, $W = 1.90(5)$ K in the notation of Lea, Leask, and Wolf.⁴ Therefore we have used the Mössbauer effect (ME) of ¹⁷⁰Yb to investigate YbBe₁₃ at temperatures from 0.065 K to 81 K.

At temperatures below $T_N = 1.27(2)$ K, the ME spectra are the typical five-line patterns of $I = 2^+ \rightarrow 0^+$ E2 transitions in magnetically ordered materials. The splittings observed are consistent with an Yb³⁺ Γ_7 ground state and follow closely the molecular field approximation for $x = 0.38(2)$ and $W = 1.88(3)$ K, in close agreement with Ref. 3. However, at temperatures above T_N we see a single line which broadens and shifts toward negative velocities with decreasing temperature, while the effect of electronic relaxation of Yb³⁺ with a Γ_7 ground state would be an apparent shift toward positive velocities. Thus interpreting the shift toward negative velocities as an isomer shift seems to imply a shift toward a valence of Yb²⁺ in support of Refs. 1 and 2.

A possible but as of yet highly speculative suggestion for resolving the discrepancies between Refs. 1, 2 and 3, and between our own results above and below T_N is that the intermediate valency of YbBe₁₃ is highly field dependent. Both EPR and magnetization measurements require external magnetic fields and below T_N there is a considerable molecular field, whereas above T_N there is no significant molecular field (and the Mössbauer effect involves no external fields). Further careful analysis of this system is necessary.

(3) Crystal Field Effects and the Interpretation of Magnetism in Mixed-Valent TmSe

Graduate Students: N. S. Dixon

L. S. Fritz

Mössbauer observations of magnetic dipole and electric quadrupole hyperfine interactions in TmS, TmSe, and TmTe measure two 4f electronic

moments which rather completely characterize the 4f ground state wavefunctions in these materials. These measurements when coupled with a recent neutron diffraction determination of the soft magnetic axis in TmSe, show that the behavior of the ground state in TmSe is largely consistent with the properties expected for the Γ_1 singlet ground state of Tm^{3+} . A simple linear interpolation of the properties expected for the ground states of Tm^{2+} and Tm^{3+} leads to magnetic order along the $\langle 100 \rangle$ crystal axis in agreement with the neutron diffraction experiment, rather than along $\langle 111 \rangle$ as expected from pure Tm^{3+} .

(4) Electronic Relaxation in Magnetically Ordered Tm Compounds

Graduate Students: L. S. Fritz
N. S. Dixon

The effects of electronic relaxation on Mössbauer effect spectra in magnetically ordered rare earth compounds has been a subject of interest in recent years. The behavior of several metallic Tm compounds including Tm, TmAl , TmCu and $\text{Tm}_x\text{Y}_{1-x}\text{Cu}$ was studied over a temperature range of 65 mK to $T > T_{\text{Néel}}$. The Tm, TmAl and TmCu materials all show spectra which can be described well by including electronic relaxation. The general form of the spectra is similar for the three compounds even though Tm is hexagonal and shows a spin-wave structure in neutron diffraction, TmAl is orthorhombic, and TmCu is cubic. To investigate the nature of the relaxation mechanisms, the TmCu was diluted with Y (non-magnetic) to modify the exchange interaction between the Tm atoms. These experiments have led to a consistent description of Tm in magnetic compounds over the entire temperature range studied.

(5) In-Beam Implantation of Iron into Germanium, Silicon and Diamond Studied by the Mössbauer Effect

The Mössbauer effect of ^{57}Fe implanted into diamond structure semiconductors, Ge, Si and C, has been studied by in-beam implantation of ^{57}Fe ions, which were excited to the 14 keV state by a ^{35}Cl beam from a tandem Van de Graaff accelerator. The time between the stopping of the ^{57}Fe nucleus and the emission of the 14 keV gamma ray is determined by the lifetime (140 ns) of the 14 keV state. In each material the Möss-

bauer spectrum exhibits a doublet with velocity coordinates in (mm/s) at room temperature, relative to a sodium ferrocyanide absorber, as follows: diamond (-0.99, 1.10), silicon (-0.80, 0.21), and germanium (-0.88, -0.02). In silicon and germanium crystals the spectra were observed over the temperature range between 13°K and 870°K. The relative line intensities changed dramatically and the positions of the lines shifted systematically with temperature. In addition, channelling studies were made on iron that had been implanted into silicon.

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- (2) I. Nowick, I. Felner, and R. Yanowsky, J. de Phys. C6 (1976) 431.
- (3) G. Heinrich, J. P. Kappler, and A. Meyer, Phys. Lett. 74A (1979) 121.
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- "Electronic Relaxation in Rare Earth Metals and Alloys - A Non-Kramers Example: Tm^{3+} ," N. S. Dixon, L. S. Fritz, Y. Mahmud, B. B. Triplett, S. S. Hanna, G. von Eynatten, J. de Phys. Vol. 41, C1-25.
- "In-Beam Implantation of Iron into Germanium in an External Magnetic Field Studied by the Mössbauer Effect," G. Langouche, N. S. Dixon, L. S. Fritz, and S. S. Hanna, submitted to *Hyperfine Interactions* for publication.
- "In-Beam Implantation of Iron into Germanium, Silicon and Diamond Studied by the Mössbauer Effect," G. L. Latshaw, P. B. Russell, and S. S. Hanna, submitted to *Hyperfine Interactions* for publication.

Papers Presented at Conferences:

- "Crystal Field Effects and the Interpretation of Magnetism in Mixed-Valent $TmSe$," L. S. Fritz, N. S. Dixon, B. B. Triplett, S. S. Hanna, Y. Mahmud: International Conference on Mössbauer Spectroscopy 10-14 September 1979, and International Conference on Magnetism, 3-7 September 1979, Munich, W. Germany and Portoroz, Yugoslavia.

"Electronic Relaxation in Magnetically Ordered Tm Compounds," L. S. Fritz, N. S. Dixon, B. B. Triplett, Y. Mahmud, and S. S. Hanna: International Conference on Magnetism, 3-7 September 1979, Munich, W. Germany.

"Recoil Implantation Mössbauer Experiment on ^{57}Fe in Ge in the Presence of an External Field," G. Langouche, N. S. Dixon, L. Gettner (L.S.Fritz), and S. S. Hanna: International Conference on Mössbauer Spectroscopy, 7-10 September 1979, Portoroz, Yugoslavia.

25. PSEUDOPOTENTIAL METHODS IN PHYSICS

W. A. Harrison, Professor of Applied Physics

Professional Associate:

Shang-Yuan Ren

Graduate Students:

S. Froyen
S. Bending

Agency Support:

NSF DMR 77-21384
ONR N00014-79-C-0072
NSF-MRL through CMR

Technical Objectives:

To understand the electronic structure of solids and its relation to the properties of the solid.

Research Report:

Most of our research this year has been directed at the theory of the properties of insulators in terms of their microscopic electronic structures. Our earlier work established universal matrix elements for LCAO representations of the electronic structure and a "Bond Orbital Approximation" made possible the elementary calculation of dielectric and bonding properties of semiconductors and insulators. We turned this year to more accurate calculations of properties in terms of the same universal matrix elements but without the Bond Orbital Approximation. The results were of fundamental significance in showing that the principal discrepancies between theory and experiment came from the approximation rather than from the use of universal parameters. An error in the form of the conduction bands remains even without the Bond Orbital Approximation but it does not strongly effect many properties.

Our studies included three major efforts. First was a systematic study of bonding in ionic solids in which we began in an ionic limit and systematically added the effects of interatomic matrix elements in perturbation theory. The leading term, called "the covalent contribution to the bonding of ionic crystals" was of second order and corresponded to a purely radial interaction. Fourth-order terms have angular dependence and include a "chemical grip" responsible for tetrahedral structures in strongly covalent systems and for the bend in the oxygen bridge in SiO_2 . It also included an "sp-hybridization energy" which opens up the angle at oxygen from 90° in SiO_2 . An analogous "sp-hybridization" favors the 90° orientations in the cubic perovskites. Finally, an "ion distortion" term softens the noble-metal halides to shear.

A second program used our method of "extended bond orbitals" to improve upon the calculation of transverse charges and piezoelectric charges. The only prior microscopic theory of these charges was based upon our Bond Orbital Model; the use of extended bond orbitals removed the principal discrepancies with experiment.

We also carried out detailed calculations of the dielectric properties of semiconductors with no approximations other than the use of universal matrix elements. This included the first calculation of the photoelastic coefficients of semiconductors. The results appear to be in agreement with experiment on the scale of the accuracy of most experimental determinations.

Our continuing effort on the electronic structure of transition metals and compounds, described under the Thrust Program on Alloy Catalytic Materials, is closely related to these studies of simple semiconductors and insulators.

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26. HIGH-RESOLUTION AND IN-SITU INVESTIGATIONS OF SMALL PARTICLES AND REACTIONS ON SURFACES

K. Heinemann, Adjunct Professor, Materials Science and Engineering

Professional Associates:

H. Poppa	G. M. Pound
R. Anton	C. Y. Yang
R. Sinclair	M. J. Yacamán

Graduate Students:

K. W. Carey
M. Avalos-Borja
K. Furuta (received Engineer's degree during report period)

Agency Support:

NASA - NSG 2249
NASA - NCA 2-Or-745-901
NSF - 77-05958

Technical Objective:

Increase the understanding of fundamental aspects in thin film growth and catalysis.

Approach:

- (a) Characterize nanometer-size metal particles, deposited on substrates, by sophisticated methods of high-resolution transmission electron microscopy.
- (b) Determine the growth behavior of small metal particles during vapor deposition by in-situ transmission electron microscopy studies under controlled conditions (uhv and deposition parameters).
- (c) Investigate the reaction of deposit small metal particles with gases under controlled vacuum and temperature conditions, using the in-situ transmission electron microscopy approach.

Research Report:

1. THE CHARACTERIZATION OF SMALL MULTIPLY TWINNED, VAPOR-DEPOSITED METAL PARTICLES

Research Associate: C. Y. Yang
Professional Associate: H. Poppa
Visiting Scholar: M. J. Yacamán

Based on the exact crystal structure of decahedral and icosahedral particles, high energy electron diffraction patterns and

image profiles have been derived for various high symmetry orientations of the particles with respect to the incident beam. These results form a basis for the identification of small metal particle structures with advanced methods of transmission electron microscopy.

The crystallographic structure of small gold particles vapor-deposited on NaCl substrates was investigated using high resolution, selected-zone dark field (SZDF), Bragg reflection imaging (BRI), moiré fringe imaging, and strong beam and weak beam dark field (WBDF) transmission electron microscopy (TEM) imaging techniques. Those particles that exhibit uniform contrast in bright field (BF) and have a distinct triangular shape are perfect single crystals with a face-centered cubic (fcc) structure. The particles with pentagonal profile were determined to be regular decahedra composed of five identical tetrahedral building units of non-fcc structure. Each unit has a body-centered orthorhombic crystal symmetry, slightly distorted from the fcc structure. The experimental evidence for this particle model and for the conclusion that the older model based on fcc tetrahedral building units does not apply includes (a) SZDF-BRI micrographs demonstrating the nonexistence of gaps between the tetrahedral units; (b) WBDF images showing thickness fringes that exclude nonuniform lattice strains that would result from an fcc model with closed gaps; and (c) micrographs exhibiting characteristic moiré fringes in well-defined parts of the composite particles.

"Multiply-twinned" gold particles with hexagonal bright field TEM profile were determined to be icosahedra composed of 20 identical and twin-related tetrahedral building units that do not have an

fcc structure. The crystal structure of these slightly deformed tetrahedra is rhombohedral. Experimental evidence supporting this particle model was obtained by selected-zone dark field and weak beam dark field electron microscopy. It has been concluded that multiply-twinned gold particles of pentagonal or hexagonal profile that are found during the early stages of the vapor deposition growth process on alkali halide surfaces do not have an fcc crystal structure, which is in obvious contrast to the structure of bulk gold.

2. THE CHARACTERIZATION OF SMALL SINGLE CRYSTALLINE, VAPOR-DEPOSITED METAL PARTICLES

Professional Associate: H. Poppa
Visiting Scholar: M. J. Yacamán
Graduate Student: M. Avalos-Borja

The three-dimensional habit of small metal crystallites (> 5nm in size) can be determined by a combination of selected-zone dark-field (SZDF) and weak-beam dark-field (WBDF) transmission electron microscopy. The information can be obtained from one electron micrograph which is taken in a defocused SZDF condition where all reflection images are clearly separated. The method is based on an evaluation of a) the general intensity of corresponding reflection images, which gives rise to the orientation of the particles with respect to the electron beam, and of b) the weak-beam thickness fringes which appear in those reflection images that were subject to a relatively large excitation error. The particular advantage over the WBDF method proposed earlier by Yacamán and Ocaña⁽¹⁾ is that no tilting sequence is required.

The habit faces of various single crystal vapor deposited metal particles in the 5-15 nm size range were determined, using the method

described above in conjunction with multibeam computer calculations of image intensifiers. Particles exhibiting square and rectangular shapes in bright field TEM were often found to be truncated pyramids with {001} base and top surfaces and {111} faces. Sometimes {001} based cubes with {001} faces could be identified. Single crystalline pentagonal particles were found frequently and determined to have {001} base and surfaces, as well as three {111} and two {011} side faces. Particles with triangular bright field profile had a {111} base and three {001} faces. Gold crystallites growing on KCl substrates were found, under certain conditions during the coalescence stage, to form large, irregularly shaped, very flat islands with {001} top surfaces.

Reference:

- (1) M. J. Yacamán and T. Ocaña, phys. stat. sol. (a) 42, 571 (1977).
3. IN-SITU TEM OBSERVATIONS OF DIFFERENT GROWTH MODES OF SMALL IRON PARTICLES ON SAPPHIRE.

Research Associate: R. Anton

An in-situ study was performed of the growth kinetics of individual crystallites during the deposition of iron onto electron-transparent single-crystalline α -Al₂O₃ (sapphire) substrates. Clean sapphire films were produced in-situ under UHV conditions by electron-beam induced crystallization of amorphous Al₂O₃ (1). Iron was electron-beam vapor-deposited at constant rates (0.2 - 0.5 nm/min) and elevated substrate temperatures (750 - 900°C) immediately following the crystallization. The nucleation, growth, and eventual coalescence of the metal particles were observed in-situ by transmission electron microscopy and recorded on video tape at 30 frames per

second, at high electron optical magnifications.

The mean diameters of the growing particles as calculated from the projected areas, are plotted vs. the deposition time t , the growth can be represented by a $t^{0.5}$ -dependence. This is expected for three-dimensional growth of a particle (2,3) when the capture rate for adatoms is proportional to the circumference of the particle, and when the contribution of the directly impinging vapor beam can be neglected, e.g., if the particle is small.

Whereas the early stages of growth of most particles can be described with this $t^{0.5}$ -dependence, after a coalescence event the growth mode of a particle may suddenly change to a linear increase of the mean diameter with time. This behavior can be related to a two-dimensional expansion of the particle (1). In some cases, a $t^{1.8}$ -dependence was observed. This observation was concomitant with a distinct particle elongation in one direction. A calculation revealed that this can only be the case when most of the captured adatoms, including those impinging on the crystallite itself, contribute to the preferred growth in one direction.

This observation of various growth modes is an indication of preferred surface and/or bulk diffusion of adatoms during vapor depositions.

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4. THE NUCLEATION, GROWTH, AND OXIDATION OF IRON PARTICLES ON α -ALUMINA

Professional Associate: H. Poppa

Research Associate: R. Anton

In an attempt to correlate the crystallographic structure and shape of small transition metal particles with their chemical activity, we have studied the low-pressure oxidation of small iron particles nucleated on clean α - Al_2O_3 substrate films. We have used an in-situ transmission electron microscopy (TEM) approach for substrate preparation, subsequent iron deposition, and subsequent oxidation, in order to maintain optimum control of the surface crystallography and cleanliness, which influence decisively the oxidation reaction.

Single crystalline areas of sapphire were produced by electron-beam flash-heating of amorphous films that had been prepared externally by anodic oxidation of aluminum.

Iron was deposited at a rate of 0.1 nm/min on recrystallized Al_2O_3 at various substrate temperatures: $T_s \approx 100^\circ\text{C}$ was chosen to achieve nearly continuous films; temperatures above 700°C were used to obtain large iron crystallites with lower number density and highly epitaxial orientation. Oxidation was performed by introducing oxygen into the chamber to a partial pressure of 10^{-3} Pa at specimen temperatures starting at 70°C and slowly increasing up to 500°C .

First oxide diffraction intensities were observed after 30 min. of oxygen exposure at 70°C . A slow increase of the temperature to 200°C under continued oxygen exposure increased the oxide diffraction intensities which appear next to the iron arcs and reproduce their texture, indicating that the oxide is growing epitaxially on the iron.

Further oxidation at 330°C for 30 min. yielded large grains of

apparently completely oxidized iron. Additional heating at 440°C under continued oxygen exposure resulted in a near-perfect epitaxial reorientation of the iron oxide on the substrate, concomitant with transformation to rhombohedral α -Fe₂O₃. The rate of oxide growth was different on different faces of the iron particles.

During vacuum annealing (without oxygen exposure) of partially oxidized iron at 450°C, fluid-like coalescence of the oxide with the iron particles was observed. Evaluation of diffraction patterns and the moiré-spacings leads to the tentative conclusion that during this high-temperature annealing phase, the oxide had been transformed to very large, thin FeAl₂O₄ crystals that are perfectly epitaxial to the substrate. The observed spreading of the oxide over the substrate, and the concomitant re-orientation, is believed to be due to a high mobility of the oxide species on the α -alumina substrate. Our observations are in qualitative agreement with recently reported results by Chen et al. who reported a spreading of PdO [1] and, to a lesser extent of Rh₂O₃ on amorphous SiO₂ substrates, and who argued that this effect is due to a stronger interaction between the substrate and the oxide when compared to the substrate-metal interaction. Our investigations are continuing with emphasis on the influence of the sapphire substrate on the oxidation product.

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27. ELECTRON-DENSITY APPROACH TO BINDING ENERGIES OF MOLECULES AND
CONDENSED SYSTEMS

Conyers Herring, Professor, Applied Physics

Technical Objective:

To develop a new technique for estimating the ground-state electronic energy of an arbitrary configuration of atoms, that will be accurate enough to give useful results, and at the same time significantly less laborious computationally than existing methods that involve the self-consistent determination of many-electron wave functions.

Approach:

Ways of approximating the ground-state energy of a many-electron system in terms of the electron density distributions are being explored. The long-familiar Fermi-Thomas method does this, but is far too inaccurate to be useful for detailed calculations. The accuracy can be greatly improved if, in addition to the often-studied "gradient corrections," functionals of the density are employed that are fully nonlocal, i.e., that depend on the entire form of the density distribution, rather than being integrals of a function of the local density and its derivatives.

Publications:

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28. STRUCTURAL STUDIES OF METALLOENZYMES AND METALLOPROTEINS

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Agency Support:

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Research Areas:

(1) EXAFS Studies of Metals in Biomolecules

A substantially enhanced capability for recording EXAFS spectra of dilute metals in biological systems has evolved over the past year at SSRL. We have concentrated on the use of EXAFS to probe structural questions about bioinorganic systems containing molybdenum, copper and iron. In parallel, we have carried out numerous studies on model systems which have demonstrated that EXAFS analysis can provide first shell distances to an accuracy of about 0.02 Å and coordination numbers to about 20%.¹

Recent work has concentrated on using EXAFS to probe how the structure of the metal site of a protein is involved in its function especially when the protein is under physiological conditions.

Examples for which EXAFS has provided accurate structural information include the "blue" copper and cytochrome (iron-containing) electron transport proteins. Our EXAFS studies of azurin and plastocyanin (both "blue" copper proteins) revealed the presence of the shortest known Cu-S bond (2.10 Å) in the oxidized form of these proteins. There is also a surprisingly long Cu-S bond around 2.70 Å. Upon a 1 electron reduction, the short Cu-S bond is observed to lengthen by a full 0.1 Å. We have also succeeded in elucidating the active site structure of hemocyanin (an invertebrate oxygen transport protein). The oxygen binding Cu site is dimeric with a Cu-Cu distance of 3.58 Å. The Cu-Cu distance lengthens on loss of oxygen and this fact may be related to the observed cooperativity of hemocyanin.² In contrast, the reduction of ferric to ferrous iron in cytochrome c is not accompanied by changes in metal ligand geometry.

(2) Anomalous Scattering Studies Using Synchrotron Radiation

The earliest uses of anomalous scattering were in single crystal diffraction measurements where the consequences of the effect were used in the determination of absolute configuration (handedness) of chiral molecules in crystals. More recently, the effects have been used extensively in macromolecular crystallography for locating anomalously scattering atoms, in refining their positions, and in assisting in phase determination. Other applications, such as unique phase determination using multiple wavelengths and extraction of elemental specific radial pair correlation functions in polycrystalline or disordered systems have been suggested.

Before synchrotron radiation became available, the measurement of anomalous scattering terms was impractical except at specific wavelengths since the emission of standard anode X-ray sources yield photons predominantly at discrete wavelengths. This discreteness limits the measurement of f' and f'' to specific photon wavelengths not necessarily close to an absorption edge. Since the largest changes in the anomalous scattering are within a few electron volts of the edge, the large magnitude of the effects could not be accurately measured (or

used experimentally) with characteristic lines from these anode sources. Calculations of the anomalous scattering terms based on Hartree-Fock atomic methods have been tabulated, but we have shown them to be accurate only in regions that do not include absorption edges.⁶ Since the potential usefulness of anomalous scattering is dependent on the maximum change in f' and f'' that can be attained by varying the wavelength, previous methods of determining the anomalous scattering factors do not illuminate the most interesting regions of the anomalous scattering spectra.

Synchrotron emission is a source of photons in which the photon energy can be varied continuously over a wide range limited only by the monochromator and operating conditions of the electron storage ring used to produce the radiation. Our X-ray absorption studies using synchrotron radiation indicate that large anomalous effects are present as the incident photon energy approaches an L absorption edge (p-state ionization). The failure of the Hartree-Fock atomic calculations in predicting these features implies that the effects are not describable solely in terms of atomic states and that transitions into excited molecular electronic states must be included. Our calculations indicate that, indeed, transitions into bound states or molecular shape resonances just above the continuum threshold give rise to complex edge structure as observed. (Transitions to highly excited continuum states give rise to extended fine structure - EXAFS.) With the availability of an X-ray diffractometer on a synchrotron radiation source,³ anomalous scattering terms can be measured at arbitrary energies for a crystal of known structure. The anomalous scattering terms for cesium in cesium hydrogen tartrate have been determined near the L_1 , L_2 , and L_3 edges.^{4,5} These studies revealed values of f' of -26.7 electrons at the L_3 edge (5016 eV) and of -13.5 electrons 50 eV below and 5 eV above the L_3 edge.

We performed a survey of high energy resolution absorption spectra of a variety of lanthanide and heavy metal complexes using synchrotron radiation.⁶ The survey revealed even larger changes in absorption at

L_3 and L_2 edges than was found in the cesium study. Similar sharp changes were earlier dubbed "white lines" because of their characteristic trace left on photographic negatives in absorption measurements. Since f'' is related to the absorption cross section by the optical theorem and f' can be derived from f'' using the Kramers-Kronig dispersion relation, we have carried out a systematic study of the absorption spectra of a large number of L edges for the lanthanide and other heavy metal complexes in order to assess their anomalous scattering terms. These substantial changes in the anomalous scattering factors have applications to deriving structural information for macromolecules from X-ray diffraction studies. The magnitude of the changes indicate that the anomalous scattering technique is a powerful means of obtaining structural parameters for macromolecules in single crystals, in solution, and in biological membrane samples.

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29. . SOLID STATE ELECTROCHEMISTRY

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Institute for Energy Studies, Stanford
National Science Foundation through CMR

Technical Objectives:

SOLID STATE IONICS

- (1) Development of new materials for use in solid state electrochemical systems. This involves design, synthesis and characterization of new inorganic materials as well as evaluation of their structure, thermodynamic and kinetic properties.
- (2) Achievement of understanding concerning the important phenomena involved in the rapid transport of ionic and electronic species in solid electrolytes and mixed ionic-electronic conductors, and their structural basis.

- (3) Development of relevant experimental and theoretical techniques for the evaluation of thermodynamic and kinetic properties of molten salts and solids with mobile ionic species.
- (4) Investigation of various areas of potential application of solids with fast ionic transport, such as materials and phenomena involved in high performance battery and fuel cell systems, catalysis, selective ion sensors, electrochromic display devices, etc.

MATERIALS PREPARATION METHODS

Investigation of new techniques for materials synthesis and the preparation of special microstructures, including electrocrystallization of metals, alloys, semiconducting materials, and metal-metalloid compounds, as well as the synthesis of metals and ceramics by the decomposition of infiltrated polymeric precursors.

Research Report:

(1) Lithium-Based Electrochromic Materials

A new program of research has been undertaken to investigate the possibility of using the color change observed on electrochemical injection of lithium into some transition metal compounds as a display device. The ultimate objective is to develop an all solid state system. The program involves the discovery of new electrochromic materials and the development and use of equilibrium, steady-state and transient electrochemical techniques for the assessment of their utility.

(2) Materials for Advanced Lithium Batteries

Theoretical models have been developed and experimental measurements made of the defect structure, and ionic and electronic conductivity in several groups of solids with highly mobile atomic species. Particular attention has been

devoted to materials with crystal structures containing crystallographic tunnels and sparsely populated sites. These have included beta alumina, alkali metal ferrocyanides, titanates, germanates, silicates, aluminosilicates, fluorides and related materials. Current work concentrates on materials which show very high lithium ionic conductivity at ambient and elevated temperatures. Materials include solid solutions with structures related to lithium orthosilicate and lithium phosphate, which have high conductivities at about 400 C, the temperature of interest for some advanced lithium batteries. A second material of importance is lithium nitride, which has a layer type crystal structure with very high lithium ion conductivity at ambient temperatures. While this behavior is very anisotropic, it has been found that appropriate control of the microstructure can produce polycrystalline bodies with very high lithium ionic conductivity values at ambient temperatures, close to those in the "fast" direction in single crystals. Other materials include alkali metal aluminum halides, and pure and doped materials with the anti-fluorite structure.

A number of potentially interesting electrode materials are also being investigated. A new galvanostatic intermittent titration technique has been developed to evaluate the chemical diffusion coefficient and other kinetic parameters of mobile ionic species in mixed ionic-electronic conductors. This method is especially powerful when used in conjunction with coulometric titration, which allows the composition of a single phase sample to be changed quantitatively, thus avoiding reproducibility and analytical problems normally encountered in the production of a series of separate samples of different compositions. By these means, both thermodynamic and kinetic data can be obtained on appropriate materials with an unusual combination of precision and compositional

resolution. Especially interesting is the ability to evaluate thermodynamic quantities, such as the free energy of formation, as a function of composition within narrow intermediate phases. Likewise, kinetic quantities such as the chemical diffusion coefficient, self diffusion coefficient, partial ionic conductivity, and tarnishing rate constant can be obtained as functions of the stoichiometry - and thus defect concentrations - in narrow phases. These techniques are being applied to the lithium-aluminum negative electrode, and to a variety of new positive electrode materials, which include ternary oxides, sulfides and nitrides.

(3) Electrodeposition from Molten Salts

Theoretical and experimental work are underway on the use of electrochemical techniques for the growth of both single crystals and polycrystalline materials, as well as for the preparation and purification of selected materials. Of special current interest is the inexpensive preparation of silicon by electrocrystallization from molten salts.

(4) Use of Solid State Ionics to Influence Heterogeneous Catalysis

It has been shown that electrochemical cells involving solid electrolytes and mixed ionic-electronic conductors can be used to control the concentrations of specific species at solid-gas interfaces, and to greatly influence the rates of heterogeneous reactions.

Experiments have shown that the rate of decomposition of NO can be increased by a factor of a million by the use of solid state ionic techniques, achieving greater specific reaction rates on certain oxides than on platinum.

Current work is aimed at the extension of these concepts and techniques to influence heterogeneous displacement reactions upon the surfaces of solids.

(5) Use of Anion-Conducting Solid Electrolytes in Coal-Consuming Fuel Cells

The mass transport and thermodynamic properties of several groups of new materials are being investigated as oxide ion-conducting solid electrolytes. A second goal of this work is the investigation of the potential utilization of such materials in novel types of moderate temperature fuel cells for the combustion of coal and related carbonaceous materials.

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30. ACOUSTIC INTERACTIONS WITH SOLIDS

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F49620-79-C-0217

Nondestructive Testing

Technical Objective:

To use acoustic techniques to determine the location and size of flaws in materials and determine more subtle properties of materials such as microstructural properties and hardness.

Approach:

Acoustical image techniques in which an array of piezoelectric transducers is employed have been shown to produce good images of flaws in metal samples. Related techniques operating at high frequencies are being used to measure and characterize extremely small flaws in ceramics. Similar techniques are also being developed for surface wave probing of surface cracks and for measurement of microstructure in metals.

Research Report:

We have continued our construction and examination of acoustic imaging systems. A 32 element real-time synthetic aperture digitally processed acoustic imaging system has been built and is being tested. We have used this device to image surface cracks and holes in aluminum and steel. We have also been employing it to image simple objects like wires and metal plates in water. Theoretical studies have begun on the nature of the images to be expected from simple shapes of defects and in particular specular reflectors. Experimental results seem to be in reasonably good agreement with our expectations.

A second system is being constructed. The second computer processed, mechanically scanned, synthetic aperture system is being constructed for detecting and analyzing flaws in ceramics. It will operate at a frequency of 50 MHz. We have used our detailed numerical scattering theory from spherical defects in a solid matrix as an input to our synthetic aperture image reconstruction computer program. This makes it possible to predict in detail the image of a spherical defect. We have carried out theoretical reconstructions using 32 elements in a complete circle around the cylindrical object to be examined, and also theoretical reconstructions in three dimensions using elements located on the peripheries of 16 discs with 32 points around the circumference of each disc. A resolution of a point source of .2 wavelengths is possible in the circumferential direction with a resolution of approximately .5 wavelengths in the axial direction. In these theoretical reconstructions, specular reflectors and spherical reflectors are not reproduced with such accuracy, but we should be able to pick out the radius of voids and the required information about the size of spherical inclusions.

An experimental system has been built for examining cylindrically shaped silicon nitride ceramics and will shortly be tested in the imaging mode. It is possible to scan a single transducer with an 8 μ m accuracy in two directions and rotate the cylindrical sample accurately in the angular direction. A 50 MHz transducer has been built with excellent operating characteristics for use in this system.

We have been measuring scattering of 3.5 MHz surface acoustic waves from surface cracks in ceramics. We have been able to predict breaking stress of small half-penny shaped surface cracks of the order of 100 μm diameter with accuracy. We have observed acoustically that many cracks are closed at the top and that plasticity is an important effect in structural ceramics such as silicon nitride. The results we are obtaining appear to be in good agreement with the materials properties predicted by Evans and Marshall at Berkeley. However, this is the first analytic tool that has been available for making such measurements. The same techniques are being developed for use with conically-shaped acoustic surface wave wedge transducers, so as to be able to measure surface cracks in cylindrically-shaped ceramics. Later, after measuring natural cracks in these ceramics, the ceramics will be stressed in a stressing rig, and the breaking stress determined. We will then compare our acoustic predictions with the actual measured breaking stress.

We have perfected our techniques for measuring attenuation in metals and can carry out scans of attenuation over the cross section of a metal sample in much the same manner as we already do with velocity. We have observed that with samples of aluminum, attenuation can vary from the center to the edge, as does the acoustic velocity. In both cases, there is a monotonic change of these parameters; this appears to be associated with variation of grain size and texture of rolled samples over their area. The velocity measurement techniques seem to provide a very useful method of determining texture variation while the attenuation measurements are associated with both texture and grain size variation. Thus we believe that with these techniques we have arrived at important new methods of measuring microstructural properties of metals.

Other related work on measuring stress and stress intensity factor has been carried out on our Thrust Program on Nondestructive Testing. This is reported separately.

Acoustic Surface Wave Correlators and Convolvers

Technical Objective:

To construct devices which can correlate two electrical signals

with each other, take transforms of signals, and act as variable programmable delay lines, and in particular, programmable inverse filters and adaptive filters.

Approach:

We are constructing acoustic surface wave devices on silicon substrates. A sputtered zinc oxide layer is used to provide piezoelectric coupling.

Research Report:

We described last year an acoustic surface wave correlator which employs zinc oxide laid down on silicon. During the year, we have developed our magnetron sputtering system further and have carried out very complete tests on it.

The system is now extremely reliable, and we have obtained ZnO films of outstanding quality. We find that we can grow excellent ZnO on top of the thermal SiO₂ grown on Si. We have observed x-ray rocking angles as low as 0.27°, a result which is almost as good as we would observe with our x-ray system on perfect single crystals. The acoustic coupling coefficients that are measured appear to be at the full value to be expected; RED measurements again indicate almost perfect material.

A method of measurement has been developed in cooperation with T. Evans at Berkeley in which he uses a Knoop hardness indenter to test the adherence of the ZnO layer to the substrate. This material appears to have uniform adherence over the area of the substrate and to be far better in quality than any other material he has tested.

Similar measurements have been made with zinc oxide deposited on gold, on platinum, on aluminum, on sputtered SiO₂, and directly on Si. In all cases, we are obtaining high quality zinc oxide layers. With oriented platinum, the layers are as good as those observed on silicon dioxide. With most of the other materials, there is only a very slight deterioration of quality.

We are therefore very pleased with the results of this deposition technique. Acoustically, the results we have obtained by these test methods bear out our predictions. We have made surface wave correlators

and convolvers with better performance than any of those we have made previously. Only one problem appears to have remained: this is associated with the fact that after the system has been used for some time, ZnO collects on various parts of it and can flake off during the deposition producing spots on the ZnO layer. This deteriorates the performance of acoustic surface wave devices but is a problem which we believe we can eliminate with care.

31. ELASTIC-PLASTIC STRESS ANALYSIS WITH PARTICULAR EMPHASIS
ON METAL-FORMING APPLICATIONS

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NSF-ENG-77-16342
NSF-MRL Through CMR - Thrust Program on Plasticity
and Metal Working

Technical Objective:

In order to be able to predict that a metal-forming process will produce a satisfactory product, free from defects such as internal and surface cracks, high residual stresses or local concentrations of high strain, it is necessary to carry out a complete elastic-plastic stress and deformation analysis of the process. The Thrust Program on Metal-working and Plasticity is concentrating on particular aspects of this area of technology: a.) the finite-element analysis of cold extrusion and comparison of the residual stresses evaluated with acousto-elastic measurements of them, and b.) the finite-element analysis of warm rolling of steels and comparison of the resulting predictions of process characteristics with those observed in rolling experiments. Much of the group's research supports this thrust program and is described in the

Thrust Program on Metalworking and Plasticity contribution to this Annual Technical Report. In the course of that investigation, a basic error was uncovered in the currently accepted elastic-plastic theory for finite deformation. What led to the discovering of this problem and the basic reason for it were presented in a report on the project [1]. Since the development of elastic-plastic theory stimulated by this anomaly falls outside the main scope of the thrust program, this facet of our research is reported separately. The objective of this part of our work is to correct the basic structure of elastic-plastic theory, hence to improve the accuracy of the theoretical evaluation of stress and deformation distributions by ascertaining in what circumstances the approximation involved in the currently accepted approach is adequate.

Approach:

The adjective "incremental" is commonly used to describe plasticity theory since the increment of strain due to elastic-plastic loading is a function of the stress and increment of stress defining the loading, in addition to the history of previous plastic deformation. Such a relation contrasts, for example, with elasticity in which the total strain is determined by the stress acting currently, so that the initial unstressed configuration maintains an influence on the elasticity law throughout the deformation. An incremental relation can be equivalently expressed by the strain-rate being determined from the stress-rate and the stress, a relation more akin to fluid behavior than that of a solid, although plasticity commonly falls under the rubric of solid mechanics. The application of such an incremental law for the evaluation of stress and deformation distributions is commonly carried out in terms of the velocity field in the current configuration of the body, specifically the rate of strain being expressed as the symmetric part of the velocity gradient. Even when large deformations occur as in metal-forming, this approach eliminates the need to define large (finite) strains since a step-by-step evaluation is adopted with

sufficiently small time steps to ensure small increments of strain which have, in the past, commonly been considered to be adequately analyzable by linear (infinitesimal) kinematics. That coupling between these increments and elastic and plastic strains does demand a non-linear kinematic analysis, irrespective of the magnitude of the time step, was pointed out some years ago, [2], but complete formulation of the theory on this basis was not achieved.

The approach adopted in our recent elucidation of this anomaly is to utilize the full non-linear kinematics, including rate terms, which brings out the error involved in the almost universally adopted linear incremental approach.

Research Report

Graduate Student: V. A. Lubarda

When an increment of stress is applied to a body, causing elastic and plastic increments of deformation, and then removed, linear incremental kinematics defines the reversible part of the strain increment to be an increment of elastic strain, and the residual or irreversible part to be an increment of plastic strain. However, the exact non-linear kinematics shows that if the increment of deformation includes rotation, a possibility which must be incorporated into a general loading analysis, part of the residual strain increment will comprise an elastic change of strain due to the increment of rotation. If, as is the case of linear incremental analysis, this component of residual strain is ascribed to plasticity and incorporated into a variational principle through the plasticity constitutive equation, error in the resulting stress field evaluation will arise, and hence also in the finite-element code based, as is commonly the case, on such an analysis.

A variational principle based on the complete non-linear kinematics has been developed [3]. The formulation currently in common use has been shown to be an approximation to the complete formulation which is good for many situations. Analyses to determine when errors become significant are in progress.

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32. SUPERCONDUCTIVITY AND MOLECULAR PHYSICS

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Agency Support:

NSF-MRL through CMR

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ONR N00014-78-C-0514

CIT PF-185 8-808978

NSF DMR 76-82087-3CS

Technical Objective:

To study the feasibility of obtaining superconductivity at a relatively high temperature in organic and organo-metallic systems. The design and fabrication of microminiature cryogenic refrigerators using photolithographic techniques. To understand the nature of short and long term memory in neural networks; and, the development of mathematical tools to handle this problem.

Approach:

Our main line of work is the study of the possibility of high temperature superconductivity using an exciton induced electron-electron interaction rather than the phonon mechanism. Our efforts have centered on linear chain systems where we believe a sufficiently strong excitonic interaction can be obtained with suitable ligands.

We have studied the effects of impurities and imperfections on the various types of ordered phases in quasi-one-dimensional systems and the effects of the resultant localization on superconductivity. (1,2,3)

We have also considered the design of complex macrometals and the possibility of achieving superconductivity in them. (4)

An investigation of the feasibility of building micro-miniature cryogenic refrigerators using photo-lithographic techniques has yielded promising results. Techniques have been developed for building counter-current heat exchangers and Joule Thomson refrigerators on thin glass plates. The prospects of building a miniature 4K Helium refrigerator by this means looks good.

Work has continued on the study of the memory storage capacity of a neural network. A linearized approximation of the mathematical description of the problem corresponding to the high temperature expansion of the corresponding Ising model has been solved exactly.⁽⁵⁾ Some progress has been made in the solution of the general problem. We have shown that our model has a holographic-like means for the recall of information from long term memory.

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33. SURFACE REACTIVITY

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Overall Technical Objective

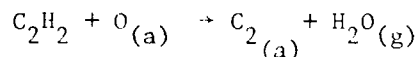
To understand the effects of the geometry and composition of metal and metal compound surfaces on chemical reactivity at surfaces.

Oxidation Reactions on Ag(110)

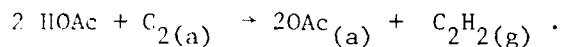
M. Barteau

Our work in this area was continued in order to probe further the basicity of adsorbed oxygen. The results are exemplified by the reactions of acetylene and Co_2 with surface oxygen. Acetylene, a very weak acid, reacts with preadsorbed oxygen on Ag(110) surfaces to form a surface acetylide, C_2 , and water. Depending on the initial concentration of oxygen, acetylides of different surface structures are

formed. When heated the acetylide decomposes to form carbon atoms which are readily oxidized to CO_2 by oxygen. The overall surface reaction



can be viewed as an acid-base reaction; $\text{C}_{2(a)}$ is then a base. It can, in fact, be protonated reversibly by



Carbon dioxide reacts with $\text{O}_{(a)}$ to form a surface carbonate. The initial rate of reaction is higher on a surface with randomly adsorbed oxygen atoms than one possessing a high degree of order. This structural dependence is apparently due to the stabilization of the oxygen atoms in the ordered state. Formation of the $\text{CO}_{3(a)}$ leads to structural domains which cause compression of the oxygen atoms along the channels in the (110) surface. The repulsive forces that accompany this compression appear to limit the extent of formation of $\text{CO}_{3(a)}$.

Photoelectron Spectroscopy of Adsorbed Species and Intermediates

M. Bowker

The adsorption of methanol on clean and oxygen dosed Cu(110) surfaces has been studied using temperature programmed reaction spectroscopy (TPRS), ultra-violet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). Methanol was adsorbed on the clean surface at 140K in monolayer quantities and subsequently desorbed over a broad range of temperatures from 140 to 400K. The UPS He(II) spectra showed the 5 highest lying emissions seen in the gas phase spectrum of methanol with a chemisorption bonding shift of the two highest lying orbitals due to bonding to the surface via the oxygen atom with which these orbitals are primarily associated. A species of quite a different nature was produced by heating this layer to 270K. Most noticeably the UPS spectrum showed only 3 emissions and the maximum coverage of this state was approximately 1/2 monolayer. The data is indicative of the

formation of a methoxy species thus showing that methanol is dissociated on the clean Cu(110) surface at 270K. The same dissociated species was observed on the oxygen-dosed surface, the main difference in this case being the production of large amounts of H_2CO observed in TPRS at 370K.

Bimetallic Alloys

E. Silverman

The chemisorption of hydrogen and carbon monoxide and the decomposition of formaldehyde and formic acid were examined on copper (10%)/nickel (90%)-(110) and nickel (76%)/iron (24%)-(100) single crystals using a combination of ultra-high vacuum surface science techniques. The Cu/Ni alloy surface was varied in composition from 100% Ni to 35% Ni by sputtering and annealing to different temperatures. The surface composition of the Ni/Fe alloy sample was found to be only slightly iron-enriched after annealing. The principal aim of this investigation was to identify changes in the chemisorption and the surface reactivity properties between the pure metal components and the resulting alloy systems in order to illustrate the different effects of alloying.

The chemisorption of carbon monoxide and hydrogen on the Cu/Ni surfaces was studied by flash desorption spectroscopy (FDS) and Auger electron spectroscopy (AES). Different adsorption sites of carbon monoxide, identified in the desorption spectra of CO from the alloy surfaces at saturation coverage, were associated with desorption from ensembles consisting of Ni atoms, Cu atoms, and Cu-Ni pairs. The weakening of the chemisorption bond strength of CO adsorbed on four-fold Ni ensembles was attributed to the Ni atoms becoming surrounded by Cu atoms (i.e., ligand effect). Saturation hydrogen coverages were initially insensitive to the addition of copper to a nickel surface, and decreased sharply on the 61% Ni/39% Cu and 35% Ni/65% Cu alloy surfaces. The results support an adsorption model where a hydrogen atom can be bound to ensembles consisting of Ni-Ni adsorption sites and Cu-Ni adsorption sites. The findings of these adsorption studies indicated that the main effect of alloying the Ni surface with Cu atoms was the variation in the

population of the different carbon monoxide and hydrogen adsorption states.

Carbon monoxide adsorption on the Ni/Fe surface was investigated by X-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), and flash desorption spectroscopy (FDS). An XPS and FDS comparative study of the CO behavior of the Ni/Fe(100) surface with the CO behavior of the clean Ni(100) and Fe(100) surfaces indicated a strong similarity in the chemisorption properties between the Ni/Fe(100) and the Ni(100) surfaces. CO adsorption states and heats of chemisorption for the Ni/Fe alloy surface were characteristic of pure Ni.

The interaction of formic acid (HCOOH) with a clean Ni/Fe single crystal was examined by XPS, UPS, and TPRS. The dehydrogenation of formic acid via a formate intermediate was the sole reaction observed on the Ni/Fe(100) surface and was similar to the behavior of the Fe(100) surface to formic acid decomposition. However, the results contrast with the Ni(100) surface where the amount of the dehydration and dehydrogenation of formic acid was identical. The difference in the selectivity between the alloy surface and nickel surface was ascribed to the destabilization of the anhydride species formed on Ni(100) which is believed to result from the necessity of an ensemble consisting of four Ni atoms. The findings of these reaction studies clearly revealed that the major effect of alloying was the dilution of active sites.

The Effect of Sulfur on Surface Reactivity of Metals

N. Abbas

S. Johnson

The effects of sulfur on the adsorption and desorption behavior of hydrogen and carbon monoxide and surface reactions on Ni(100) and Pt(111) were investigated under ultra-high vacuum (UHV) conditions by temperature programmed reaction spectroscopy (TPRS). The formation and stability of the sulfurized surfaces prepared by the thermal decomposition of H_2S adsorbed at 300K were monitored by Auger electron spectroscopy, low energy electron diffraction, and TPRS. The one-quarter

and one-half monolayer surfaces were found to be thermally stable to 900K, chemically stable under UHV conditions with respect to the adsorbates used here, and to inhibit the formation of surface carbon by promoting diffusion of carbon into the bulk. The results on Ni(100) are summarized below.

The pre-exponential factor and activation energy which characterized hydrogen desorption, a 2nd order, recombination limited process, were modified by sulfur in a continuous manner from $5 \cdot 10^2$ cm²/atom-sec and 21.3 kcal/gmole (clean surface) to $3 \cdot 10^{-8}$ cm²/atom-sec and 10 kcal/gmole on the c(2·2)₁S surface. Desorption of CO from the clean surface was a first order process with an activation energy which decreased from 26.1 kcal/gmole with increased CO coverage. The addition of sulfur reduced the amount of CO adsorbed in that state, which was eliminated on the C(2·2)₁S surface, while creating or enhancing additional peaks with binding energies of 22.1 and 19.1 kcal/gmole. The pre-exponential factors, 10^{13} /sec, and activation energies for these peaks were not altered by sulfur. These results also indicated that the low coverage binding site of CO on Ni(100) is the four-fold hollows.

Four surface reactions, two decomposition and two dehydrogenation, were identified for alcohols on clean and sulfurized surfaces. One of the decomposition reactions proceeded via a stable [COD] type intermediate. Addition of sulfur to the surfaces shifted selectivity from decomposition to dehydrogenation via alkoxide intermediates. Methane and its deuterium substituted analogs were produced by decomposition of CH₃CH₂OD. The distribution of deuterium in methane species indicated that methane was formed from adsorbed carbon by the step wise addition of hydrogen atoms.

The effects of sulfur on the surface reactions of alcohols stabilized larger molecular fragments or intermediates and may be seen as a combination of ligand and ensemble effects. The results of this study also provided insight into methanation on nickel and its poisoning by sulfur.

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8. M. A. Barteau, M. Bowker and R. J. Madix, "Acid-Base Reactions on Solid Surfaces: The Reactions of HCOOH, H₂CO, and HCOOCH₃ with Oxygen on Ag(110)," Surface Sci. 94, 000 (1980).
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34. THE ROLE OF F- AND V- CENTERS PRESENT IN OXYGEN-ION TYPE ELECTROLYTES IN ELECTROCATALYZING GASEOUS REACTIONS.

David M. Mason, Professor, Chemical Engineering and Chemistry

Visiting Scholar: Dr. Boo Goh Ong, University of Malaysia

Post-doctoral Fellow:

Dr. C.C. Chiang

Graduate Student:

B. Nguyen

Agency Support:

ACS-PRF-9864-AC7

DOE 10492

Technical Objective:

An experimental investigation of the kinetics of cathodic reduction of oxygen from air and anodic oxidation of selected fuels on a 1 cm diameter disc of stabilized zirconia with a porous metallic electrode surface has been made. The experimental results show that the electrolyte predominates in catalytic activity compared to either noble metal, platinum or gold. It is hypothesized that F-centers (or trapped electrons) formed electrochemically in the electrolyte at the cathode act as catalytic sites for reduction reactions. Correspondingly, V-centers (or holes) formed in the electrolyte at the anode are hypothesized to act as catalytic sites for certain oxidations. Support for this mechanism is being tested by irradiating the electrode-electrolyte system with β -rays, since radiation as well as electric potential is known to produce F- and V-centers. In all the studies, scandia stabilized zirconia was employed.

Research Report:

Experiments on fuel-cell anodic reactions of gaseous hydrocarbon species derived from petroleum or coal such as: CO , H_2 , CH_4 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ show that the electrolyte is playing the predominant role in the overall rate process, independent of whether porous platinum or

gold is used as the electrode. If the electrode were playing a significant catalytic role one would expect platinum which strongly absorbs oxygen and hydrocarbon species to be far more active than gold for both oxidation of hydrocarbons and reduction of oxygen (Reference 1).

By incorporating a reference electrode in the system operating under null-current conditions, separate overpotential-current relationships for the fuel anode and air cathode were obtained. Measurements were made at different temperatures in the range 700 to 800°C, allowing the activation enthalpy to be calculated. For all fuel-anodic and air-cathodic processes the activation enthalpy was found to be around 25 kcal/gmol irrespective of whether platinum or gold comprised the electrode surface. This constant-activation-enthalpy behavior further substantiates a commonality of the reaction zone; viz., the electrolyte and not the electrode.

Colored centers (F-centers), or electrons trapped in anion vacancies, created at the cathode by the imposed electrical potential may be acting as active catalytic sites for certain cathodic reactions. By the necessity of electrical neutrality V-centers (or trapped positive holes) are formed at the anode and possibly play a role in catalyzing oxidation reactions. There is a wealth of information on the mechanism of production of colored centers (in alkali halides by light or electrical potential). Only limited research on F-center formation electrochemically in stabilized zirconia has been done by Casselton (Reference 2), Guillon et al. (Reference 3) and Millet and Jacquin (Reference 4). In each of these works the F-centers were evidenced by a darkening at the cathode. The speculative electrocatalysis by F-centers and V-centers is being tested by setting up an experiment where in situ β -radiation can be directed against the anode and cathode face with ongoing electrochemical measurements. Enhancement of electrochemical rates by radiation would tend to support the F- or V-center hypothesis.

Though the controlling physical-chemical process for each system involves the electrolyte, the overpotential-current curves are quite

different for different species. In continuing work the electrocatalytic mechanisms are being studied by varying the concentration of reactant and temperature, and mathematical rate expressions are being employed to fit the experimental data.

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35. PHYSICAL CHEMISTRY OF LIPID, LIPID-PROTEIN OR LIPID-DETERGENT BILAYER
MEMBRANES

H. M. McConnell, Robert Eckles Swain Professor, Chemistry

Professional Associates:

T. Berclaz
D. G. Hafeman
G. M. K. Humphries
M. A. McCloskey

Graduate Students:

K. Balakrishnan	L. M. Smith
G. S. Cartwright	D. Torney
F. D. Howard IV	

Agency Support

NSF PCM 77-23586
NIH 5R01 AI 13587
NIH 5R23 AI14813 (GMKH)

Technical Objective:

The aim of this research is to attain a more thorough understanding of the structure and function of biological and synthetic membranes.

Approach:

Various physical chemical techniques such as electron spin resonance (ESR), freeze-fracture electron microscopy, and two-dimensional gel electrophoresis are used to study the physical nature and chemical composition of biological and synthetic membranes.

Research Report:

(1) Lateral Electrophoresis of Membrane Components

Professional Associate: T. Berclaz

Experimental evidence exists now demonstrating lateral mobility of a number of components of intact biological membranes, and also of lipids and proteins incorporated in model membranes (lipid bilayers). The aim of the undertaken research is to observe lateral electrophoresis of membrane components - spin-labeled fatty acids or phospholipids - in reconstituted membranes by the means of EPR spectroscopy and fluorescence recovery techniques.

(2) Triggering of the Macrophage Respiratory Burst

Professional Associate: D. G. Hafeman

Research is being done to characterize the mechanisms whereby immune cells, such as macrophages and neutrophils, are able to specifically recognize the surface properties of foreign bodies and to subsequently initiate biochemical responses against these bodies. The specific antibody-dependent stimulation of the respiratory burst (cyanide-insensitive oxygen consumption, L-C-glucose oxidation) of RAW264 macrophages by haptenated lipid vesicles depends strongly on the physical properties of the lipid membrane, as well as the surface density of antibodies on the vesicles. Lipid membranes that are "solid" at 37°C (dipalmitoylphosphatidylcholine, DPPC) are much more effective, per vesicle bound, than are "fluid" membranes (dimyristoylphosphatidylcholine, DMPC). Vesicle membranes that have both fluid and solid regions (DPPC containing less than 20 mol % cholesterol) show both enhanced binding rates (due to the fluid regions) and enhanced respiratory rates (due to the solid regions). In contrast to these results, the specific antibody-dependent respiratory burst of neutrophils due to haptenated vesicles parallels the antibody-dependent vesicle binding and shows no significant difference between fluid and solid target membranes.

(3) Specific Stimulation and Suppression of an In Vitro Primary Antibody-Forming Cell Response by Lipid Haptens in Fluid Liposomal Membranes

Professional Associate: G. M. K. Humphries

I have recently shown both specific stimulation and specific suppression of a primary in vitro antibody-forming cell (AFC) response by monovalent lipid haptens added to mouse spleen cell cultures as components of fluid liposomal bilayers. Selection between these two types of response is controlled by the lipid hapten concentration in the liposomal bilayers. Both types of response are given by T cell-depleted cultures but not by macrophage-depleted cultures. The role of the macrophage in this particular liposome-controlled system is not known and is currently under investigation. Preliminary results using cell supernatants suggest that its role is not that of an antigen-presenter, that function presumably being performed by the liposomes.

(4) The Effects of Cholesterol and Agents Which Modify Its Metabolism Upon In Vitro Immune Responses

Professional Associate: G. M. K. Humphries

The use of 25-hydroxycholesterol and compactin (both known to suppress HMG CoA reductase but by different mechanisms), together with the use of cholesterol, has indicated that in vitro immune responses which require cell proliferation are highly susceptible to a decrease in the availability of cholesterol. Work is in progress to elucidate the role of oxidized cholesterol as an immunosuppressant.

(5) Freeze-Fracture Studies of the Mechanism of T-Cell Cytotoxicity

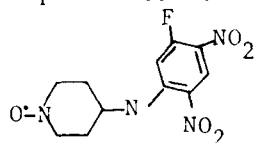
Professional Associate: M. A. McCloskey

We are using freeze-fracture electron microscopy to study the mechanism of T-cell cytotoxicity, with particular emphasis on the organization of lymphocyte membrane proteins at the junction of target and killer cells. Also, we are trying to develop a synthetic lipid membrane system which is anchored to various spherical solid substrates. This will be of interest in studies on phagocytosis and T cell-target cell interaction.

(6) Monoclonal Antibody-Producing Hybridomas

Graduate Student: K. Balakrishnan

Monoclonal hybridoma cell lines producing antibodies against a simple hapten (see below) are being generated and we hope to use them to study the first events in immune recognition of target cell membranes containing the hapten attached to phospholipids.



(7) Membrane Motion and H-2 Restriction

Graduate Student: G. S. Cartwright

My research over the past year has dealt with the phenomena of H-2 restriction both by studying the immunological process in vitro using sterile cell culture techniques and by attempting to further simplify the biological system by purifying the H-2K^k molecule and reconstituting it with synthetic membranes. The restriction phenomena itself we think is dependent on the motion of viral proteins and H-2 gene products in the plane of the membrane. Our laboratory is well suited to further define this motion.

(8) H-2 Cell Surface Motion in Virally-Infected Cells

Graduate Student: F. D. Howard IV

Cell surface motion is an important parameter in cell-cell interaction in the immune system. We are currently exploring the effect of viral infection on the major histocompatibility molecule's lateral mobility on a variety of cell types. Initial results point to a dramatic decrease in lateral mobility as a result of viral infection.

(9) Measurement of Lateral Motion by Fluorescent Photobleaching

Graduate Student: L. M. Smith

In the past year my work has been primarily concerned with the measurement of lateral motion in both model membranes and biological membranes by a fluorescent photobleaching technique. In collaboration

with Dr. Barton Smith I have made measurements of the lateral motion of a membrane protein reconstituted into model membranes, and showed that this protein (the M-13 coat protein) diffuses nearly as rapidly as the lipid molecules in fluid membranes. In collaboration with Dr. J. Wallace Parce and Dr. Barton Smith I have measured the rate of lateral motion of antibodies bound to lipid haptens in model membranes, and showed that these antibodies diffuse as rapidly as the lipids themselves. Drs. Parce and Smith and myself have designed and built a highly sensitive photobleaching apparatus in this laboratory, and this system is presently my primary research tool. With this apparatus I have recently measured the rate of diffusion of the M-13 coat protein as a function of cholesterol concentration and temperature, and discovered a new method for the measurement of lateral motion which is not limited by the wavelength of light. I am presently collaborating with Frank Howard to determine the effect of viral infection of cells on the motion of histocompatibility antigens on the cell surface. I am also collaborating with Dr. Howard Petty in this laboratory to measure the distribution and rate of motion of the C3 receptor on different cell types.

(10) Molecular Probes

Graduate Student: D. Torney

We have designed, constructed and studied the physical properties of molecules which are fluorescent and paramagnetic. As probes, these molecules are both antigenic and soluble in phospholipid membranes.

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36. COMPUTER-AIDED ENGINEERING OF SEMICONDUCTOR INTEGRATED CIRCUITS

J. D. Meindl, Professor, Electrical Engineering

Professional Associates:

R. W. Dutton	J. D. Plummer
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Consultants:

J. J. Barnes	T. I. Kamins
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Graduate Students:

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L. Christel	S. A. Schwarz *
D. C. D'Avanzo *	A. Shah
H. G. Lee **	B. Swaminathan
M. M. Mandurah	M. A. Taubenblatt
D. N. Modlin	

* Received PhD during Report Period.
** Expect PhD to be conferred during Report Period.

Agency Support:

DARPA

Technical Objectives:

Economic procurement of small quantities of high performance custom integrated circuits for electronic systems is severely impeded by inadequate process, device and circuit models to facilitate accurate computer-aided design at low cost. The salient objective of this program is the development of new basic models for integrated circuit fabrication processes which will permit accurate prediction of the characteristics of a monolithic structure on the basis of its proposed process parameters. The four generic fabrication processes which are considered here: 1) ion implantation, 2) thermal diffusion, 3) thermal oxidation and chemical vapor deposition, and 4) epitaxy.

Approach:

In military systems in particular, although to a growing extent in commercial applications as well, there is often a necessity to customize the design of an integrated circuit to fulfill the critical needs of a specific system or class of systems. A major barrier which prevents the economic production of small quantities of high performance custom integrated circuits is the cost of design. The source of this difficulty lies in empirical, and costly, engineering techniques used currently both in integrated circuit design and production. Optimal and efficient system design requires accurate computer models for silicon fabrication processes, elemental device structures, monolithic circuit configurations and system architectures. Current capability to predict changes in system performance resulting from silicon fabrication process modifications is impeded by deficiencies in process, device, circuit, and system models.

The overall objectives of this program are:

- (1) To develop process models based upon fundamental physical phenomena which accurately predict device structures which would result from a given process sequence.
- (2) To integrate these process models in a comprehensive, user-oriented computer simulator (SUPREM) which is generally useful for silicon structures.
- (3) To develop methods to utilize geometrical and process information to specify simple device models including two-dimensional effects.
- (4) To develop circuit analysis capabilities which reflect statistical model effects including parameter correlations.
- (5) To disseminate the results to industry.

The results described in this report build upon an established program which has resulted in the release of a second generation process modeling computer program--SUPREM II--which is generally regarded as the pre-eminent tool of its type available today. It is used by more than 100 industrial firms and university research groups for the simu-

lation and design of state-of-the-art MOS and bipolar fabrication processes. The development of accurate physical models for SUPREM has been a principal objective of this program for the past four years. The work described here extends these models and their implementation in SUPREM to the small geometry device structures which are expected to be used in VLSI circuits in the next several years.

The historical trend in silicon integrated circuit technology has been towards increased complexity and smaller active device dimensions. This has resulted today in lateral device dimensions on the order of 2-3 μm and vertical dimensions well below 1 μm in many commercially available circuits. There are no basic physical mechanisms which prevent a reduction in each of these dimensions by an order of magnitude; such device structures are widely projected for the 1985-1990 time period. Such projections are predicated, however, on our ability to understand physically and accurately model the fabrication techniques which will be used in the construction of such devices.

For devices with relatively large geometries ($>5 \mu$) and loose processing tolerances, relatively simple models suffice for prediction of vertical impurity profiles resulting from a given fabrication sequence. As device dimensions shrink, however, it becomes essential to employ more robust process models and to consider the interaction both laterally and vertically of various processing steps, if accurate simulation of structures is to be obtained. This is important even with today's 2-3 μm device geometries; it will become essential for smaller devices.

Larger geometry devices can be successfully modeled as one-dimensional structures. This is true for both process models and electrical models. Devices with lateral dimensions below a few microns, however, require two-dimensional models for accurate simulation. This need has stimulated a large body of work in recent years on two-dimensional electrical models of device current-voltage characteristics. This work has resulted in remarkable advances in our understanding of small geometry device physics. Recent work under this program in this area is described in Section 6 of this report.

Progress has not been as rapid, however, in two-dimensional process modeling. This is a direct result of our need for improved physical models of oxidation, ion implantation, diffusion, and CVD. It is quite clear that these processes are not one-dimensional. Recent experimental evidence has clearly indicated that oxidation or impurity diffusion in a localized region of a silicon substrate can substantially affect oxidation or diffusion rates in laterally or vertically adjacent regions of the substrate. There is no clear agreement at the present time on the basic physical mechanisms responsible for such results. It is clear, however, that we must quantitatively understand such phenomena if we are to accurately model small device structures.

A specific goal of this program is to understand and model these two-dimensional effects. We have made substantial progress in this regard in the past year. It appears now that the basic physical phenomena underlying these interactions are the roles of point defects--silicon vacancies and interstitials--in impurity diffusion, thermal oxidation, and other processes. The generation and consumption of these point defects during high temperature fabrication steps appear to be the unifying physical effects which can explain many of the phenomena which have been regarded as anomalous to date. We have used such models to quantitatively understand a variety of process phenomena and have incorporated some of these models in SUPREM II. The unifying role of these mechanisms is a cornerstone of the work described in this report. We regard such models as absolutely essential to accurate modeling of two-dimensional effects in small devices.

The most widely used model of the thermal oxidation kinetics of silicon is that provided by Deal and Grove [1], who suggest an initial reaction rate limited linear relationship between oxide thickness and time followed by a transport limited parabolic form. Although this model is useful, it does not include the effects of substrate orientation, multiple species in the oxidation ambient, and substrate doping levels. It does not explain the enhanced kinetics of thin SiO_2 layers, has no predictive capability for oxide charge densities and is one-dimensional. A major part of our activity in this area has been aimed

at examining the interface reaction which converts silicon to SiO_2 . This work has pointed out the important roles of silicon point defects in this reaction [2,3], and has led to a generalized model for thermal oxidation which has quantitatively modeled for the first time the effect of substrate doping levels on oxidation kinetics [4]. This model has been incorporated in SUPREM II. The role of these point defects in oxidation is fundamental to the work which is described in Section 1 of this report. Such phenomena are the means of coupling oxidation to diffusion and oxide charge densities, and are expected to play important roles in our studies of thin oxide kinetics. In addition, generation of these point defects during oxidation is regarded as the key mechanism in understanding two-dimensional effects of thermal oxidation.

The most widely used model for ion implantation is based upon Linhard, Scharff and Schiott (LSS) range theory [5]. Although the LSS model is indeed useful, the approach fails to account for two important features of ion implantation in integrated circuits: the effects of implanting in multilayer targets as encountered in threshold shifting of MOS transistors and the effects of upper layer "knock-on" ions on device characteristics. Also not modeled is the experimentally observed dopant profile's deep channeling tail that results from ions scattered into relatively unobstructed channels in the crystalline silicon substrate. To overcome these shortcomings, a new ion implantation model based on the Boltzmann transport equation which predicts the flux of incident and "knock-on" ions at a series of closely spaced distances within a multilayer target has been developed [6]. This model has also recently been applied to the prediction of channeling tails on implanted profiles.

Many of the physical phenomena associated with ion implantation and other processes are transient in nature (damage annealing and gettering for example). As a result, physical modeling has been difficult due to the need for obtaining a large number of experimental data at closely spaced time intervals. In the past this has implied a large number of experimental samples. A major effort has been initiated in the past year to develop a temperature tolerant metallurgy for elec-

trical contact to bulk regions and for MOS structures. Such a metallurgy would make possible in-situ or time dependent monitoring of a single sample and greatly improve our understanding of these transient processes. This work is regarded as vital for developing improved models for many of the processes described in this report. Recent work in ion implantation modeling and in the development of this temperature tolerant metallurgy is described in Section 2 of this report.

The most widely used model for thermal diffusion is based upon Fick's second law or the so-called diffusion equation assuming a constant diffusion coefficient. It is quite clear that this model is inadequate at high dopant levels, or during thermal oxidation, or in the presence of multiple diffusing species. A new multistream diffusion model which describes the interaction of diffusing ions with silicon point defects has been developed and demonstrated substantial improvements in modeling capability [7]. Models involving point defects have also been developed which explain the enhancement of diffusion coefficients during thermal oxidation [8]. The large amount of work in this program related to point defect phenomena is expected to further improve impurity diffusion models.

Current models of dopant inclusion in silicon epitaxial layers are based upon simple steady-state boundary layer concepts [9]. Such approaches cannot account for gas flow transients and their impact on doping, especially in very thin epitaxial layers. A new physiochemical model for dopant inclusion has been developed, based upon a transfer function approach. It achieves accurate prediction of arbitrary epitaxial layer doping profiles through convolution of the reactor transfer characteristics with appropriate gas flow functions [10,11]. Modeling of this type has recently been extended to thin epitaxial layers ($\sim 2 \mu$) which will be required for VLSI devices. Because polysilicon is so widely used in MOS devices, it has become the subject of a significant portion of our CVD activities. The physical structure and thermal stability as well as electrical conductivity of doped films have been studied in layers deposited both at atmospheric and low pressures. Refractory metal silicides hold great promise for reduced inter-

connect resistances in VLSI structures. For this reason, a detailed study of their physical, electrical, and chemical properties is underway with the aim of evaluating their potential for small geometry devices. Recent work in the polysilicon area is described in Section 3; activity in the Refractory Metal Silicides is described in Section 4.

In cooperation with the physical modeling of fabrication processes described above, we have also developed advanced materials analysis techniques based upon the use of Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). These techniques are routinely used to analyze samples and provide experimental inputs to the oxidation, ion implantation, and CVD activities. In addition, both AES and SIMS have been used extensively in careful studies of the segregation of impurities in the Si-SiO₂ structure, the atomic nature of the Si-SiO₂ interface and the grain boundary chemistry in polysilicon [12,13]. This work is described in Section 5 of this report.

The new process models for oxidation, ion implantation, diffusion, and CVD outlined above and described in detail in the remainder of this report, are specifically being developed for incorporation in a new version of SUPREM [14]. SUPREM III which is projected for release during the current calendar year, will for the first time enable simulation and accurate modeling of many of the technologies associated with small geometry devices. In order to model shallower junctions and thinner oxides and epitaxial layers, transient kinetics must be included in the process simulator. In addition, most VLSI device structures employ multilayer structures--for example polysilicon layers for diffusion contacts and SiO₂-Si₃N₄ layers both for active devices and for local oxidation masking. SUPREM III will have to be substantially altered to accommodate these capabilities. In addition to these fundamental changes in simulation capability all of the models in SUPREM will be upgraded to incorporate results generated by the oxidation, ion implantation, diffusion, and CVD groups. One final change which will be made in the program is to alter its output format and structure so that the process variables being used at any time by the simulator are accessible. This improvement is expected to be highly useful to the

groups developing improved physical models for SUPREM and should allow for closer coordination of basic physical work and SUPREM implementation.

The viability of process modeling for IC design hinges on prediction of device performance. The final section of this report provides a comprehensive review of device modeling results based on SUPREM as the cornerstone. Semiconductor Device Analysis both for one-dimension (SEDAN) and for Two-dimensional Analysis (TANDEM) are described. Moreover, the applications of process and device analysis to test structures and circuit simulator model development are presented.

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37. DEFORMATION AND FRACTURE IN STRUCTURAL MATERIALS

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**Received MS during report period.

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EPRI RP-1123-1

Research Report:

(1) MODELLING OF DEFORMATION AND FRACTURE IN HIGH-TEMPERATURE STRUCTURAL MATERIALS (with Professor Oleg D. Sherby)

The general objective of this research project is the development of improved quantitative methods for predicting deformation and fracture of metals and alloys under the complex histories and environments which are typical of energy-related systems. This work will, hopefully, bring a greater physical content to the methods used by the high-temperature design community. At the same time, the research aims to extend the applicability of our scientific understanding of deformation and fracture processes to more complex technologically-important situations.

In the area of modelling of non-elastic deformation, the general approach has been to develop improved understanding of the various quantitative interrelationships, and to use this understanding to improve our constitutive equations, starting with the MATMOD equations (previously utilized for Zircaloy for light-water reactor applications). The MATMOD equations contain structure variables which represent three

major categories of strengthening mechanisms: (1) solute strengthening (and other mechanisms which do not depend on work hardening), (2) isotropic work hardening, and (3) directional work hardening. We have undertaken studies in each of these three areas.

With respect to solute strengthening, and especially its sometimes synergistic interaction with deformation strengthening, we completed an improved version of the MATMOD equations. The improvement ($F_{sol,2}$) represents interactive solute elements, generally interstitials, which enhance the work hardening rate in specific temperature and strain rate regimes. One particular mechanism may be the formation of vacancy-interstitial pairs. The model was applied, with reasonable success, to type 316 stainless steel. A complete set of materials constants was calculated, and a number of independent comparisons of predictions against data (such as the effect of cold work on creep, the amount of primary creep, stress relaxation, and cyclic stress-strain behavior) indicate fair quantitative accuracy over a broad range of conditions.

With respect to isotropic work hardening, we have undertaken a unique experimental investigation motivated by the fact that the MATMOD equations contain only one variable (F_{def}) representing isotropic work hardening, whereas at least two physical entities (forest dislocations and subgrains/subcells) can be responsible. The experiments involve warm working to produce a well-defined subgrain size, cold working to produce various subgrain sizes, and elevated-temperature compression testing (750°C) to determine the flow strength. Based on the data, we have developed an equation for the separate influences of subgrain strengthening and forest dislocation strengthening in type 304 stainless steel, which lays the groundwork for a more complete quantitative understanding of, and constitutive model for, transient hardening in subgrain-forming materials.

With respect to directional work hardening, another experimental investigation has explored cyclic behavior at very high strain ranges, so that we can compare back stresses generated during monotonic, steady-state flow against those generated during cyclic deformation. This investigation, using both aluminum and type 304 stainless steel, has shown

that the level of back stress can be a function of the isotropic strength level, and that back stresses measured by Bauschinger effect can be (understandably) different from those measured by stress-transient or strain-transient techniques. The same experiments have provided valuable data on local strain softening during fully reversed straining (Figure 1). The data are being used to check and improve the MATMOD equations in this area.

In another study, the topic of strain softening is being studied in detail for its possible implications with respect to flow concentration and possibly fatigue crack initiation. The objectives are to understand the role of physical variables such as stacking fault energy and to be able to model the many manifestations of strain softening more precisely.

Notwithstanding these rather extensive studies of deformation, a major objective of this program is to improve our ability to predict fracture under complex histories and environments. This objective is, in part, related to our constitutive equations work in that the equations provide improved ability to predict details of the stress and strain histories for complex loadings, for example, in situations where creep-fatigue interaction is known to be life-limiting. But our fracture-related research has also involved additional topics and findings. In our study of the effect of hold periods on the fatigue resistance of 2½Cr-1Mo steel at elevated temperature, we conclude that oxidation, in conjunction with deformation, is responsible for the observed (unusual) laboratory behavior (especially the detrimental effect of compressive hold periods). Proof that oxidation, rather than creep, is the detrimental effect during elevated-temperature hold periods in this material was provided by critical tests ("zero stress hold tests") run during the past year. We have developed this understanding into a predictive model. The model works quite well (Figure 2) and appears far more physically correct and appropriate for extrapolation to real-world, long-life situations than existing design approaches.

(2) ZIRCALOY CLADDING DEFORMATION AND FRACTURE ANALYSIS

K. D. Challenger, Research Associate
A. Tasooji, Graduate Research Assistant

Technical Objective:

To develop a physically-based model for the stress-corrosion-cracking (SCC) fracture of Zircaloy nuclear fuel cladding due to pellet-clad interaction (PCI).

Approach:

The model developed is required as part of a larger EPRI code development project which seeks to predict the durability of light-water nuclear reactor fuel under transient power conditions. The researchers at Stanford University have had the responsibility for developing an appropriate SCC fracture model, utilizing experimental data generated mostly by other participants in the overall project. Therefore our approach has been mainly to conduct physically-based analyses of the outside data, to develop mechanistic interpretations of the material's behavior, and to distill the results of these analyses into a useable mathematical framework.

Results:

During the past two years, a new approach to modelling of fracture in general, and iodine-induced stress-corrosion cracking of Zircaloy in particular, has been developed. This "bundle-of-sticks" approach is computationally very simple which allows modelling of the complex interactions among intergranular failure, transgranular quasi-cleavage, ductile rupture, crack growth due to these processes, changing stress fields due to this crack growth, and iodine penetration along the crack, with a minimal expenditure of computer time. The model's ingredients arise from both physical reasoning as well as phenomenological data.

A major advantage of the model is that it treats, in a unified manner, both SCC crack "formation" in initially smooth material as well as crack propagation; in other words the model covers the entire possible range of crack sizes starting from zero.

The model simulates details of non-SCC fracture fairly well with

respect to (1) predicted stress and strain distributions, (2) the effect of crack size, (3) the effect of specimen width, (4) the effect of material ductility, and (5) prediction of the plastic zone size. In treating Zircaloy SCC, the model correctly simulates the failure time versus stress curve and its dependence on yield strength, temperature, iodine concentration, and neutron fluence. It also gives reasonable simulations of crack growth rate versus stress intensity including an apparent K_{ISCC} . The model's predictions compare well against data on SCC resistance under variable stress conditions (cumulative damage), and the simulated fracture surface appearance (degree of intergranular vs. transgranular fracture) agrees with the data.

The model's "crack formation and growth" format has permitted it to be coupled to a statistical distribution of initial flaw sizes measured on as-manufactured cladding. This coupling has allowed us to make predictions of the expected differences in SCC behavior between the large quantities of Zircaloy cladding present in nuclear reactor cores and the much smaller quantities tested in laboratory experiments.

(3) EVALUATION OF MULTI-AXIAL FATIGUE (with Professors H. O. Fuchs and D. V. Nelson)

See research report of Professor H. O. Fuchs

Publications Since June 1979

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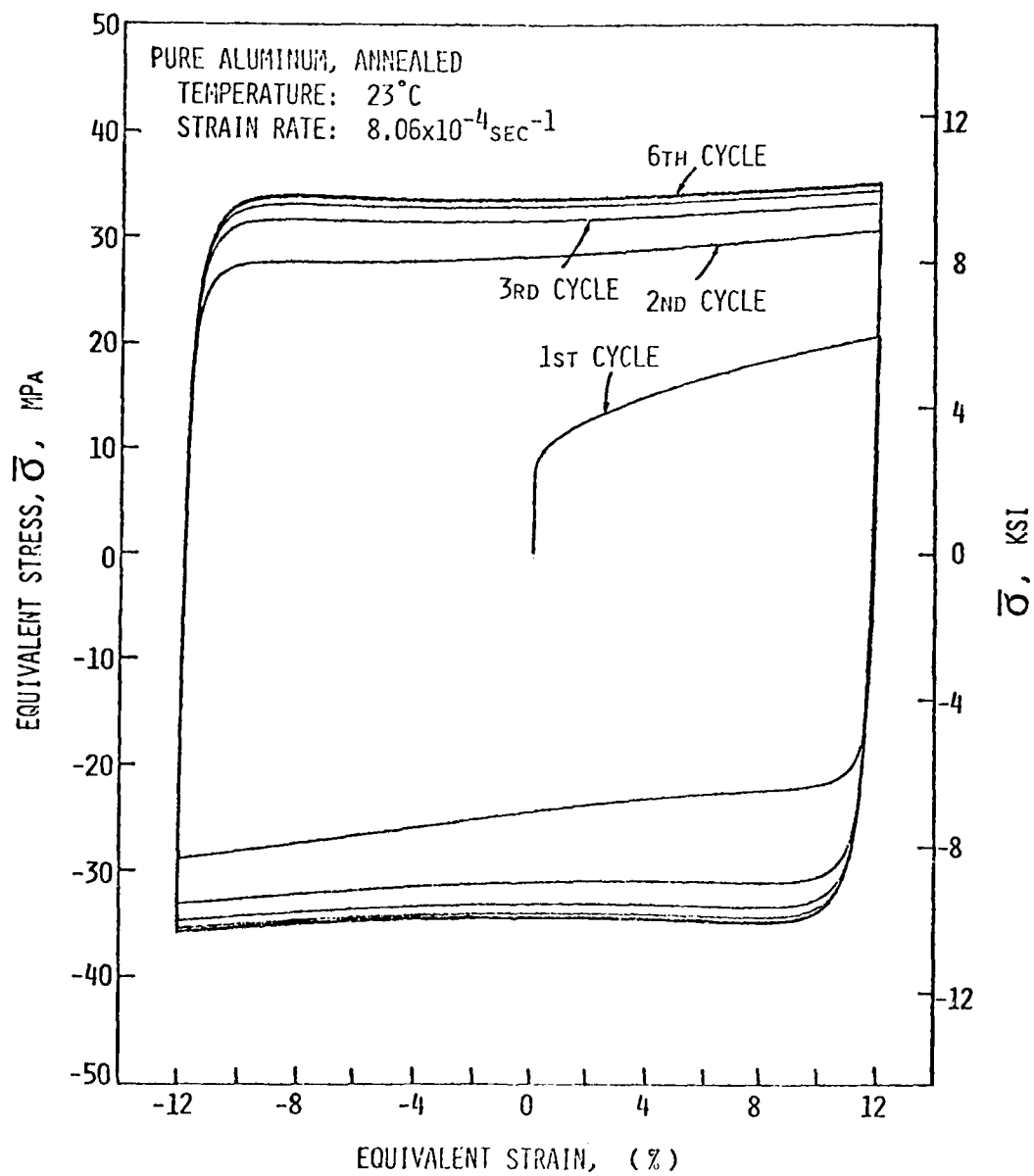


Fig. 1. Hysteresis curves of annealed pure aluminum at 23°C.

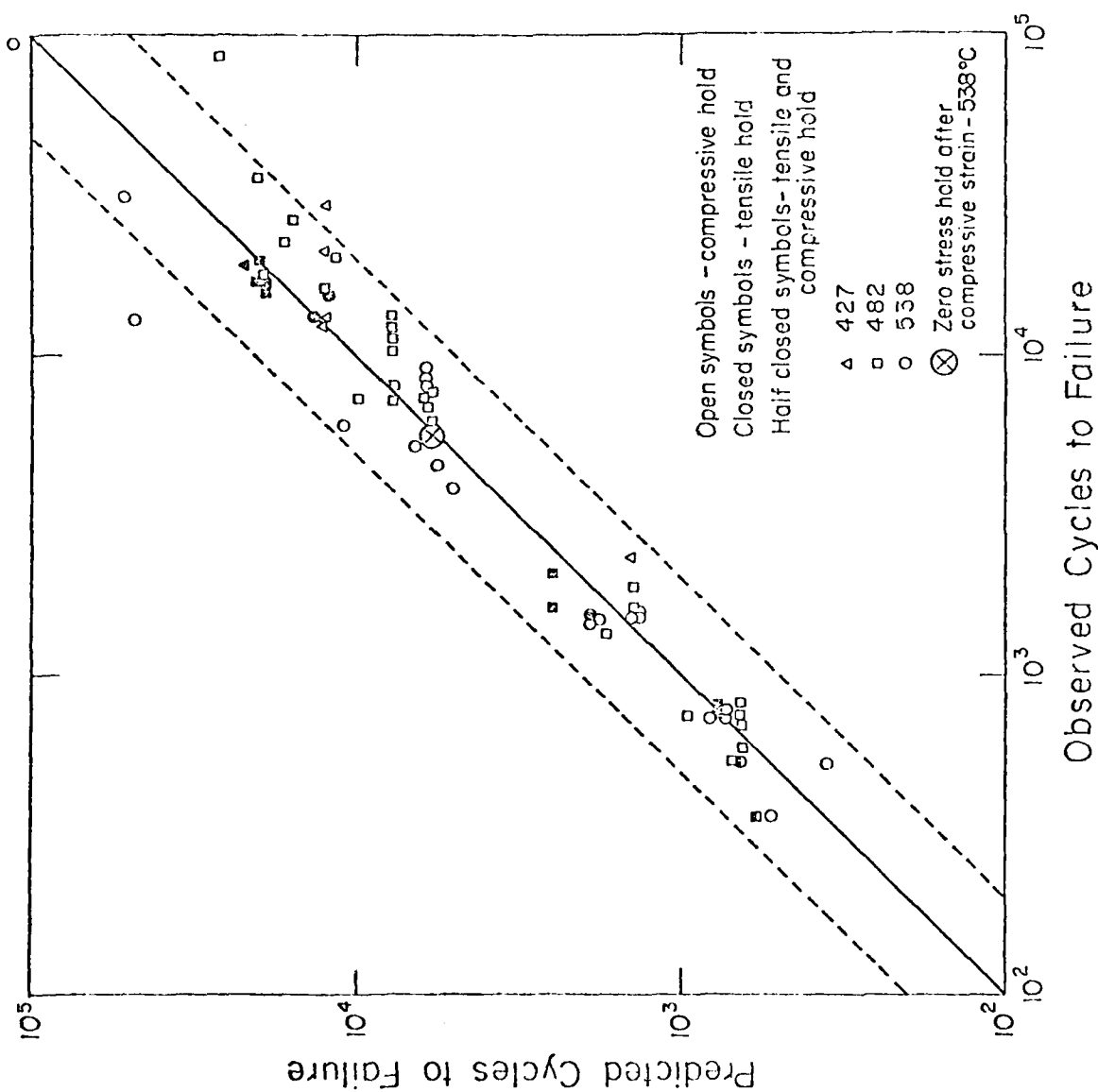


Figure 2. Comparison of the EFL predicted fatigue life with experimental data.

38. MULTIAXIAL FATIGUE OF STRUCTURAL METALS

D. V. Nelson, Assistant Professor, Mechanical Engineering

Graduate Student:

J. S. Chung

Agency Support:

NSF-MRL through CMR

NSF CME 8006692

Technical Objective:

Many structures and mechanical components experience multiaxial cyclic stressing and resulting fatigue damage. In most cases, the stressing is non-proportional (i.e., principal stresses vary in ratio and/or directions). The objectives of this research are: (a) to improve the fundamental understanding of multiaxial fatigue behavior, which lags the corresponding state of knowledge for uniaxial fatigue by several decades, and (b) to use this increased understanding to develop better analytical methods for predicting fatigue life.

Approach:

This program was begun in October 1979 and presently consists of the following activities:

- (a) The influence of normal stress on multiaxial fatigue behavior is being investigated experimentally.
- (b) A cooperative university - industry research program is being established to study the multiaxial fatigue behavior of test specimens containing stress concentrations.
- (c) The use of surface acoustic wave transducer technology is being investigated as a means for detecting microcrack initiation and monitoring propagation. This capability will significantly improve the understanding of both uniaxial and multiaxial fatigue damage at the microstructural level.

Research Report:

Traditionally, the Tresca (range of maximum shear stress) and the von Mises (range of octahedral shear stress) criteria have been used to correlate multiaxial fatigue data, with reasonable success for high-cycle, proportional cyclic stressing of smooth specimens made of ductile metals. However, these criteria often fail to correlate data for different stress-states (e.g., uniaxial vs. pure torsion) in low-cycle, proportional stressing tests. Also, they can seriously underestimate the damage due to non-proportional stressing, such as occurs in combined axial and torsional loading applied out-of-phase.

There are a number of possible reasons for the apparent inadequacies of such shear stress based criteria. First of all, they are insensitive to the possible influence of normal stress on planes experiencing maximum shear stress range. Second, their "performance" has been assessed in terms of life to fracture, whereas cyclic shear stress is associated with the microstructural mechanisms which nucleate micro-cracks. The ratio of life spent in nucleating a crack to that spent in propagating it to fracture is believed to be large in the high cycle fatigue regime and vice versa in the low-cycle regime.

A series of tests begun by S. B. Lee to investigate the effect of normal stress on multiaxial fatigue is being continued under this program. The tests utilize 90° out-of-phase bending and torsion to produce non-proportional stressing. Results to date for A533B steel show that for a fixed range of maximum shear stress, the life to visible cracking is reduced as the amplitude of normal stress is increased on planes of maximum range of shear stress. However, the mean normal stress appears to have little or no effect, at least for the given test conditions. A better understanding of the effect of normal stress on multiaxial fatigue behavior could be gained by distinguishing the effect on microcrack nucleation and on crack growth. This understanding may be attained through the use of advanced acoustic techniques which can detect and monitor microcrack nucleation and growth. It is hypothesized that normal stress influences most strongly the crack propagation phase of total life. Tests to investigate this are being planned.

A cooperative multiaxial fatigue research effort has been formally established between Stanford and several U.S. companies. Specialized test equipment is currently being fabricated at two of the companies. The bulk of the expensive and time-consuming testing will be done by industry, while most of the analytical development will be carried out at the University. The program has the following objectives:

- (a) to investigate multiaxial, elastic-plastic cyclic stress-strain behavior at stress concentrations, initially for proportional and later for non-proportional loadings;
- (b) to develop a generalized multiaxial fatigue damage parameter (e.g., plastic work per cycle) capable of predicting fatigue life under complicated multiaxial loadings, and
- (c) to use the results from items (a) and (b) to develop a fatigue evaluation method suitable for use in design.

39. RELATIONS BETWEEN CRYSTALLINE IMPERFECTIONS AND THE PHYSICAL PROPERTIES
OF CRYSTALS

William D. Nix, Professor, Materials Science and Engineering

Professional Associates:

J. C. Gibeling
L. Martinez
R. Singer

Graduate Students:

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D. T. Guidry**	R. Fuentes-Samaniego*
J. K. Gregory**	J. D. Smith
A. C. Holk**	J. C. Wei
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period

Agency Support

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DOE DE AS03-326-PA ER 103 78
NSF-MRL through CMR
NSF DMR 79-23942

Technical Objective:

To understand and exploit the relation between imperfections and the physical properties of crystalline solids. To develop techniques for predicting and controlling the mechanical and electronic behavior of crystalline materials in order to establish guidelines for making both structural and electronic materials.

Approach:

To carry out both theoretical and experimental investigations of crystalline solids with known concentrations of various types of defects.

Research Report:

(1) Theoretical Study of High Temperature Fracture

Research Associate: L. Martinez

Many structural materials subjected to high temperature creep fail by the growth and coalescence of cavities at the grain boundaries. Diffusion controlled mechanisms have been proposed wherein the growth results from atomic transport of material away from the cavity, mainly along the cavity surface and through the adjoining grain boundary. The models can be divided in two categories: those considering that the diffusion process is controlled at the grain boundary, $D_B \ll D_S$, (Hull and Rimmer, Speight and Harris, Raj and Ashby) and at the cavity surface, $D_S \ll D_B$, (Chuang and Rice, Pharr and Nix, Fuentes-Samaningo and Nix). In order to explore the wide region between these two limiting cases, we developed a numerical model to simulate the time dependent diffusive cavity growth for different grain boundary to cavity surface diffusivity ratios ($0.5 \leq D_B \delta_B / D_S \delta_S \leq 10^4$). The results we obtain confirm that the cavity tip grows like a crack of the model of Chuang and Rice and that the power law for growth predicted by them is essentially correct.

(2) A Study of the Mechanisms and Mechanics of Creep Crack Growth in Metals at High Temperatures

Research Associate: J. C. Gibeling

Although creep and creep fracture are important deformation and fracture processes at high temperatures, actual failure usually occurs by the initiation and growth of cracks. The prediction of failure requires not only some knowledge of the microscopic mechanisms of decohesion (fracture), but also some understanding of the mechanics of cracks. Our research is aimed at extending our understanding of the microscopic mechanisms of intergranular fracture to the study of cracked samples which are tested under creep conditions. Our experiments with Ag, Cu and Ni containing water vapor bubbles and dispersions of stable second phase particles clearly demonstrate that we can control

the matrix strength, grain boundary properties and fracture mechanisms in these materials. Our goal is to study creep crack growth for various material conditions to determine whether deformation or fracture dominate the crack growth process.

(3) Applications of Stress Change Experiments to the Study of High Temperature Creep

Research Associate: J. C. Gibeling

During the past ten to fifteen years stress change experiments have gained widespread acceptance as a means to probe the mechanisms of dislocation creep at elevated temperatures. By changing the applied load during creep and monitoring the resultant stress or strain transient, numerous investigators have attempted to learn more about the deformation process. However, many of these experiments have resulted in disagreements with regard to matters of fact and matters of interpretation. The present work is aimed at clarifying some of these questions in order to learn more about creep mechanisms.

Our work on pure metals (Al, Cu and Pb), including polycrystalline and single crystal specimens has resulted in several important new observations. These experiments have demonstrated that recovery is not required for forward creep to continue at the reduced stress. Using both conventional and newly developed high resolution strain measuring techniques, we have also determined that anelasticity provides an important contribution to stress drop transients.

This anelastic process can be modeled using a simple mechanical analog, incorporating linear and nonlinear dashpots. This mathematical description of backflow has been combined with measured constant structure forward creep data in a phenomenological description of creep transients. This model provides the first quantitative demonstration of the idea that these strain transients can be described by a superposition of forward and reverse flow. These techniques are now being extended to other materials and testing conditions to examine carefully the ways in which the backflow effects are influenced by temperature, substructure and material composition.

In addition, we have developed a new theoretical framework which combines the diffusion controlled recovery and thermally activated glide approaches to creep. This description is based on the idea that the inherently inhomogeneous dislocation substructures that form during creep produce inhomogeneous stresses that enhance the rate of recovery in "hard" regions and inhibit thermally activated glide in "soft" regions of the substructure. This "composite" model of creep has been used to explain both steady state and non-steady state creep properties in a semiquantitative way.

(4) A Study of Internal Back Stresses in Pb-In Solid Solutions

Graduate Student: J. C. Wei

In our work to date we have fully characterized the creep behavior of the Pb-In solid solution alloy system. We have studied the steady state creep properties as a function of composition, temperature, stress and grain size. We have also conducted several preliminary anelastic creep experiments on Pb-30 In. This alloy obeys all the rules for glide controlled creep and thus would not be expected to exhibit large long range internal stresses. However, the significant amount of backflow recovered upon full unloading in the anelastic experiment implies a very large internal back stress. This backflow phenomena is important and needs to be studied further. We have now completed the work to improve the accuracy of our measurements in order to probe the behavior in a more complete and quantitative way.

(5) Elongated Grain Formation in Oxide Dispersion Strengthened Nickel Alloys

Graduate Student: J. K. Gregory (jointly with Professor Sinclair)

One beneficial and peculiar aspect of oxide dispersion strengthened alloys involves the microstructure. Annealing above some critical temperature causes grains of submicron size in an as-extruded sample to grow anisotropically. For ODS nickel superalloys, this temperature is approximately 1250°C. Below this temperature, only grain coarsening

occurs, inhibiting subsequent elongated grain formation.

For this study, Transmission Electron Microscopy will be used to examine Inconel Alloy MA 754 and MA 753 to answer the following

- questions:
1. What is responsible for the anisotropy of the grain growth ?
 2. What is the process which is triggered above 1250°C and inhibited below 1250°C ?

(6) The Interaction of Dispersion Strengthening and Solute Strengthening in Al-Mg

Graduate Student: W. C. Oliver

The mechanical properties of dispersion strengthened Al-3.6% Mg (IN-9051) are being studied. The purpose of this work is to better understand the interaction of dispersion strengthening and solute strengthening in metals.

The steady state creep characteristics of this material are being determined using compression tests. A constant crosshead speed Instron machine in conjunction with an H-P 9825 data acquisition system is being used.

The steady state creep properties of dispersion strengthened Al-3.6% Mg demonstrate several interesting characteristics. Serrated yielding, yield points, negative stress exponents, and high activation energies are all present and are characteristic of solute effects. The material also shows high stress exponents in certain domains of strain rate and temperature, and this is characteristic of many dispersion strengthened alloys.

The deformation microstructures are being studied using a Philips 400 transmission electron microscope. Preliminary results indicate that the annealed grain size is extremely fine (approximately 0.2 μm). This indicates that recrystallization and grain growth are limited by the presence of the dispersoid.

(7) Application of Mechanical Alloying to the Synthesis of Superconducting Wire

Graduate Student: J. D. Smith

Mechanical alloying has been used to produce an intimate mixture of elemental Nb and Sn powders. These powders have then been isostatically compacted into a Cu matrix, with subsequent hydrostatic extrusions as high as 100/1. Annealing in the 650°C-850°C range then transforms the elongated Nb/Sn powders to the desired Nb₃Sn, an A15 superconducting phase.

We are presently investigating the effects of interstitial impurities on the ductility of Nb/Sn powders for the purpose of obtaining higher reductions and thus better superconducting properties. We also plan to adopt wire drawing in place of hydrostatic extrusion in order to obtain microcomposite wires as small as 0.002 inch in diameter with as many as 10^5 Nb₃Sn filaments per cross section.

(8) A Study of the Mechanical Properties of Metallic Glasses

Graduate Student: D. T. Guidry

During the past two years we have conducted a study of the creep properties of METGLAS 2826 (nominal composition: 40% Ni, 40% Fe, 14% P 6% B). Tension creep experiments were conducted and the strain rate-stress relation was found to be highly nonlinear, but could be described by a power law relationship. The temperature dependence of creep flow has also been measured but sufficient information to identify a mechanism for creep was not obtained. The measured creep ductilities were found to be as high as 20% with very high local ductilities indicated on the fracture surfaces. Room temperature tensile fracture stresses were found to be highly dependent on sample preparation with properly prepared specimens having a fracture stress three times greater than unprepared samples.

Annealing studies of as-received materials show no signs of crystallization at creep testing temperatures. Room temperature microhardness versus time after annealing at temperatures above the crystal-

lization temperature show a pattern of initial crystallization followed by possible phase separation. The hardness for samples annealed below the crystallization temperature remain unchanged, suggesting that recrystallization does not occur under these conditions. Similar studies on copper-zirconium alloys show the same pattern with a possible microhardness dependence on sample thickness.

(9) Studies of the Fracture Surfaces of Cu Alloys by Scanning Auger Spectroscopy

Graduate Student: K. S. Yu (jointly with Professor Heinemann)

The presence of impurities such as oxygen and bismuth in copper have a significant effect on the mechanical properties. In addition to solid solution strengthening, such impurities produce an embrittlement effect as well. It is generally believed that the embrittlement effect is due to the impurity atoms that segregate at the grain boundaries in copper and consequently reduce the cohesive forces between the grains. Cu-O alloys crept almost to fracture in air and then placed into a high vacuum environment have been studied by scanning Auger spectroscopy in order to determine the nature of the segregation effect. A fracture stage to break the samples in-situ in a high vacuum chamber has been designed and installed to avoid contamination of the samples at the time of fracture and to obtain with more accuracy the depth profile of the solute concentration.

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40. WAVE PROPAGATION IN SOLIDS WITH FLUID FILLED PORES

A.M. Nur, Professor, Geophysics

Graduate Students

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NSF-MRL through CMR

Technical Objective:

To understand the physical processes involved in wave propagation in porous, fluid bearing solids, by measuring velocities and attenuation of compressional and shear waves. The results are essential for utilizing elastic, acoustic or seismic waves as diagnostic tools for the state of fluids and pores in soil, rock, bones and other porous, fluid containing media.

Approach:

Resonant and pulse transmission methods were used to determine the dependence of long wave velocities and attenuation on porosity, confining pressure, fluid type, pore pressure and temperature.

Research Report:

Compressional wave attenuation has a peak in porous solids when water-/gas are mixed in the pores at 65/35 to 95/5 volume ratios, with a 3-4 fold increase of attenuation from the dry of fully saturated conditions. The results promise to have major impact on diagnostic methods for determination of gas saturation in porous media.

Reference Publication:

A. M. Nur, K. Winkler, J. DeVilbiss, and J. Walls, "Effects of Fluid Saturation on Waves in Porous Rock and Relation to Hydraulic Permeability," Soc. Petroleum Engineers, 8235 (1979).

41. PHOTON PRODUCTION FROM HIGH ENERGY ELECTRON BEAMS

R. H. Pantell, Professor, Electrical Engineering

Professional Associates:

J. R. Fontana
M. A. Piestrup
W. Zakowicz

Graduate Students:

A. N. Chu	J. C. Sheppard
J. A. Edighoffer	R. L. Swent
P. F. Finman	D. F. Wang
W. D. Kimura	

Agency Support:

DE-AS03-76ER71042, P.A. 42
DE-AT03-78ER70064, P.A. 64
NSF ENG76-11244
ONR N00014-78-C-0403
NSF-MRL through CMR

Technical Objective:

To obtain sources of optical, x-ray and γ -ray radiation for materials research.

Approaches:

We are currently studying three methods for the generation of electromagnetic radiation using high energy electrons. Two methods, transition and channeling radiation, generate soft and hard x-rays. Successful experiments have been performed in the last year for both phenomena.

We have also been studying a device we have termed the optical klystron which will generate visible and ultraviolet radiation. This device utilizes

a high energy electron and laser beam interaction to produce bunched electrons which are then allowed to reradiate with gain. The bunched beam will also have high harmonic content allowing for possible harmonic generation into the ultraviolet.

Research Report:

- (1) Transition Radiation as a Source of X-ray Radiation (NSF-MRL supported Research)

Relativistic charged particles crossing the boundary between two media with different dielectric constants produce x-rays by a process known as transition radiation. The photon yield is small for a single interface between two dielectrics; however, a summation from each of a large number of interfaces is possible resulting in a large flux. A two orders of magnitude greater than synchrotron radiation is possible.

This year we have performed two major experiments. Soft x-rays (2 keV to 6 keV) were observed using thin Mylar foils using electron beam energies of 104 and 66 MeV. Various stacks of mylar of 2.5, 3.5 and 6.35 μm thickness were used to produce the radiation. Optimum foil thicknesses and number were calculated and found experimentally to be correct.

In another experiment, soft x-rays were observed from three transition radiators using 90 MeV electrons. The radiators consist of 30, 1.0 μm foils of Al; 25, 1.5 μm foils of Mylar; and 23, 1.0 μm foils of Be. The photon energy spectra for each radiator peaked at 1100, 1000, and 800 eV respectively. This is the first observation of such soft x-rays from Transition Radiation.

Reference Publications:

- (1) A. N. Chu, M. A. Piestrup, T. W. Barbee, Jr., and R. H. Pantell, "Transition Radiation as a Source of X-rays," J. Appl. Phys. 51, 1290 (1980).
- (2) A. N. Chu, M. A. Piestrup, T. W. Barbee, Jr., R. H. Pantell, and F. R. Buskirk, "Observation of Soft X-ray Transition Radiation from Medium Energy Electrons," Rev. Sci. Instrum. 51, 597 (1980).

(2) X-ray and γ -ray Emission from Channeled Electrons and Positrons

Relativistic electrons and positrons traverse periodic trajectories when channeled in a crystal lattice. This results in the emission of forward-directed electromagnetic radiation of relatively narrow linewidth. For incident particles with energies in the range from 25 MeV to 60 MeV, the photon energies are in the range from 20 keV to 130 MeV.

Radiation from planar-channeled positrons has now been measured under a variety of conditions. The {110} planes of Si have been used at several beam energies, and crystals of different thickness have been used. Measurements were also made with the {110} planes of Ge. In all cases, the peak energies agreed very well with theoretical calculations.⁽¹⁾ The best results to date have been with 9 μ m Si, with a positron energy of 54 MeV. The photon energy was 39 keV, with 26% linewidth (FWHM). The peak/background ratio was ≈ 3 . It is believed that detector collimation can reduce the linewidth by another factor of 2, and that the peak/background ratio can also be increased.

Radiation from planar-channeled electrons in Si was observed for the first time in July 1979.⁽²⁾ In this case, several spectral lines were seen for each set of planes. Using the data for the {110} planes at beam energies of 28 MeV and 56 MeV, a theoretical model was created,⁽³⁾ which allows one to reconstruct the interplanar potential with a resolution of $\approx .1 \text{ \AA}$.

Future plans include further studies of the parametric dependencies of electron and positron planar-channeling radiation, as well as refining the theoretical model for electron axial-channeling radiation.

In addition to providing a potentially useful source of x- and γ -radiation for other applications, channeling radiation can be related to properties of the crystal itself, such as imperfections, bending potentials, and impurities.

Reference Publications:

- (1) R. H. Pantell and M. J. Alguard, "Radiation Characteristics of Planar Channeled Positrons," J. Appl. Phys. 50, 798 (1979).
- (2) R. L. Swent, R. H. Pantell, M. J. Alguard, B. L. Berman, S. D. Bloom, and S. Datz, "Observation of Channeling Radiation from Relativistic Electrons," Phys. Rev. Lett. 43, 1723 (1979).
- (3) R. H. Pantell and R. L. Swent, "The Emission Spectrum from Planar-Channeled Electrons," Appl. Phys. Lett. 35, 910 (1979).

(3) Optical Klystron

A device known as the optical klystron has been designed. This device uses the inverse Cerenkov effect to momentum modulate electrons. This process works as follows: The phase velocity of a laser induced electromagnetic wave is retarded by a gaseous medium. By intersecting the laser and the electron beams at the Cerenkov angle, the electrons remain in a field of constant phase, resulting in a cumulative energy exchange.

An experiment was performed this year using the 102 MeV electrons generated by Stanford's Superconducting Accelerator (SCA) intersecting a laser beam in hydrogen gas. The Nd:YAG laser delivered 30 Mw of 1.06 μm radiation. This corresponded to a peak field of $\approx 10^6$ V/cm or a peak acceleration gradient of ≈ 1 MeV/m. The beams overlapped in the interaction region for approximately 10^5 optical wavelengths. After the interaction region, the energy spectrum of the electrons was measured using a spectrometer. The effect was observed at the proper gas pressure and Cerenkov angle.

An experiment designed to observe bunching from such a beam is currently being investigated.

Reference Publications:

- (1) R. H. Pantell, W. D. Kimura, J. A. Edighoffer, and M. A. Piestrup, "Energy Exchange between Free Electrons and an Electromagnetic Field," Physics of Quantum Electronics, Reading, Mass.: Addison-Wesley Publishing Company, 7, 15 (1979).

42. PHYSICAL CHEMISTRY OF OXIDES AND OXIDE SURFACES

G.A. Parks, Professor, Applied Earth Sciences

Graduate Students:

S.G. Marshall (received MS degree during report period)
V.S. Tripathi (Applied Earth Sciences)
Demetrius Pohl (Geology Department)

Agency Support:

Stanford Institute for Energy Studies
NSF CPE-7920012

Technical Objectives:

1. Collection, through experiment and literature search, of intrinsic surface ionization constants and adsorption equilibrium constants needed for solute transport modelling. Contexts include radioactive waste disposal, mineral exploration, wastewater treatment and reinjection and solution mining.
2. Evaluation and experimental determination of the water solubility of UO_2 , and stability constants for formation of carbonate complexes of U(IV) under conditions ranging from 100 to 500°C and 1 to 1000 bars.

Research Reports:

Intrinsic Adsorption Constants (Parks and Tripathi). NSF funding has been received for a collaborative effort with Lawrence Berkeley Laboratories through which we intend to determine equilibrium constants for adsorption of UO_2^{2+} onto goethite ($FeOOH$) and their variability with respect to adsorbate concentration, pH, salinity, and complexing ligand concentration. This work will require acid dissociation constants and adsorption equilibrium constants for Ca^{2+} , Na^+ , Cl^- , and CO_3^{2-} , for example, on the $FeOOH$ surface.

We have developed software with which it will be possible to recalculate intrinsic dissociation constants and simple ion adsorption

constants from data in published literature. During the summer of 1980, these programs will be used to collect and evaluate what is known about these data.

Tripathi has developed sensitive analytical techniques for uranium in water solution and completed preliminary adsorption experiments. The results indicate general agreement with earlier work on adsorption of UO^{2+} and are sufficient to design the more complete investigation needed to determine intrinsic adsorption constants for this system.

Solubility of UO_2 (Pohl). The determination of the solubility of uranium (IV) dioxide and elevated temperatures and pressures in a variety of aqueous fluid compositions has direct application to radioactive waste disposal; hydrothermal uranium deposit genesis, uranium resource exploration, and solution mining.

The solubility of uranium (IV) dioxide is very poorly defined. It is proposed to experimentally determine the equilibrium solubility of uraninite in aqueous media from 100°C to 500°C and 500 to 1000 bars pressure. A synthetic, stoichiometric uranium (IV) dioxide will be reacted with solution in Dickson hydrothermal equipment. Equilibrium may be tested by sampling of the solution as a function of time and reversibility from undersaturated and supersaturated conditions. Initially, the systems $UO_2 - H_2O$ and $UO_2 - H_2O - CO_2$ will be investigated and hopefully extended to $UO_2 - H_2O - HF$ and $UO_2 - H_2O - \text{rock}$ buffer systems. The systems to be investigated have been chosen to approximate important radioactive waste disposal and natural hydrothermal environments.

This project is to be initiated during June 1980.

43. GAS-LIQUID METAL REACTIONS AND INTERACTIONS

Norman A. Parlee, Professor, Applied Earth Sciences

Professional Associates:

R. N. Anderson (San Jose State University)
M. Hassan (American Microsystems, Inc.)
Prof. D. A. Stevenson (Dept. of Mat. Sci., and Eng.)

Graduate Students:

C. H. Hua
B. Heshmatpour* (with Prof. Stevenson)
J. R. Hwang*
S. Slivinsky

*Received PhD during report period.

Agency Support

NSF-DMR 75B0168A01
NSF-MRL through CMR

Technical Objective:

- (1) To measure and predict solubilities and diffusivities of gases (e.g. H_2 , N_2 , O_2) in liquid metals and multicomponent alloys;
- (2) To elucidate the laws controlling the effects of surface active elements (O, S., Se etc.) on the rates of absorption and desorption of gases in stirred liquid metals and alloys and thus to predict these affects;
- (3) To find cheaper ways of making expensive reactive metals (e.g., Ti, U, Zr, Mg);
- (4) To develop better ways of recovery-processing fuel and waste disposal;
- (5) To study selective hydriding, nitriding and oxidizing of reactive metals in liquid metallic solvents.

Approach:

Determination of the thermodynamics and kinetic relations from equilibrated and dynamic systems in the laboratory. Development of methods for quantitative prediction of the behaviour in real industrial

systems.

Research Report:

(1) The Prediction of Solubilities (S_N , S_H), Diffusivities (D_N , D_H), and Rate Constants of Absorption and Removal, of Nitrogen and Hydrogen in Liquid Multi-Component Iron Alloys and Steels.

Graduate Student: C. H. Hua

The gases (hydrogen, nitrogen and oxygen) must be removed from the liquid metals and alloys before they are cast if optimum final solid properties are to be achieved (nitrogen is often an exception where it is added in highly alloyed special austenitic steels to save expensive nickel, etc.). Gas solubilities are important, but rates of gas removal are basically controlled (in liquid vacuum degasification or argon flushing, etc.) by gas diffusivities - in the absence of excessive amounts of a surface active element, (e.g., O), which are generally previously removed if possible to below critical levels if they are known. Thus, for example, the knowledge of gas diffusivities in complex liquid iron alloys is just as important as the knowledge of gas solubilities in the making of complex iron alloys and steels by all the most advanced special steelmaking processes.

The research reported here is part of the NSF (US-USSR) sponsored project on "Plasma Arc Melting of Metallic Materials - Part 1 High Temperature Interactions Between Gases and Liquid Metals," Nitrogen is of particular importance in the plasma arc process as applied to multi-component alloys of very high alloy content (up to at least 50% alloy). The plasma arc is very adaptable to making very highly alloyed steels, and particularly to those of very high nitrogen content.

The background experience of this laboratory for this work is considerable - many studies of solubilities, rates of absorption and effusion of gases in stirred and stagnant melts, and diffusivities of H, N, O in a considerable number of gas-metal and gas alloy systems having been made. Diffusivities have been measured by both the "unsteady state" (1) and "steady-state" (2) methods developed here, which give identical results. A new superior method (1, 15) of measuring both gas solubility and diffusivity essentially simultaneously by using the combined "steady" and "unsteady" state techniques was discovered here.

This latter technique (15) was the one mainly used in the work on multi-component iron alloys here. Earlier work on hydrogen by Sacris and Parlee (2), and Depuydt and Parlee (3), discovered an inverse linear relationship between log of the diffusion coefficient ($\log D_H$) and hydrogen solubility (S_H), which apparently applied to pure metals but very definitely to Fe-X binary alloys, particularly when applied to alloying elements of any one period (in the periodic table), and at fixed X% composition. Lee and Parlee (4) found an analogous linear relationship to exist between $\log D_N$ and S_N in Fe-X alloys at 1600°C for any particular percentage of alloying element. Auza, Jayarajan and Parlee (5, 14) recently showed that this relation could be extended to Fe-W-X-Y-Z alloys for any fixed total alloy content. Thus D_N prediction in complex alloys is possible by this means, but it is rather complex and would require a great deal more basic data before the method would be very useful. Auza, Jayarajan and Parlee also developed a completely new and spectacular graphical method of predicting D_N in alloys of Fe-U-V-W-Y-Z composition, or in any steel, up to about 15% total alloying elements, regardless of periodic table position. This method is based on data taken from known curves of $\log D_N$ vs. %X in Fe-X alloys. The data for each alloying element at its concentration is plotted as a vector on a graph of $\log D$ vs. %X, then the vectors are summed graphically. The resultant values gives the predicted D_N for the complex alloy. Results compare beautifully with experimental values to 15%

total alloy content (5, 14). The basis of this method is that it represents a rough Taylor expansion.

This led in 1978 to the development of a modified advanced Taylor expansion method by Dr. Jayarajan (16), who used and evaluated higher terms of the expansion. The general method applies both to prediction of diffusivity and to solubility. Whereas in the case of diffusivity the basic data are curves of $\log D_N$ vs. ΔX , for solubility the basic data are curves of $\log f_N^X$ vs. ΔX , in FeX alloys, (where f_N^X is the activity coefficient). The ability to predict D_N and S_N in complex alloys up to 50% alloy content is excellent.

During the last three years, Mr. Hua (6) has been measuring S_H and D_H values in complex alloys and has completed the adaptation and improvement of Jayarajan's method for the prediction of S_H and D_H in nearly all complex liquid iron alloys and steels up to at least 50% total alloy content. Mr. Hua has also established a complete new basic table of improved hydrogen-alloy element interaction parameters, which will make solubility prediction more precise in the future. These new and reliable methods of predicting solubilities and diffusivities of nitrogen and hydrogen in the most complex liquid iron and steel, will be of great assistance to the steel industry for the estimation of the rates of gas absorption and removal. These methods should be applicable also to O and N in non-ferrous alloy making, given sufficient basic S and D data.

(2) Elucidation of the Laws Controlling the Effect
of Surface Active Elements (S, O, Se, etc., on the
Rates of Nitrogen and Hydrogen Absorption and Desorp-
tion in Stirred Liquid Metals and Alloys

Graduate Student: C. H. Hua

Mr. Hua (6) has developed the following new equation representing the rate constant or mass transfer coefficient, k , for the absorption of gas by stirred liquid metal:

$$k = D^{1/2} V_e^{3/2} \rho^{1/2} \sigma^{-1/2} \sqrt{1-\theta} \quad (1)$$

where D is gas diffusivity, V_e = eddy velocity, ρ is liquid density, σ is surface tension, and θ = fractional coverage of the surface by any poisoning (surface active) elements that may be present. He has extended the methods developed by Belton for calculating θ for single surface active elements from "surface-tension lowering" measurements so that θ can now be calculated for the presence of any number of such elements, such as O, S, Se which may be simultaneously present in any concentration. This equation can be used to predict several things. For example (a) for any particular alloy, the rate constant for hydrogen k_H can be predicted if k_N , the rate constant for nitrogen, D_H and D_N are known, i.e., $k_H/k_N = D_H^{1/2}/D_N^{1/2}$; (b) for iron alloys that are not very high in alloy content (i.e. where V_e , ρ and σ are not very different from pure iron) the rate constant for an alloy, k_A , can be predicted satisfactorily from the known rate constant for iron, k_{Fe} , and the known diffusivities of the gas (e.g., nitrogen) in iron, D_{Fe} , and in the alloy, D_H , --i.e., from $k_A/k_{Fe} = D_A^{1/2}/D_{Fe}^{1/2}$; (c) the effect of one or more surface active elements, such as S, Se and O, on the rate constant for any iron alloy can often be predicted from Hua's calculated values of θ , by making use of Hua's proof that the relationship between k and the square root of the fraction of clean surface, $\sqrt{1-\theta}$ is always linear. Similar linear relation exists for different metals and alloys.

Although this new relationship is very useful it suffered from the fact that (for prediction) it was often only useful for prediction of surface active element effects in a metal and its closely similar alloys and only under the same hydrodynamic conditions.

During the last few months it has been discovered that if all rate constants are converted to a dimensionless or fractional rate constant k_N^F ranging from 0 to 1--then data plots of k_N^F (for nitrogen) vs. $\sqrt{1-\theta}$ representing 33 different researches on iron and iron alloys (some as complex as stainless) all fall essentially on the same straight line--for both nitrogen absorption and desorption, as affected by one or more surface active elements. This means now that if one knows, for example, the rate of degasification of a liquid iron alloy containing known amounts of $\underline{S}$ and $\underline{O}$ (say 0.01% $\underline{S}$ and 0.005% $\underline{O}$) then one can easily calculate the degasification rate at any other $\underline{S}$ and $\underline{O}$ contents, (such as 0.1% $\underline{S}$ and 0.05% $\underline{O}$). This is easily done by use of one master graph or the simple linear equation for 1600° C

$$k_N^F = 1.19 \sqrt{1-\theta} + 0.19 \quad (2)$$

The graphs and equation 2, based on experimental findings show that the rate becomes practically zero, i.e., immeasurably slow, at 97.5% coverage of the surface by surface active element atoms instead of at 100% as predicted by equation (1) and by all early theory. This is explainable on the basis that, at 97.5% coverage, the surface is too "busy" with rapidly vibrating surface active atoms for nitrogen molecules or atoms to "land". Grabke, Paulitschke and Viefhaus (7) have established, in work on "catalysis," that two adjacent sites are needed for a gas particle to land and pass through the surface. At 97.5% coverage the chances become very small.

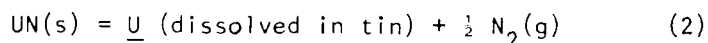
Temperature coefficient relations have been also established for calculating surface coverage and its effect on rates at other temperatures. The effects of surface active elements becomes very small at very high temperatures and this helps to explain the phenomenal absorption rates at the tip of the plasma-arc "flame".

Relations similar to equations 1 and 2 are found for the effects of surface active elements on hydrogen kinetics in liquid Fe and Fe alloys, also for liquid Cu and Ni; however more data are needed to firmly establish their validity for predictive purposes.

(3) The Use of Induction Plasma for Decomposition of Uranium Nitride

Professional Associate: Mohammed Hassan

An induction plasma torch was designed and built for use as a chemical reactor for work on the extractive concentration of gallium from fly ash (8). Argon is the carrier gas. This equipment was applied to the decomposition of pure UN but failed as expected. However, when powdered tin was fed along with UN, some decomposition was found according to



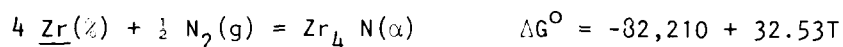
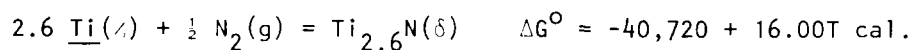
More work needs to be done to determine what is the maximum degree of decomposition possible by one pass through the apparatus. Considerable U was collected in the form of solid U-Sn alloy. This may possibly have some potential in the nuclear fuel reprocessing area.

(4) Selective Nitriding, Hydriding etc. of Reactive Metals (U, Th, Ti, Zr, Hf, etc.) in Liquid Metallic Solvent Solutions--and Applications

Graduate Student: J. R. Hwang

The stoichiometry and thermodynamics of the following reactions in liquid tin solvent solution have been established which are generally applicable to the 1 to 15% concentration and 1200 to 1550° C temperature ranges as follows---the exact ranges being given in Mr. Hwang's disser-

tation (9):



Studies of this kind on 7 very reactive metals have now been done here. Hafnium forms a carbide (in the graphite crucibles along with the nitride above 4% Hf. No carbide forms below 0.5% Hf. Studies on Hf are incomplete. Small additions of Ca markedly increase uranium nitriding rates.

Selective nitriding work (9) established that the following separations were possible:

- (a) Th from U--for advanced breeder reactor cycles
- (b) Zr from Hf--for cheaper production of reactor grade (cladding) zirconium.
- (c) Zr from U--for recovery of Zr from spent zircalloy reactor "hulls".
- (d) U + Pu from fission products in spent reactor fuel to return the U + Pu to the reactor as "new" fuel and avoid Pu proliferation.

Broad-brush hydriding studies (9) were done on 4.64 to 14.71 wt% of Ti, Zr, Mg, U, Gd, Pr and Y respectively in liquid tin and certain other metal solvents in the 300 to 1200° C range. In most cases rates were

too slow to give consistent equilibrium data. Only in the case of Gd and Y were fairly good equilibrium data obtained and the stoichiometry of the hydride phase roughly established.

While selective nitriding offers great promise for re-processing nuclear fuels and components by methods and processes developed at Stanford (10, 11, 12, 13)--also for other refining applications, e.g. Nb, Zr, Ti, etc. (10, 11)--the applications for selective hydriding seem limited. They could have special applications, if future research found ways of improving kinetics. At least one other exciting method of selective precipitation refining has been uncovered which will be described in the next report.

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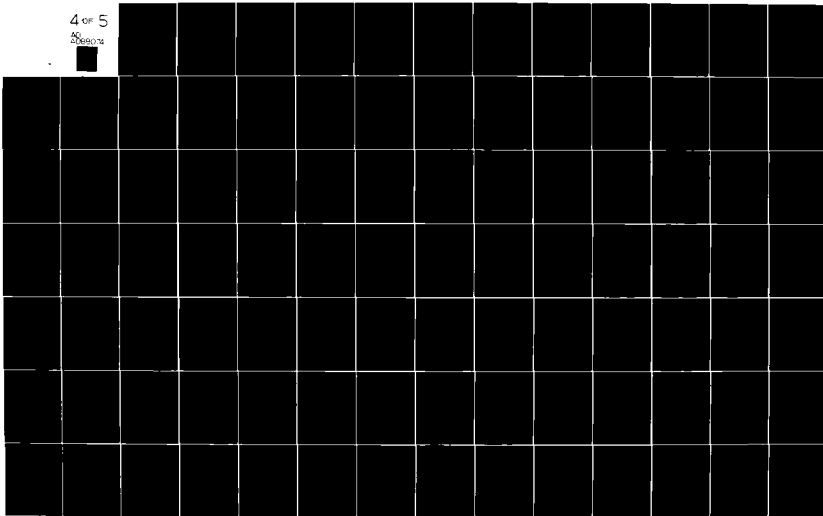
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PATENT

N. A. D. Parlee and R. N. Anderson, "Carbothermic Reduction Methods for Converting Metal Oxides to Metal," Patent from the Japanese Government. (1980).

44. ELECTRICAL, OPTICAL AND METALLURGICAL PROPERTIES OF SEMICONDUCTING MATERIAL

G. L. Pearson, Professor, Electrical Engineering

Professional Associates:

W. S. Feng
P. Kordos
D. D. Lee

Graduate Students:

Y. F. Jan
K. G. Jew
M. I. Landstrass
S. C. Lee
K. J. Malloy*

*Received M.S. during report period

Agency Support:

Navy N00014-78-C-0297
AROD DAAG-78-C-0018
NSF DMR-79-01661
SERI XI-9-8030-1

Technical Objective:

To prepare new semiconducting materials, measure their pertinent properties, and construct novel devices therefrom.

Research Report:

(1) Preparation and Properties of AlGaAs-GaAs Double Hetero-junction Devices.

Graduate Students: S. C. Lee

The key to success when using two different semiconductors to form useful heterojunction (HJ) devices is that the lattice constants must be closely matched so that interface states has only a minor effect on the electrical properties. There are a limited number of semiconductor combinations that fulfill this requirement of which the $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ system is the most widely studied.

Double layer Au-(n)AlGaAs-(n)GaAs Schottky barrier (SB) devices were grown and their carrier transport properties investigated. The interaction of closely spaced Au-AlGaAs SB and the AlGaAs-GaAs HJ was found to produce a novel phenomenon termed "band readjustment". This effect was used in the design of high efficiency solar cells. Three criteria are presented by which the open circuit voltage and the short circuit current of the solar cells can be controlled separately. Several new designs including n-p-p and p-n-n $\text{Al}_y\text{Ga}_{1-y}\text{As}-\text{Al}_x\text{Ga}_{1-x}\text{As}-\text{GaAs}$ layers dramatically reduced the dark 2 kT recombination current without altering either the diffusion or photocurrents. As a result, the 1 kT diffusion current dominates at current densities as low as 10^{-5} A/cm^2 thus improving solar cell efficiencies. These structures also have potential applications in heterojunction transistors and double HJ lasers.

The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers were grown on GaAs substrates by liquid phase epitaxial (LPE) techniques. Several experimental observations led to a theory of the "etchback-regrowth" effect which sometimes occurs during LPE growth. This theory deals with the physical processes which occur immediately after the substrate is inserted into the melt. It predicts that, if the saturated melt and the substrate are not in chemical equilibrium, a thin graded-bandgap epilayer can grow on the substrate even under isothermal conditions.

During investigation of the electrical properties of single $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers grown on Cr-doped semi-insulating GaAs substrates, it was found that an embedded n-type layer, which had formed on the thermally converted substrate surface during crystal growth, caused van der Pauw measurements to be in error. A modified thermal probe technique, termed "cold probe", was developed to determine the surface carrier type of the grown layers. The SB technique was found to be reliable for measuring the carrier density.

The energy band diagrams of three (n) $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ -(n)GaAs HJs with different doping densities were analyzed, based on the simplified graded-bandgap HJ model developed by Cheung, Chiang and Pearson. Several

modifications were also incorporated into the calculations. The theoretical current density vs voltage (J-V) curves of these HJs were derived using thermionic emission theory. It was found that unless the doping densities of the AlGaAs layers were low, i.e., $\leq 10^{16} \text{ cm}^{-3}$, a 50 Å metallurgical grading width at the n-n HJ interface produced either an ohmic or a weak rectifying characteristic. These results explain the lack of rectification in most n-n $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs HJs reported in the literature.

Studies of the temperature dependent I-V characteristics of p-n and SB diodes reveal that the diode n factor, which takes values between 1 and 2 at room temperature, increases with decreasing temperature. Values between 1.5 and 4 were usually observed at temperatures around 70 K. A model which takes temperature induced interface states into account is used to explain this behavior. It is demonstrated that experimental data obtained on SB diodes are in good agreement with this theory and that n must be taken into account when determining SB heights from forward bias I-V curves.

(2) Electronic Transport Properties of $\text{Al}_x\text{Ga}_{1-x}\text{As}$

Graduate Student: K. G. Jew

$\text{Al}_x\text{Ga}_{1-x}\text{As}$ has been widely studied because of its applications in optoelectronic devices such as semiconductor lasers and solar cells. While there have been many reports of studies on crystal growth, device fabrication and device performance, relatively little work has been done on the electrical properties of this material. The goal of this project is to perform a systematic study of the transport properties of free carriers in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The electronic parameters of interest include free carrier mobility, minority carrier diffusion length and dopant impurity activation energy.

In the course of this work, both p-type and n-type epitaxial layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (doped with Ge and Sn) have been grown throughout the composition range $0.0 < x < 1.0$ using liquid phase epitaxy techniques. Hall measurements have been performed over the temperature

range 77° - 300°K to obtain mobility, carrier concentration and resistivity as a function of temperature. Presently, work is proceeding on an analysis of the experimental data.

Recent efforts have been on the development of a model for the electrical properties of n-type and p-type $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as both composition and temperature are varied. The transport mechanisms which determine the carrier transport in the material can be studied by analyzing the temperature dependence of mobility. Each scattering mechanism has a characteristic temperature dependence. By comparing calculated and experimental mobilities, the contribution of each scattering mechanism to the mobility can be obtained. The scattering mechanisms involved include polar-optical, nonpolar-optical, deformation potential, piezoelectric, equivalent and nonequivalent intervalley, ionized impurity, alloy, space charge and neutral impurity scattering.

In the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system, where several conduction bands contribute to the carrier transport, interpretation of experimental data becomes complicated. Each conduction band valley must be analyzed since each valley has different transport parameters. After performing theoretical calculations of the mobilities in each valley, they can be combined to obtain the net mobility. Since many of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ physical constants needed for the theoretical calculations are not well known, the compositional dependence of the transport parameters must be investigated. Values for deformation potentials, electron-phonon coupling constants, etc., are being estimated or derived by analyzing the existing data.

(3) Fundamental Studies of Photocarrier Tunneling in GaAs Thin Solar Cell Structures

Graduate Student: K. J. Malloy

During the past year, the $\text{Au-(n)AlGaAs-(n)GaAs}$ heterojunction Schottky barrier solar cell was studied in detail. Hole photocurrent in the structure was modeled as consisting of three components:

(1) Thermionic emission of holes over the heterojunction valence band hole barrier.

(2) Tunneling of holes through the hole barrier.

(3) "Warm" hole transport of holes over the barrier.

In the last transport process, holes traverse the barrier region without loss of energy because of long mean free paths between scattering events. This process dominates transport in the barrier region under reverse bias.

It was also shown that compositionally grading the aluminum content of the AlGaAs layer can reduce or even eliminate the hole barrier under operating conditions. We anticipate improvements in overall cell efficiency through the use of a high-low (n)GaAs minority carrier mirror in conjunction with a graded AlGaAs layer. Current experiments and computer modeling are aimed at verifying this conclusion.

Finally, heavily doped $(p^+)AlGaAs-(n^+)GaAs$ and $(n^+)AlGaAs-(p^+)GaAs$ tunnel diodes have been grown using LPE methods. These ohmic p-n junctions permit the construction of a monolithic cascaded junction solar cell composed of a high band gap $(n)AlGaAs-(p^+)AlGaAs$ cell on top of a low band-gap $(n^+)GaAs-(p)GaAs$ cell. In future work on this structure, we hope to demonstrate greatly enhanced open circuit voltages with only slight reductions in short circuit current.

(4) Preparation and Properties of Semi-Insulating $Al_xGa_{1-x}As:Cr$ Single Crystals and MIS Devices

Graduate Student: M. I. Landstrass

The objective of this research program is to prepare semi-insulating $Al_xGa_{1-x}As:Cr$ -GaAs heterojunctions and to determine the utility of this system for MISFET applications.

Semi-insulating (SI) $Al_{0.5}Ga_{0.5}As:Cr$ layers were grown by Cr doping (0.5 mole percent Cr in the melt) a closely compensated Ga melt. Close compensation of n- and p-type impurities was achieved by baking out the Ga melts in flowing H_2 for ~100 hrs. at 475°C. At this temperature, equal amounts of n- and p-type growth system contaminants are incorporated in the melt. As long as the Cr concentration exceeds the residual uncompensated donor concentration, the grown crystal will be semi-insulating. Preliminary experiments are also under way on stress compensation of Cr so as to achieve higher solid solubility in the

crystal. Boron is being used since it is isoelectronic with Ga but will compensate the lattice strain produced by Cr.

Crystals grown by this technique have a resistivity of $\sim 10^{11}$ ohm-cm. This yields crystals in which the Fermi level positions itself ± 0.17 eV from the intrinsic level. This fluctuation causes scatter in the dominant conduction mechanism in the crystal. Some crystals have been ohmic until breakdown is reached while others are ohmic at low fields and dominated by Fowler-Nordheim tunneling at higher fields.

C-V measurements from 10 Hz to 1 MHz have been performed on Cr/Au-Al_{0.5}Ga_{0.5}As:Cr-GaAs MIS capacitors. Only measurements on n-GaAs (10^{15} - 10^{16}) have been performed to date. Fabrication of p-type capacitors is in progress.

All samples to date have exhibited frequency dispersion in the SI Al_xGa_{1-x}As:Cr layer due to charge injection with no measurable dispersion due to interface states. Capacitors whose leakage current was below detection limits at 10 volts (10^{14} amps or 10^{-11} amp/cm²) had C-V characteristics which saturated at negative bias voltages. Capacitors whose leakage current exceeded this value went into deep depletion. The capacitors which had capacitance saturation did not exhibit inversion type behavior at low frequencies.

Work is in progress to fabricate an MIS inversion mode transistor on MIS layers having low leakage currents. The aim of this study is to determine if these devices can support an inversion layer of injected minority charge.

(5) Growth and Properties of AlGaAs-GaAs Photoelectric Devices Prepared by Liquid-Phase Epitaxial Techniques

Visiting Scholar: W. S. Feng

Graded and constant band-gap Al_xGa_{1-x}As layers for solar cells and voltage-controlled light-switching (VCLS) diodes were grown by liquid phase epitaxial techniques and characterized by means of electrical and optical measurements. Several device configurations were investigated but the one to be described here is (p⁺)Al_xGa_{1-x}As:Ge-(p)GaAs:Ge-(n⁻)GaAs-(n⁺)GaAs:Te with Au-Zn and Au-Ge-Ni alloyed ohmic contacts on the front and back surfaces, respectively. An antireflection coating (AR) was

applied to the front surface by anodic oxidation.

The double-drift fields in the devices were formed by (1) thermal diffusion of Te impurities from the n^+ substrate into the n^- undoped GaAs active layer and (2) growth of the surface $Al_xGa_{1-x}As$ layer in an isothermal As-undersaturated solution which caused an increase in both x and E_g as one approaches the surface. The impurity gradient was measured by electrolytic etching and Schottky barrier techniques. Characterization of the graded band-gap layer was provided by Auger spectroscopy.

The optical constants of the anodic oxides and AlGaAs layers were measured with an ellipsometer and step-profiler. A computer-aided simulation was carried out which provided for adjustments in impurity concentration, energy band-gap, and built-in field. The results were used in the design and construction of devices with optimum characteristics. Several completed cells were tested under an AM1 (100 mW/cm^2) solar simulator. An open-circuit voltage of 0.86 V, short-circuit current density of 25.2 mA/cm^2 , a fill factor of 0.69 and a conversion efficiency of 15% were obtained.

The VCLS diodes were made by successive crystallization of epitaxial layers of AlGaAs and GaAs on GaAs substrates. By controlling the thickness, impurity concentration, and energy band-gap of these materials, the light turn-on voltage, breakdown voltage, and absorption spectrum could be adjusted. VCLS diodes constructed in this manner exhibited maximum turn-on and breakdown voltages of 500 V and 1000 V, respectively.

Reference Publications:

1. K. I. Chang and G. L. Pearson, "Defects in As-Grown and Annealed $Al_xGa_{1-x}As$ Single Crystals," J. of Luminescence 20, 131 (1979).
2. P. Kordos, G. L. Pearson, and M. B. Panish, "Isothermal LPE Growth of Thin Graded Band-Gap $Al_xGa_{1-x}As$ Layers From Saturated Solutions," J. Appl. Phys. 50, 6902 (1979).
3. P. Kordos and G. L. Pearson, "Grown Junction GaAs Solar Cells With a Thin Graded Band-Gap $Al_xGa_{1-x}As$ Surface Layer," Solid State Electronics 23, 399 (1980).

4. Y. D. Shen and G. L. Pearson, "Preparation and Properties of Au-(n)Al_xGa_{1-x}As(n)GaAs Schottky Barrier Solar Cells," Solar Energy Materials 2, 31 (1979).
5. C. M. Garner, C. Y. Su, W. A. Saperstein, K. G. Jew, C. S. Lee, G. L. Pearson and W. E. Spicer, "Effect of GaAs or Ga_xAl_{1-x}As Oxide Composition on Schottky Barrier Behavior," J. Appl. Phys. 50, 3376 (1979).
6. C. M. Garner, C. Y. Su, Y. D. Shen, C. S. Lee, G. L. Pearson, W. E. Spicer, D. D. Edwall, D. Miller and J. S. Harris, Jr., "Interface Studies of Al_xGa_{1-x}As-GaAs Heterojunctions," J. Appl. Phys. 50, 3383 (1979).
7. S. C. Lee and G. L. Pearson, "Interaction of Closely Spaced Junctions," IEEE Trans. on Electron Devices ED-26, 1839 (1979).
8. S. C. Lee and G. L. Pearson, "Band Readjustment Effect with Applications to Solar Cells," IEEE Trans. on Electron Devices ED-27, 844 (1980).

45. STUDIES OF THE DYNAMICS OF MOLECULES AND MACROMOLECULES IN LIQUIDS

R. Pecora, Professor, Chemistry

Professional Associates:

S. P. Michielsen
K. Moro*
W. H. Nelson

A. C. Ouano*
C.-C. Wang

*Left during report period

Graduate Students:

S. E. Bott
A. Flamberg
K. R. Maier
N. H. Oliver

S. G. Stanton
B. E. Zebrowski
K. M. Zero

Agency Support:

NSF CHE 79-01070
NIH 5R01 GM 22517

Technical Objective:

To formulate theories of and to develop experimental techniques for studying the dynamics and motions of molecules in condensed systems.

Approach:

Theories of molecular motions and experimental techniques are formulated in terms of time-correlation functions. Experimental studies are carried out using dynamic light scattering, and other types of fluctuation spectroscopy.

Research Report:

1. Molecular Motions in Glassy Materials

Professional Associate: A. C. Ouano

Graduate Student: N. H. Oliver

Studies have been completed on the rotational motion of chlorobenzene dissolved in polymethylmethacrylate. Depolarized time correlation functions and Fabry-Perot spectra have been obtained as a function of temperature and chlorobenzene concentration. Theoretical models utilizing the restricted rotational diffusion model and the free volume concept have been used to interpret the results.^{1,2}

Experiments have also begun on the rotational motion of molecules in glasses composed of small organic molecules (orthoterphenyl, triphenylphosphite, etc.). An apparatus for obtaining the required low temperatures and a suitable sample block have been constructed.

2. Theoretical Studies of the Dynamics of Flexible Polymer Chains

Professional Associates: K. Moro
C.-C. Wang

The depolarized light scattering spectrum from a freely, rotating polymer chain has been calculated using the Zwanzig-Bixon projection operator approach.³

A theory of rotational diffusion of rod-shaped molecules in a conical volume has been formulated and applied to such problems as the rotation of molecules in glasses (see 1 above), and the intramolecular motions of broken-rod macromolecules.⁴

3. Experimental Studies of the Intramolecular Dynamics of Flexible Macromolecules

Professional Associates: S. Michielsen
C.-C. Wang

Polarized and depolarized light scattering studies have been performed on some polyamic acids and polyhydroxyphenylmethanes. There is evidence that intramolecular motion influences the line width of the depolarized scattering of both series of compounds. These results are, however, preliminary. Further data analysis is now in progress.

4. Studies of Polypeptides and Proteins

Professional Associate: C.-C. Wang

Graduate Students: A. Flamberg
N. Oliver
B. E. Zebrowski

Experimental work has been performed on

- 1) bovine pancreatic trypsin inhibitor (BPTI)
- 2) ribonuclease (RNase)
- 3) myosin rods and light meromyosin
- 4) poly- γ -benzyl-L-glutamate
- 5) F-actin
- 6) lambda-phage DNA.

For BPTI and RNase, we have, as previously reported, obtained translational and rotational diffusion coefficients for the intact molecules. There is evidence from our more recent experiments that for both of these molecules there is a strong concentration dependence of the rotational diffusion coefficient. Further experiments are being done on BPTI to confirm this dependence. For RNase, we have also studied the thermal unfolding transition in the presence of 1 M guanidine. There is evidence of a pretransition "swelling" of the protein.⁵ Data on the thermal unfolding of RNase has also recently been obtained in the absence of guanidine.

5. Rotational Motion in Semi-Dilute and Concentrated Solutions

Professional Associates: C.-C. Wang

Graduate Students: K. Zero

Rotational motion of long, rigid rod polymers has been studied in the semi-dilute region, that is, the region in which polymer rods cannot rotate significantly without hitting each other, but in which large amounts of solvent are still present. Studies of light meromyosin⁶ and poly- γ -benzyl-L-glutamate indicate that the rotation is much faster than predicted by scaling theories. Studies of the myosin rod also indicate fast rotation and show evidence that it may be flexible.

6. Studies of Phospholipid Vesicles and Micelles

Graduate Students: S. Bott
A. Flamberg
B. E. Zebrowski

A reliable and rapid cumulant method, assuming a Schulz distribution of vesicle sizes, has been developed to study sizes and size distributions of phospholipid vesicles. A major problem for precise studies of these systems is a method for the routine preparation of ultra-dust free samples. A new method of sample preparation gives dust-free samples most of the time.

Dynamic light scattering studies of micelles of dodecyldimethylammonium chloride as a function of NaCl concentration have also been performed in our laboratory. A transition from roughly spherical micelles at low NaCl concentration to rod-like micelles at high concentrations is observed. Attempts are now being made to study the rotation of the rod-like form and to determine whether or not it is rigid.

7. Resonance-Enhanced Scattering

Professional Associate: W. H. Nelson
Graduate Student: S. Stanton

Extensive tests of parinaric acid and some of its esters for resonance-enhancement have been conducted. Although it was found that these compounds exhibit large enhancements, they also exhibit large amounts of fluorescence and are also photochemically unstable, rendering precise light scattering experiments difficult. We found on introducing these compounds into vesicles, that the resulting depolarized signals exhibited too much noise for quantitative data interpretation. We have concluded that these compounds are not suitable as light scattering labels in vesicles. Light scattering labels should not photochemically decompose and should not exhibit strong fluorescence.

We have found that resonance enhancement is exhibited by many compounds--for instance the coumarins (which are fluorescent) and

cyanine dyes (some of which are nonfluorescent and photochemically stable).

Experiments are now being conducted on para-nitrophenol and picric acid, both of which have very large scattered intensities.

Reference Publications:

1. A. C. Ouano and R. Pecora, "Rotational Relaxation of Chlorobenzene in Poly(methylmethacrylate) Part I. Temperature and Concentration Effects," *Macromolecules* (in press).
2. A. C. Ouano and R. Pecora, "Rotational Relaxation of Chlorobenzene in Poly(methylmethacrylate) Part II. Theoretical Interpretation," *Macromolecules* (in press).
3. K. Moro and R. Pecora, "Theory of Dynamic Depolarized Light Scattering from Non-Rigid Polymer Chains II Freely-Rotating Chains," *J. Chem. Phys.* (in press).
4. C.-C. Wang and R. Pecora, "Time-Correlation Functions for Restricted Rotational Diffusion," *J. Chem. Phys.* (in press).
5. C.-C. Wang, K. H. Cook, and R. Pecora, "Dynamic Light Scattering Studies of Ribonuclease," *Biophysical Chemistry* (in press).
6. C.-C. Wang and R. Pecora, "Dynamic Light Scattering Studies of Molecular Reorientation in Liquids," *Kagaku no Ryoiki* 33, 996 (1979)(in Japanese).

46. CONTINUUM CHARACTERIZATION OF BEAM STRUCTURES - APPLIED TO CANCELLOUS BONE

R.L. Piziali, Associate Professor, Design Division, Mechanical Engineering

Professional Associates:

T. A. Koogle
L. W. Swenson, Jr.

Graduate Students:

Kil Soo Kim

Agency Support:

Veterans Administration Hospital

Technical Objective:

To obtain an understanding of the characteristics of human cancellous bone in order to better model the failure of vertebral bodies and loosening problems associated with joint transplants.

Approach:

Human cancellous bone has been considered as a continuum by researchers in the past. However, cancellous bone looks something like a sponge, having a series of beam and platelike elements. We are developing techniques in which the characteristics of the structure are maintained in the development of a continuum type constitutive relationship. The latter allows us to model large areas of cancellous bone using standard finite element methods with the ability to also return back to look at the stresses in individual beams and plates.

Research Report:

No publications in this area yet.

47. MICROMECHANICAL MODELS FOR THE EXPANSIVE PROCESS IN EXPANSIVE CEMENT CONCRETE

C. W. Richards, Professor, Civil Engineering

Graduate Students:

M. D. Cohen

Agency Support

NSF ENG 77-03947

Technical Objective:

Continued development of microstructural and micromechanical models for the expansive process in calcium sulfoaluminate expansive cements. Experimental study of the causes of certain types of anomalous behavior.

Approach:

Continuation of study of the effects of parameter variations on free expansion behavior of cement pastes. A series of blends has been designed to produce specific types of behavior, based on the results of previous analysis. Blends include a) expansive clinker, ground to specific controlled particle size distributions, b) sulfate sources of known characteristics (e.g., reagent grade calcium sulfate hydrates), and c) ordinary portland cement or portland clinker. Specimens are made by mixing a given blend with water to give the desired water/cement ratio and casting in molds. During the hardening/expanding process the following properties of the pastes are monitored:

- a. Free expansion
- b. Dynamic modulus of elasticity
- c. Formation of ettringite
- d. Nonevaporable water content
- e. Morphology of ettringite crystals
- f. Presence of microcracks.

The effects of restraints, including uniaxial and biaxial, have also been investigated, using specially designed molds.

Research Report:

More than forty blends have been investigated during the year covered by this report. Free expansion measurements indicate the control or lack of control provided by each blend. Lack of control is shown by such phenomena as "double curvature" in the expansion curve as a function of time, and "delayed expansions" occurring after several months of curing in water under constant conditions. Dynamic modulus measurements indicate variations in stiffness (and by inference variations in strength) and can be correlated with variations in the rate of expansion.

Since the formation of ettringite is believed by many to be the cause of expansion, it is important to correlate the time variation of ettringite formation with that of expansion and other variables. The morphology of the ettringite crystals also seems to have a bearing on the expansive process.

Measurement of nonevaporable water content provides an indication of the strength of the paste which may be correlated with dynamic modulus. SEM studies of microcrack formation also provide evidence of strength. Clues as to the morphologies of the various types of structures, such as ettringite crystals and C-S-H gel particles are also provided by SEM

Data from the experimental investigation are being analyzed and correlated through various models of the expansive process. Results will be presented in a final report at the end of the grant period.

48. PROTEIN ADSORPTION TO POLYMER FILMS

C.R. Robertson, Professor, Chemical Engineering

Graduate Students:

E. K. Austin-Lange
Y. L. Cheng
D. S. Inloes
K. E. Lange
K. V. Lemley
B. K. Lok
W. J. Smith
J. C. Wright*

Undergraduates:

D. A. Hoagland
D. W. Mewes
S. S. Snapp
A. S. Yoshimura

*Received Engineer degree
during report period.

Agency Support:

None

Technical Objective:

To develop a new technique for the quantitative investigation of protein adsorption to polymer films.

Research Report:

Protein Adsorption to Polymer Films

Graduate Students: B.K. Lok, Y.L. Cheng

Undergraduate Students: H.B. Rosen, D.A. Hoagland

The initial event upon contact of blood with an artificial surface is the immediate deposition of a layer of plasma proteins. Often the compatibility of such a surface may be correlated to the type and amount of protein originally deposited. For this reason, protein adsorption to several important materials is being studied using a total internal reflection fluorescence technique. Based on the same physical principles as Multiple Attenuated Infrared Spectroscopy, the adsorption of a fluorescently labeled specie (in this case a protein -- fluorescein isothiocyanate complex) may be followed

continuously.

Experiments using this technique are devoted to developing adsorption isotherms for protein adsorption under both static and laminar flow conditions. Later studies will be expanded to cover a broader range of biomaterials and adsorption conditions.

Reference Publication:

1. R.W. Watkins and C.R. Robertson, "A Total Internal Reflection Technique for the Examination of Protein Adsorption," J. Biomedical Materials Research 11, 915 (1977).

49. SPECTROSCOPY AND QUANTUM ELECTRONICS

A. L. Schawlow, J.G.Jackson-C.J.Wood Professor of Physics
T. W. Hansch, Professor of Physics

Professionals Associates:

R. Abreu (Venezuela), Visiting Scholar
E. Arimondo (Italy), Visiting Scholar
B. Couillaud (France), Visiting Scholar
H. Gerhardt (Germany), Visiting Scholar
S. Haroche (France), Visiting Scholar
Susan M. Kay (England), Visiting Scholar
J. E. Lawler, Postdoctoral Research Affiliate
G. W. Series (England), Visiting Senior Research Associate
A. Siegel (Germany), Visiting Scholar
Z-Y. Wang (People's Republic of China), Visit. Res. Assoc.
H-R. Xia (People's Republic of China), Visit. Res. Assoc.
G-Y. Yan (People's Republic of China), Visit. Res. Assoc.

Graduate Students:

N. W. Carlson *	
W. T. Hill III	G. P. Morgan**
D. J. Jackson	D. R. Lyons
K. M. Jones	A. J. Taylor
L-S. Lee	J. C-C. Tsai

* Received Ph.D. during
Report period
**Received MS during
Report period

Agency Support:

NFS PHY-77-09687
NSF PHY-78-23532
U.S. Navy - ONR N00014-78-C-0403

Technical Objective:

To study the interaction between electromagnetic radiation and matter, to extend the range of coherent light techniques, to apply coherent and conventional light to elucidate problems in atomic, molecular and solid state physics.

(1) High Resolution Spectroscopy of Atomic Hydrogen

Visiting Scholars: Dr. B. Couillaud
Dr. A. Siegel

Current research is directed toward measuring the wavelength of the hydrogen 1S-2S transition with higher accuracy, by using a continuous, rather than pulsed, laser. This requires a continuous-wave laser source at a wavelength 2430 Angstroms, but there is no known laser operating at that wavelength. Moreover, there is no crystal that gives good phase-matching for harmonic generation of that wavelength. Ammonium dihydrogen phosphate (ADP) cooled close to its Curie temperature can provide sum-frequency generation of blue light from a krypton laser and yellow light from a dye laser. There have, however, been persistent problems with rapid damage of the surface of the mixing crystal. Some relief was obtained by cleaving the crystal in vacuum and coating the surfaces with evaporated magnesium fluoride. But this treatment is insufficient to permit pumping by the recently acquired ring dye laser, or indeed by any dye laser that gives enough power to carry out the experiment. It is hoped that adequate power levels will be obtainable by using even greater precautions to ensure that the crystal surfaces are clean and completely free from oil films.

(2) Measurement of the Wavelength of Continuous Lasers

Professor T. W. Hansch

The moving-mirror wavemeter of Kowalski and Schawlow has been modified to make it insensitive to sidewise translation of the reflecting prism. This has been done by adding an additional mirror so that the beam passes twice through the prism before completing its path through the interferometer. The interferometer system was already insensitive to twisting of the prism support, and now it is not troubled by motion from side to side as it moves along the track. Consequently, a very simple support may be used, and a toy electric train has proven very effective. The train has the advantage that more tracks can be added to give a longer translation distance, and so to increase the

accuracy.

(3) Measurement of Wavelength of Pulsed Lasers

Graduate Students: K. Jones
L-S. Lee

It is desired to be able to measure the wavelength of each individual pulse of a dye laser. These pulses typically have lengths of only a few nanoseconds, and so moving-mirror techniques are not applicable. Instead, we are investigating a new technique using three wedge interferometers, one above the other. A collimated light beam illuminates the three interferometers and produces three interference patterns, one above the other, on the cathode of a television pickup tube (vidicon). The image is captured and digitized in the time of a single television frame, and stored in the memory of a microcomputer. Fringes from a wavelength-standard laser are recorded at the same time. Preliminary tests have shown an accuracy of about one part in 500,000.

(4) Color Center Lasers

Postdoctoral Research Affiliate: J. E. Lawler
Graduate Student: D. J. Jackson
Visiting Scholar: Dr. H. Gerhardt

A continuous-wave laser, using stimulated emission from color centers in alkali halide crystals, has been used for spectroscopy in the near infrared. A number of helium and hydrogen lines have been observed by opto-galvanic detection. The sensitivity to small numbers of atoms is good, although even the lower levels of these transitions are not very far from ionization.¹

The laser is being improved, so as to run in an single axial mode, and will be used for Doppler-free spectroscopy in helium.

¹D. J. Jackson, J. E. Lawler, and T. W. Hansch, Opt. Comm. (1980).

(5) Doppler-Free Spectroscopy in Hollow-Cathode Gas

Postdoctoral Research Affiliate: J. E. Lawler
Visiting Scholars: Dr. B. Couillaud
Dr. A. Siegel

High resolution spectra, free from Doppler broadening, have been obtained inside the hollow cylindrical cathode of a low-pressure discharge tube. The cathode has a large diameter (3 cm), in order to permit operation at low gas densities, so as to minimize pressure broadening. As in other Doppler-free techniques, the laser beam is divided into two parts, which are sent in opposite directions along the same line through the discharge. Simultaneous absorption of light from both beams by one atom can occur only for those atoms which have zero velocity component along the beam direction. The lines have been observed opto-galvanically, by the change in the discharge current. They have also been observed with good sensitivity by intermodulated fluorescence from the level to which they are raised by absorption of the laser light.

The hollow cathode is especially suited for observation of the spectra of refractory metals. We have observed and measured hyperfine structures and isotope shifts in atomic molybdenum, by this method.

(6) Doppler-Free Spectroscopy in Radiofrequency Discharges

Postdoctoral Research Affiliate: J. E. Lawler
Graduate Student: D. R. Lyons
Visiting Scholars: Z-Y. Wang
G-Y. Yan

We are attempting to detect Doppler-free spectra of absorption lines from high states excited in a radiofrequency electrodeless discharge. Such a discharge is especially suitable for use in studying corrosive gases which may attack metallic electrodes or seals.

Good Doppler-free lines have been observed in a helium radiofrequency discharge, by intermodulated fluorescence. So far, radiofrequency power leakage has prevented observation of optogalvanic signals in these discharges, but the investigation is continuing.

(7) Sensitive Intracavity Absorption Spectroscopy

Graduate Student: W. T. Hill
Visiting Scholar: Dr. R. A. Abreu

It has been shown previously that a broadband dye laser, without tuning elements, is a particularly sensitive detector for weak absorption lines of any substance inside the resonator.¹ In such a laser, there are very many modes of oscillation competing for the supply of excited molecules. Any slight additional absorption causes the oscillation to cease at the absorbing wavelength. Indeed, the absorption lines from water and oxygen in the air of the laboratory are observed so strongly as to obscure anything else in their region, even in the visible where we usually consider air to be completely transparent. We have, therefore, constructed an untuned dye laser in a hermetically sealed box. The laser can be filled with any gas of interest, and can be operated at pressures as low as 50 torr.² With it, we have resolved fine structures of closely-spaced lines in oxygen, and have measured isotope shifts of weak lines in oxygen 16 and oxygen 18.

¹T.W.Hansch, A.L.Schawlow, and P.Toschek, IEEE J. Quant. Electr. QE-8, 802 (1972).

²W.T.Hill, R.A.Abreu, T.W.Hansch, and A.L.Schawlow, Opt. Comm. 32, 96 (1980).

(8) Excited Electronic States in Molecular Sodium

Graduate Students: N. W. Carlson
A. J. Taylor
K. Jones
Visiting Scholar: H-R. Xia

A pulsed dye laser has been employed to excite a chosen level in the A electronic state of the diatomic sodium molecule. As the laser is polarized, the excited molecules are oriented so that they can alter the polarization of a probe beam at any wavelength corresponding to transitions to a still higher electronic level. Probe delays of several nanoseconds distinguish lower-level depolarization from upper-level

depolarization.

A large number of new excited states in Na_2 have been identified by this technique, and their constants have been measured. Two sequences of Rydberg states have been observed, each of which permits a good extrapolation to the constants of the molecular ion.^{1,2}

¹N.W. Carlson, F.V. Kowalski, R.E. Teets, and A.L. Schawlow, Opt. Comm. 29, 302 (1979).

²N.W. Carlson, A.J. Taylor, and A.L. Schawlow, submitted to Physical Review Letters.

(9) Superradiance Triggering Spectroscopy

Graduate Students:	N. W. Carlson
	D. J. Jackson
Visiting Scholar:	Dr. S. Haroche

A superradiant state can be created if enough atoms or molecules are excited to a given state within a time shorter than the phase relaxation time of these excited molecules. Then, after a short delay, the intensity of emission from both ends of the column of molecules builds up rapidly, as the phases of the emitting molecules become synchronized. In these experiments, it has been found that the superradiant output can be triggered by a weak light beam, to emit sooner and in a different direction. Thus the weak light source can be detected, or used to do spectroscopy on the excited state ensemble.¹

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50. INTERACTIONS OF OPTICAL AND ACOUSTIC RADIATION WITH SOLIDS

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Research Report:

(1) Inertial Rotation Sensing

(In collaboration with M. Chodorow)

There is an increasing interest in inertial rotation sensing for navigation using optical waves. This is currently accomplished in a device commonly known as a ring laser gyro, which contains a laser oscillator in a closed optical loop whose frequency is affected by mechanical rotation through an effect known as the Sagnac effect. We have proposed and are currently studying an alternate approach, also based on the Sagnac effect, which has potential for higher sensitivity to rotation and is applicable to solid-state construction. This system has several essential features which are not found in combination in any other approach. In its final form, the optical loop will contain an optical amplifier, to allow a large number of circulations of optical waves around the loop, which multiplies the Sagnac effect and increases the sensitivity. The system is non-oscillating, optical signals being

introduced from an external laser, which avoids a basic mode locking phenomenon that limits the sensitivity of ring laser gyros. The system is an integrating rate gyro, and uses digital cycle counting to measure the rotation, giving an absolute scale factor which does not require calibration.

We have shown experimentally that it is possible to recirculate optical pulses around a single-mode fiber optic sensing loop, to multiply the sensitivity obtainable with a given length of fiber. A total of five passive recirculations, without internal amplification, have been observed using bulk optical components external to the loop for signal injection and recirculation. A new fiber optic circuit for this purpose, replacing the hybrid bulk components with fiber optic integrated components, has been devised and is presently being assembled. This system will be tested first in a passive mode, and later with an internal fiber optic amplifier in the loop.

We have studied the subject of noise in fiber rotation sensors, and feel we have identified the source which presently limits the sensitivity of cw fiber gyros. We are presently constructing a breadboard cw gyro to test the predictions experimentally.

It is anticipated that solid state systems of this kind could increase the accuracy available in inertial navigation of vehicles and in geophysical measurements.

(2) Fiber Optic Signal Processing

Systems for high speed signal processing using optical fibers are being studied. This presently involves the development of addressable memory elements in the form of tapped optical delay lines, and the development of key fiber optic components required for these delay lines. Modern optical fibers have extremely attractive properties for use in delay lines for these purposes.

We have demonstrated basic operation of a fiber optic recirculating delay line. We are studying recirculating memories of this kind to determine their potential for long-time volatile storage of very broadband electronic signals modulated onto optical beams. Such systems

could replace microwave coax, waveguide, or acoustic delay lines used for temporary storage of broadband microwave signals, with prospects for much larger bandwidth. We are also studying fiber optic tapped delay lines, which are basic to a variety of signal processing operations, such as convolution, correlation, Fourier transformation and the various processing and filtering functions which derive from them. We have devised new ways of constructing both linear and nonlinear taps for such delay lines, and are setting up experimental laboratory systems to test these approaches.

(3) Fiber Optic Components

We are developing components for use with fiber optic systems for signal processing, sensing and communication. During the past year we have demonstrated a rugged, highly successful integrated directional coupler for single-mode fiber, having low dissipative loss, high directivity, good polarization properties, and smoothly mechanically variable coupling coefficient.

(4) Fiber Optic Amplifiers

Optical amplifiers in fiber format are being studied, which use laser amplification in lengths of single-crystal Nd:YAG fiber. Distributed side-pumping schemes have been devised which leave the ends of the fiber free for coupling to an external fiber circuit carrying the signals to be amplified. Cold testing has been carried out using tapered quartz fibers for transferring the pump power from laser pump diodes to the YAG fiber. Nd:YAG fibers are to be obtained from the Stanford Center for Materials Research, fabricated using new apparatus under construction there for pulling of single-crystal fibers.

(5) Applications of Piezoelectric PVF₂ Polymer Films to Acoustic Imaging

The polymer polyvinylidene fluoride, PVF₂, is of considerable interest in a number of fields because of its unusual dielectric, piezoelectric, pyroelectric and nonlinear optical properties. We are studying its application in a new field, namely piezoelectric acoustic

transducers and arrays for acoustic imaging devices which are used for such applications as nondestructive analysis of materials and structures. Its initial attractiveness for this purpose is its relatively strong piezoelectricity, comparable to that of crystalline quartz, combined with its mechanical flexibility and the fact that it can be fabricated in thin films of large size. In working with this material, however, further very important advantages were found in its low acoustic impedance and velocity. These parameters lie at the opposite end of the scale from those of the familiar ceramic piezoelectric materials such as PZT, and provide potential for making transducers and arrays using much simpler fabrication procedures, improved performance and high frequency operation. Such arrays could also be mechanically flexible, to conform to objects having curved surfaces. We have produced simple transducers taking advantage of these properties, which have frequency bandwidth and impulse response characteristics not obtainable with PZT.

Bulk acoustic wave and surface acoustic wave transducers have been fabricated using PVF₂ films from several sources, including commercial piezo films (no longer available) and films fabricated in the Stanford Center for Materials Research from both commercial polymer resin and from resin synthesized from the monomer in the Stanford Chemical Engineering Department. These studies have shown that PVF₂ transducers having consistent properties can be fabricated, and that their behavior agrees with theoretical predictions as to insertion loss, bandwidth and impulse response. Multielement linear transducer arrays using PVF₂ films are being fabricated for testing the applicability of PVF₂ to high speed acoustic imaging using both bulk acoustic waves and surface acoustic waves.

(6) Digitally Controlled Electronically Scanned and Focused Ultrasonic Imaging System

A new phased array ultrasonic imaging system is being evaluated for nondestructive evaluation of materials. A multilevel digital delay line under microcomputer control delivers signals with desired phase and amplitude profiles, through linear transmitter amplifiers, to a 128-element linear PZT transmitter array. An identical receiver array feeds

receiver signals through linear receiver amplifiers, back through the DDL to a CRT display monitor. Both the transmitter and receiver arrays are electronically focused. System flexibility is such that the operating frequency (1 to 10 MHz), electronically controlled focal length, number of active elements in the phase arrays, apodization, line scanning rate, CW or pulsed mode, imaging mode (A, B, C, linear scan, sector scan, differential phase contrast, double pulse) and image processing, for different NDE purposes, can be implemented by the computer software. The system has produced two-dimensional images which show the presence of internal stress in aluminum samples, operating in a differential phase contrast mode using the multielement transmitter array, with a uniform strip receiving transducer in place of the multielement receiver array.

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51. MECHANICAL BEHAVIOR OF SOLIDS

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Graduate Students:

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NSF-MRL through CMR Thrust Program on Plasticity and Metal Working

Research Report:

(1) Mechanical Behavior of Composite Materials

Graduate Students and Research Associates:

L. Eiselstein	Mu Yeh Wu
J. Wadsworth	O. Ruano

Technical Objective:

The program centers on the mechanical behavior of particulate composite materials, with special emphasis on the influence of hard particles on the strength and ductility of polycrystalline metals.

Approach:

Techniques are being developed for the preparation of composite

materials by powder metallurgy methods. Use is being made of a mechanical attritor for refining the mixing of powders prior to sintering and of a hydrostatic extrusion press for mechanical working difficult to shape particulate composites. The mechanical behavior of solids are being assessed by means of constant strain rate and constant stress creep tests. The elastic behavior of the composite materials also will be studied.

Progress:

Our research on large volume fraction composites has yielded new phenomena not previously reported. At low temperatures ($<0.35 T_m$) particles contribute to strengthening mostly through grain size refinement and partially through dispersion strengthening per se. At warm temperatures ($0.35-0.6 T_m$) particles can contribute to dispersion ductilizing when particles become active sources of dislocations and vacancies; this situation leads to high strain rate sensitivity, a factor that enhances tensile ductility. At high temperatures ($>0.6 T_m$) the large volume fraction composites exhibit strain aging and yield point effects with accompanying high strengths. In addition, a "threshold stress" appears to exist below which plastic flow apparently does not occur. Physical models to explain these effects are currently being developed.

We propose to investigate internal stress superplasticity by thermal cycling of large volume fraction composite materials. A zinc-alumina composite will be chosen since such a composite has been studied extensively for its high temperature mechanical properties. This is a particularly suitable material because it exhibits a threshold stress below which no creep will occur. Our ideas would suggest that such a material will not only creep below the threshold stress, under thermal cycling conditions, but more importantly, it will creep superplastically. Such results, if verified, can lead to new processing techniques for materials which normally are considered difficult to form at elevated temperature. A mathematical model to describe internal stress superplasticity is also being developed.

Ruano, Wadsworth, Eiselstein and Sherby are investigating the properties of white cast iron (2.4 and 3.0%C). Thermal-mechanical processing methods and powder metallurgy processing are being developed to obtain an ultrafine grain size. Success has been achieved in that fine ferrite grains of about one micron have been developed. The cementite particles in the white case iron, however, exhibit a duplex structure after thermal-mechanical processing. A large fraction of the particles are submicron in size but uniformly distributed coarse (1-5 μ m) particles are also present. The coarse particles are likely obtained from the eutectic reaction at 1160°C. These mechanically worked white cast irons exhibit superplastic properties at warm temperature and unexpectedly good ductility in compression at room temperature. We are using rapid solidification rate (RSR) processing to develop uniform ultrafine structures in white cast iron powders. These powders are then isostatically pressed at warm temperatures and superplastic properties of the compacts are being evaluated over a range of temperature. It is objective here to evaluate the mechanical properties of fine grained white cast iron containing only fine cementite particles.

(2) Deformation of Materials at Warm and High Temperatures

Graduate Students and Research Associates:

D. Bourell	B. Snyder	O. Ruano
T. Oyama	J. Wadsworth	J. Lin

Technical Objective:

To study the mechanism of deformation at high strain rate at warm and high temperature. Study of the mechanical behavior of unusual structures developed by thermal-mechanical processing operations with special emphasis in the warm working range of temperatures where subgrains and/or fine grains are developed.

Approach:

Constant strain rate tests and special thermal-mechanical pro-

cessing treatments are used with the objective of developing ultra fine structures. A rapid quenching technique during high strain rate torsional deformation has been devised to assess the deformation mechanism of warm and hot working. Superplastic characteristics of fine grained materials are being studied by means of tension and compression testing.

- a) Development of controlled fine structures in ultrahigh carbon steels by thermal-mechanical processing. (warm working and superplasticity)

We have been attempting to develop very fine grained structures in ultrahigh carbon (UHC) steels by special thermal-mechanical treatment (TMT) processing. Our research has centered on plain carbon steels containing 1.0 to 2.1% carbon (fifteen to thirty-two volume percent cementite respectively). Various TMT processing procedures have been developed which have resulted in particulate composites of cementite in iron containing ferrite grains finer than one micron in size. Such high carbon steels are superplastic at warm temperatures (elongations of over 1500% have been achieved). Furthermore, they can be made strong and ductile at room temperature. Ultrahigh carbon steels can be made more ductile than mild steel at room temperatures. A patent has been issued to Stanford for the development of these fine grained UHC steels (U. S. Patent No. 3,951,697). In addition to exhibiting superplastic characteristics, the UHC steels can be heat treated to possess exceptionally high hardnesses (R_C 69 to 70). The fine martensite needles that form from the prior fine austenite grains lead to steels with compression fracture strengths exceeding 600,000 psi and compression ductility in the order of ten percent.

The development of ultrafine ferrite-cementite structures in the UHC steels has led to other unexpected results. Such fine-structure steels, when heated to just above the critical temperature to form austenite plus cementite, will exhibit a divorced eutectoid microstructure upon transformation cooling. Pearlite will not form; the fine interparticle spacing between cementite particles apparently allows the dissolved carbon in austenite to precipitate on the pre-existing cementite during transformation. Oyama, Wadsworth and Sherby are in-

vestigating variables controlling formation of divorced structures.

The ease of deformation of superplastic materials would suggest that such materials, when in powder form, can be pressure sintered readily at warm temperatures. We are investigating the warm pressing characteristics of such materials; initial results indicate that higher densifications result when powders are warm pressed under superplastic conditions than under non-superplastic conditions. Ruano and Sherby are investigating the enhancement of densification of ferrous powders through internal stress superplasticity. Preliminary results suggest that continuous phase transformation and interdiffusion during transformation is a potentially powerful method of enhancing densification and bonding. We have coined the term DIATRIBING (Diffusion And Transformation Induced Bonding) for describing this type of bonding. New studies on solid state "fine structure" superplastic welding are being initiated. For example, experiments are being performed for the preparation of laminated composites of ultrahigh carbon steel and mild steel. The new knowledge permits the preparation of unique composites not heretofore considered. Dissimilar steels can be perfectly bonded below the A_1 temperature with no chemical interdiffusion; they can then be selectively heat treated for the development of unique mechanical properties. B.Snyder has shown that such laminated composites can be superplastic at warm temperature and hard and tough at room temperature. Ito, Wadsworth and Oyama have shown that the impact strength of such laminated composites is higher than the individual strength of the components making up the composite.

b) Mechanism of warm and hot working in crystalline solids

The factors influencing ductility and ductile fracture of materials at elevated temperature have not been studied extensively. Such studies are of paramount importance in assessing the formability of materials. A torsion apparatus has been developed at Stanford capable of deforming materials up to strain rates of 10,000 percent per second and temperatures of up to 2200°F. One of the unique features of our apparatus is that samples can be quenched instantaneously

after deformation. In this manner the exact mechanism of plastic flow during high strain rate deformation can be evaluated. We are also capable of simulating complex thermal-mechanical processing operations with small scale samples.

Our work has revealed that structural change during warm working of polycrystalline solids is characterized by the formation of well defined subgrains. The subgrain size developed depends primarily on the modulus compensated stress, $\frac{\sigma}{E}$, and is insensitive to solid solution alloying, crystal structure and stacking fault energy. The nature of the subgrain boundary, however, appears to be a function of the temperature and strain at which it is formed. For a given subgrain size, the higher the temperature of working the more effective is the subgrain boundary as a barrier to low temperature plastic flow. We have shown that subgrains can be a more potent method of hardening than grains in the fine size range (ten microns and less). Preliminary results by us suggest that warm working has higher potential for cold hardening a material than cold working. Studies include austenitic and ferritic stainless steels as well as several iron base binary solid solution alloys. We are studying the influence of large plastic strain ($\epsilon = 15$ to 20) at warm temperature on the development, and nature, of subgrain boundaries. Results on a ferritic stainless steel indicate that the misorientation angle of subgrain boundaries gradually increases with increasing strain; at strains as high as 15 , the average misorientation angle is over twenty degrees. Similar results have been obtained after extensive warm working of a mild steel ($0.2\%C$ content).

c) Large strain deformation at warm temperatures (NSF/CMR Thrust Program on Plasticity and Metal working of Materials)

Warm rolling is a promising processing technique for attainment of fine subgrain structures in crystalline solids. We have illustrated that mild steel can be strengthened considerably by warm rolling and the yield point phenomenon can be eliminated. When large strains are imposed on plates at such temperatures, however, they can alligator or edge crack. These fractures are undesirable features of roll-

ing. These defects are a result of residual stresses developed during rolling. To the best of our knowledge, no systematic studies have been performed to assess the factors leading to ductile fracture by alligatoring or edge cracking in metals during warm rolling. It is our purpose to investigate the variables that can contribute to such ductile failures.

Our newly acquired rolling equipment at Stanford will permit us to study the influence of the degree of deformation per pass, the temperature, and the time at temperature between passes. An additional important variable influencing the development of residual stresses is the microstructural state of the material considered. If a sample is ultrafine grained, it can exhibit a high degree of recovery during and after rolling which, in turn, can reduce residual stresses. Specifically, we are investigating the warm rolling characteristics of two steels. One is a mild steel (1020) with which we have had considerable experience. The other is an ultrahigh carbon steel containing fine grains. Both materials are being rolled in the temperature range of 500°C to 700°C. Preliminary studies have revealed that ultrahigh carbon steels alligator less readily than mild steel in the temperature range around 600°C. Current tests are planned to quantify the factors leading to the two principal defects observed in rolling—alligatoring and edge cracking.

d) Creep of polycrystalline solids

The importance of subgrains on the creep resistance of materials is not well understood. Our studies are directed at determining the contribution of subgrains to the creep process. Using stress-change tests and change-in-strain-rate tests, it has been possible to determine the influence of strain rate on the flow stress at constant structure. Such tests also permit determination of the possible influence of subgrain size on the creep rate. Studies on pure aluminum, coupled with other data on high stacking fault energy materials, reveal that the creep rate can be given by:

$\dot{\epsilon} \approx 10^{11} \frac{D_{\text{eff}}}{b^2} \left(\frac{\lambda}{b}\right)^3 \left(\frac{\sigma}{E}\right)^8$. Here D_{eff} is the effective diffusion coefficient, λ is the subgrain size, σ is the creep stress, E is the dynamic unrelaxed elastic modulus and b is burgers vector. There are no contemporary creep theories that can explain the eight power dependence of creep at constant structure. The practical implication of our work is clear; if one can decrease the subgrain size by a factor of a hundred, the creep rate will decrease by a factor of a million. To retain fine subgrains for high creep resistance at a given stress it will be necessary to pin such boundaries. In recent work, Luthy, Miller and Sherby have shown that the above equation is valid for analyses of steady state plastic flow down to temperatures as low as $0.20 T_m$ by the following modification $\dot{\epsilon} = \frac{10^{11} D_{\text{eff}}}{\alpha^5 b^2} \left(\sinh \alpha \frac{\sigma}{E}\right)^5$. In this equation, α is the value of the reciprocal of the modulus compensated flow stress at power law breakdown. Lin and Sherby have extended the application of the constant structure creep relation to oxide dispersion strengthened (ODS) materials by including a threshold stress. Excellent quantitative predictions of the creep behavior of ODS alloys are possible with this modified relation. Clements and Sherby are investigating the creep of polyethylene and examining the possible applicability of phenomenological relations given above for metals to polyethylene.

White, Wadsworth and Sherby have examined the superplastic behavior of all fine grained superplastic materials reported in the literature. These studies are intended to assess the phenomenology of superplastic flow and to elucidate the mechanisms and rate controlling processes taking place during such deformation. A quantitative relation has been developed which describes well the temperature, stress and grain size dependence of the superplastic creep rate, $\dot{\epsilon}_{\text{spf}}$, of fine grained materials. This is given by the relation:

$$\dot{\epsilon}_{\text{spf}} \approx 2 \cdot 10^9 \frac{D_{\text{eff}}^x}{b^2} \left(\frac{b}{d}\right)^2 \left(\frac{\sigma}{E}\right)^2.$$

In this relation $D_{\text{eff}}^x = D_L + 0.01 D_{\text{gb}} f_{\text{gb}}$ where D_L is the lattice diffusion coefficient, D_{gb} is the grain boundary diffusion coefficient

and f_{gb} is the fraction of atoms in a given material associated with grain boundaries. The term f_{gb} is generally given as $\frac{2\pi b}{d}$ where b is the burgers vector and d is the grain size. This relation predicts that at low temperatures and fine grain sizes (in the range where superplasticity is observed) the creep rate is given by $\dot{\epsilon}_{spf} \propto D_{gb} \left(\frac{\sigma}{E}\right)^2 \left(\frac{b}{d}\right)^3$ and at high temperatures and coarse grain sizes, $\dot{\epsilon}_{spf} \propto D_L \left(\frac{\sigma}{E}\right)^2 \left(\frac{b}{d}\right)^2$. This predicted temperature, stress and grain size dependence is in agreement with experimentally observed behavior. The phenomenological relations developed permit predicting quantitatively the factors which can extend the range over which superplastic flow can dominate the deformation process. Such knowledge is of great importance industrially, for economic feasibility of superplastic forming depends on enhancing the rate at which such processes can occur. Additional current studies on superplastic flow mechanisms center on the importance of size and hardness of second phase, the nature of the grain boundary (i.e. the misorientation angle) and the ease of grain boundary and interphase boundary sliding and separation.

Luthy, White and Sherby have shown that grain boundary sliding (g.b.s.) as a deformation mechanism is generally more important than diffusional creep processes at high temperatures and low stresses. The deformation maps of Ashby and of Langdon-Mohamed are altered considerably when g.b.s. is taken into account. This work is being extended by Ruano, Miller and Sherby to consider the contribution of grain boundary sliding at high stresses where dislocation short circuit pipe diffusion can contribute to the lattice diffusion coefficient.

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19. "Creep of Oxide Dispersion Strengthened Materials", talk given to DFVLR, German Aeronautics Laboratory, Köln, Germany, August 24, 1979.
20. "Mechanical Behavior of Ultrahigh Carbon Steels", talk given to Polytechnic University of Madrid, Madrid, Spain, September, 1979.
21. "Damascus Steel Rediscovered?", a talk presented to the Army Research Office, Research Triangle Park, North Carolina, October 29, 1979.
22. "Development of Superplastic Microstructures and Microstructure-Property Relations", talk by Oleg D. Sherby at 109th Annual AIME meeting, Las Vegas, Nevada, February 26, 1980.
23. "Warm Temperature Mechanical Properties of Superplastic Ultrahigh Carbon (UHC) Steel - Mild Steel Laminated Composites", talk by B. C. Snyder at 109th Annual Meeting of AIME, Las Vegas, Nevada, February 26, 1980.
24. "Impact Characteristics and Cleavage Delaminations in Warm-Rolled 1020 Steel", talk by D. L. Bourell at 109th Annual meeting of AIME, Las Vegas, Nevada, February 27, 1980.
25. "Recent Advances in Superplastic Forming", talk presented at Bendix Corporation Advanced Technology Center, Southfield, Michigan, March 10, 1980.

26. "Superplasticity - Principles and Prerequisites", talk presented at National Bureau of Standards, Gaithersburg, Maryland, March 28, 1980.
27. "Ultrahigh Carbon Steels and Their Use in Automotive Applications", talk given at Department of Transportation Workshop, Boston, Massachusetts, June 5, 1980.

52. ULTRA-SHORT OPTICAL PULSE GENERATION AND APPLICATIONS

A.E. Siegman, Professor, Electrical Engineering

Research Assistants:

J-M. Heritier

P.M. Fauchet

Agency Support:

AFOSR 80-0145

NASA NGL-05-020-103

NASA NSG-7619

Technical Objectives:

To generate the shortest possible picosecond light pulses on a continuous wave and tunable basis; and to use these pulses in making significant physical measurements on materials, particularly materials of biochemical and biophysical interest.

Research Report:

Our group has developed and used the Picosecond Transient Grating (PTG) method to measure physical phenomena with a subnanosecond or picosecond time resolution [1,2]. Accurate measurement of the photoexcitation decay in a stroboscopic fashion, coupled with an accurate and variable spatial scale at the micron level, gives readily a measure of the diffusion-like processes.

As a short-term project, we are now studying $\text{NdP}_5\text{O}_{14}$ (Neodymium Pentaphosphate) which has been used as a low threshold lasing material and could potentially be used for the fabrication of interesting optical devices.

Our next goal is to study significant physical parameters in solar cell materials. Diffusion constant, surface recombination velocity and minority carrier lifetime are three important factors for the determination of a solar cell efficiency. Using the PTG technique, we intend to measure these parameters in Zn_3P_2 and InP, two semiconductors that

have recently been shown to be very attractive as solar cells [3,4].

Our apparatus uses a continuously pumped, repetitively Q-switched, actively mode-locked Ne:YAG laser which produces bursts of 20 to 30 mode-locked pulses with several hundred kilowatts peak power and durations of ~ 60 psec at repetition rates up to 500 Hz. An LiNbO_3 electro-optic switch has been constructed to gate out a single pulse in each train of mode-locked pulses comprising each Q-switched pulse. The fundamental IR radiation at 1.064 microns can be efficiently doubled to produce some green radiation at $5320\text{\AA}$ and we can excite and/or probe with either the green pulses or the IR pulses.

Reference Publications:

1. J.R. Salcedo, "The Picosecond Transient Grating Technique: Studies on Energy Transport and Photoacoustic Effects," Ph.D. Dissertation, Department of Electrical Engineering, Stanford University, Stanford, California 94305, April 1979.
2. J. Salcedo, A.E. Siegman, D. Dlott and M.D. Fayer, "Energy Transport in Molecular Crystals: The Picosecond Transient Grating Method," Phys. Rev. Lett. 41, 131 (1978).
3. E.A. Fagen, "Optical Properties of Zn_3P_2 ," J. Appl. Phys. 50, 6505 (1979).
4. J.J. Loferski, "Photovoltaics I: Solar-Cell Arrays," and "Photovoltaics IV: Advanced Materials," IEEE Spectrum, p.26-31 and p. 37-38 (February 1980).

53. MEASUREMENT OF ULTRAFAST PHENOMENA

A.E. Siegman, Professor, Electrical Engineering

Graduate Student:

F.P. Trebino

Agency Support:

N00014-75-C-0632

Technical Objectives:

To measure ultrashort lifetimes of atomic and molecular excited states.

Approach:

To employ a "tunable transient-grating" light scattering technique similar, in principle, to the transient-grating technique, but which does not require the use of ultrashort pulses.

Research Report:

In the past few years, our group has successfully measured ultrashort molecular lifetimes with a "transient grating" technique [1] in which two picosecond pulses from the same laser arrive at an experimental sample coincident in time, but from slightly different directions, producing a transient hologram pattern or grating of excited states. By measuring the diffracted intensity of a variable delay laser probe pulse (averaged over many pulses) as a function of the delay between excitation and probe pulses, one can measure the photo-excited state decay time with a resolution of approximately the laser pulsewidth. This method has been used successfully to measure relaxation times from 10^{-8} to 10^{-11} second, a resolution unobtainable using conventional optical detectors and measurement methods.

The tunable transient-grating technique [2] is similar in principle to the transient grating technique, but does not require the use of

ultrashort pulses and has potential time resolution approaching the femtosecond range. Two frequency-tunable Q-switched laser pulses are allowed to interfere in an experimental sample producing a moving grating of excited states. The diffracted intensity of a simultaneously incident probe pulse of appropriate wavelength is then measured as a function of the grating velocity or frequency difference between the two exciting laser beams. Break points in this curve determine the excited decay time.

We have constructed the necessary apparatus to demonstrate the tunable transient grating technique, which consists of three tunable dye lasers to produce the two excitation pulses and the probe pulse, and a Q-switched Nd:YAG laser whose output beam is frequency-doubled and split to pump the three dye lasers. We are at present preparing to demonstrate the technique on samples consisting of laser dyes - molecular systems known to have excited states with ultra short lifetimes. Once these initial experiments are completed, a computer-interfaced detection system will be constructed and other molecular systems, such as semiconductors, organic molecules, and saturable absorbers will be studied.

Reference Publications:

1. Donald W. Phillion, Dirk J. Kuizenga, and A.E. Siegman, "Subnanosecond Relaxation Time Measurements Using a Transient Induced Grating Method," Appl. Phys. Lett. 27, 85-87 (1975).
2. A.E. Siegman, "Proposed Picosecond Excited-State Measurements Method Using a Tunable-Laser-Induced Grating," Appl. Phys. Lett. 30, 21-23 (1977).

54. PICOSECOND RESONANT RAMAN SPECTROSCOPY OF THE VISUAL PIGMENT RHODOPSIN

A.E. Siegman, Professor, Electrical Engineering

J. Strer, Professor, Structural Biology

Graduate Students:

G. Hayward

W. Carlsen

Agency Support:

NIH EYO 2387-01

Technical Objectives:

To elucidate the conformational dynamics of visual pigments by resonance Raman spectroscopy. Our goal is to understand how visual pigments tune the color of their retinal chromophore, enhance and channel their photochemistry, and convert the energy of light into molecular motion.

Research Report:

Light driven changes in chemical or crystalline structure are receiving widespread attention in pure and applied research. The common goals include understanding and improving the selectivity, sensitivity, and yield of photochemical processes. Vision in nature is an example of a highly evolved and optimized system with a photochemical basis. We have extended the techniques of resonance Raman spectroscopy to the picosecond domain to study the dynamics of the principle photo receptor of vision, the molecule rhodopsin.

We showed that the first large scale effect of photon absorption by rhodopsin is a cis to trans isomerization of the retinal chromophore within the rhodopsin complex. (Fig. 1). This isomerization is reversible and occurs in less than 10psec with high efficiency. This isomerization speed is surprising for a large molecule imbedded within a much larger protein. We are now studying the role played by the protein in directing and enhancing this photoisomerization process.

A picosecond dye laser with an adjustable mirror gap of 20 to 300 microns was developed as a part of the preceding work. This unusual laser can lase following a single laser pump pulse of picosecond duration. Construction and analysis of several stable and unstable resonator designs showed that the design may be enhanced to provide a large improvement in the spectral and modal output of these devices. A version designed as a probe laser for resonance Raman spectroscopy now operates stably in just two axial modes following a 30 psec pump pulse. Work is underway to ensure single axial mode operation and frequency stabilization.

The resonator analysis performed for these lasers is applicable to a broad range of dye and semiconductor lasers operating in the picosecond time domain.

Reference Publications:

Gary Hayward, William Carlsen, Anthony Siegman and Lubert Stryer, "Picosecond Resonance Raman Spectra of Visual Pigments," submitted to Nature, May 1980.

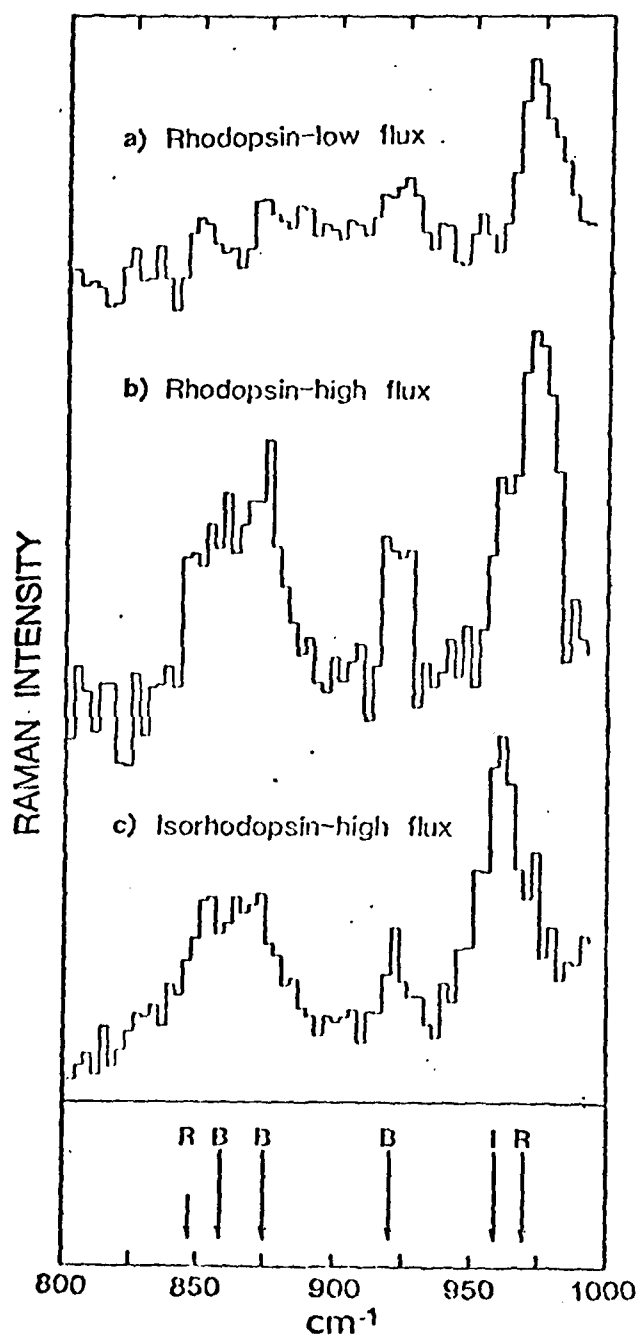


Fig. 1 - Resonance Raman spectra of flowing samples of rhodopsin and isorhodopsin photolysed and simultaneously probed by low-energy, 30 psec, 532 nm pulses. The arrows indicated positions of known Raman lines characteristic of rhodopsin, isorhodopsin, and strained all-trans bathorhodopsin

55. STUDIES OF SURFACES AND INTERFACES IN SILICON USING TEM AND AES

R. Sinclair, Associate Professor, Materials Science and Engineering
C. R. Helms, Adjunct Professor, Electrical Engineering

Graduate Students:

J. C. Bravman
R. Barton

Agency Support:

NSF/MRL through CMR

Technical Objective:

To determine the structure and segregation effects at interfaces in silicon based materials.

Approach:

Use of Auger Electron Spectroscopy (chemical distribution) and Transmission Electron Microscopy (structure) to provide complementary information about silicon interfaces.

Research Report:

1. Auger Electron Spectroscopy

Recent work [1,2] has shown that significant amounts of phosphorus segregates near the Si-SiO₂ interface upon oxidation of phosphorus-doped silicon. The distribution is independent of oxidation kinetics [1]. Figure 1 shows a typical phosphorus profile determined by AES. Upper and lower limits may be given to the degree (m) and extent (δ) of the segregation, which are compiled in table 1, and to a "heat of segregation" (Q) to the interface derived from $m = \exp(Q/kT)$ [3]. However these results do not show whether phosphorus is uniformly distributed or, as recently indicated, it is present as precipitated islands approximately 10 μ dia. [4]. This is important in modelling the segregation mechanism, and it is hoped that TEM will clarify the situation.

2. Transmission Electron Microscopy

Much of our initial efforts, during the first six months of the program, have gone into specimen preparation. The optimum configura-

tion for new data and for comparison with AES results is to arrange the interface to be parallel to the investigating electron beam, and thus parallel to the thin direction of the sample. This is quite difficult to achieve, but when realized opens up the possibility of examination close to the atomic level, as recent work by Krivanek et.al. [5] on the MOS Si-SiO₂ interface has shown.

The following procedure has been adopted. Two small strips of <100> silicon are cemented together, with the oxide layers (~1000 Å thick) facing each other. The joined strips, approximately 1.5 x .5mm, are then embedded in bakelite; this is ground thin, and polished, making the 110 direction the plane normal for convenience of the microscopy. From this, the standard 3mm discs are cut, with the two silicon pieces at the center. The specimen is thinned mechanically, until a thickness of approximately 100μ. Using a rotary grinding machine designed and built for this process, the center 1mm of the disk is then further thinned to about 75μ. Finally, the specimen is ion-beam milled, until perforation, when hopefully there is a region suitable for transmission experiments.

To date, the thinned region produced this way has not been coincident with the Si-SiO₂ interface. Structure images at 3Å resolution have been taken, however, of the perfect crystal silicon.

3. Future Work

The progress of the AES experiments is well-in-hand. Of critical importance is the perfection of the TEM specimen preparation. Once this is achieved it is planned to obtain structural information directly from conventional and high resolution TEM images, chemical information from scanning TEM energy dispersive analysis and energy loss spectroscopy (when our new spectrometer becomes available) and localized lattice parameter variations from convergent beam electron diffraction. Correlation of AES and TEM will then be carried out. A related set of experiments on dopant grain-boundary segregation in polycrystalline silicon, for which the specimen preparation is more straightforward, is also planned.

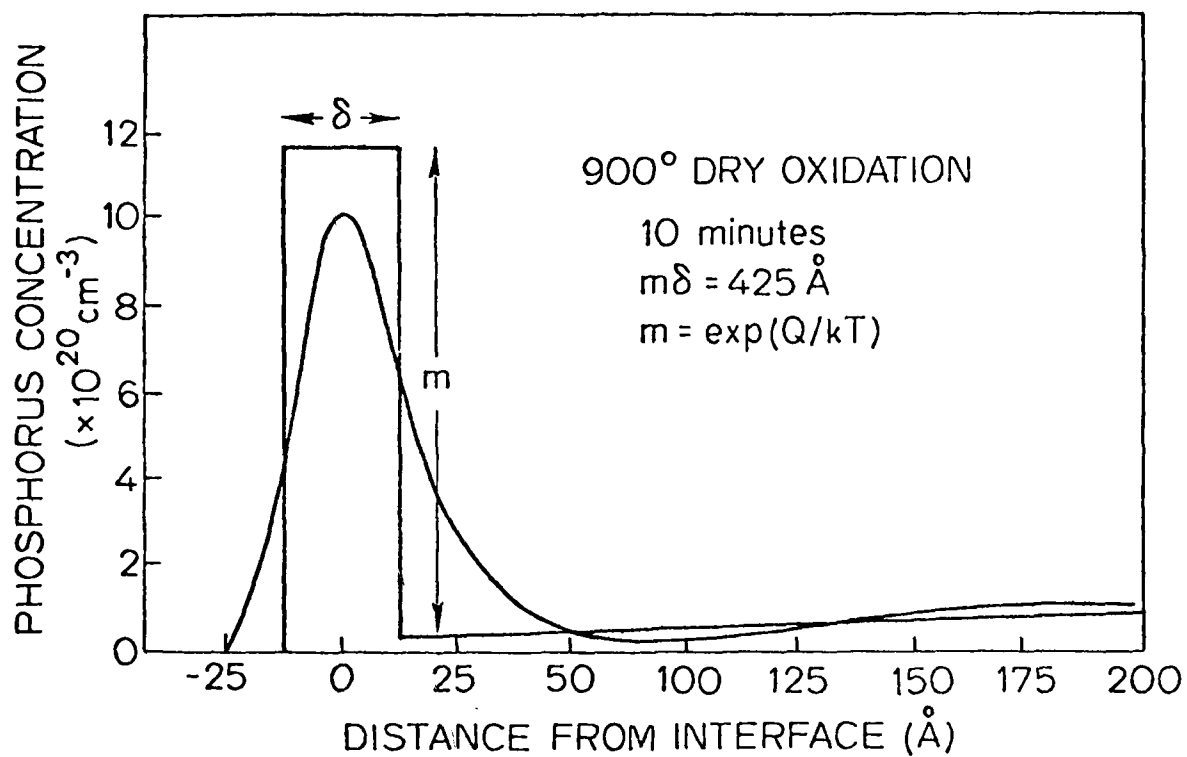


Figure 1

Table 1

	Peak/Bulk Ratio m	Pileup Width δ ($\text{\AA}$)	Heat of Segregation Q (eV)
Minimum value	9	47	0.22
Maximum value	170	2.5	0.52

56. HIGH RESOLUTION ELECTRON MICROSCOPY OF PHASE TRANSFORMATIONS

R. Sinclair, Associate Professor, Materials Science and Engineering

Graduate Students:

G.M. Michal

Agency Support:

NSF/MRL through CMR

NSF through University of California, Berkeley

Technical Objective:

To understand the fundamental atomic mechanisms of solid state phase transformations.

Approach:

To study the initial stages of transformation reactions by high resolution transmission electron microscopy techniques, particularly direct lattice imaging.

Research Report:

The structures and transformation behavior responsible for the memory and superelastic effects in TiNi have been a source of speculation and confusion since the alloy's inception in the early 1960s. The present study has employed various techniques of high resolution transmission electron microscopy to obtain a more thorough characterization of the premartensitic and martensitic transformations in TiNi than previously obtainable. Using a Philips EM400 equipped with a LaB₆ filament more detailed aspects of the structure have been obtained through structure and high resolution dark field imaging, in situ heating and cooling experiments and 2¹/₂D microscopy, due to the superior vacuum and image brightness of this system.

The technique of 2¹/₂D electron microscopy has been shown to have a much greater potential than previously thought in determining the orientation changes or difference in lattice plane spacings in crystalline solids. A theoretical model and experimental evidence are presented to determine the limit of how closely-spaced diffraction vec-

tors may be and still be correlated with their microstructural features. The present treatment indicates that the depth of field in an electron microscope, under conditions of diffraction contrast and a very low beam divergence, is much greater than commonly believed. The results indicate that diffraction spot separations of 0.5nm^{-1} can be measured and unambiguously correlated with features in the dark field stereo pair while maintaining an image resolution of 1nm . If the resolution required is reduced to 10nm , separations of less than 0.05nm^{-1} are feasible to study.

An atomistic mechanism has been proposed for the martensitic transformation which takes into account the premartensitic lattice displacement waves and the differing sizes of the Ti and Ni atoms. The resulting monoclinic martensite structure is able to reconcile both the available powder X-ray diffraction and single crystal SAD data observed in many different laboratories while maintaining a set of atomic bond lengths commensurate with those observed in other structures in the Ti-Ni system.

Starting from the high temperature phase which has a B2(CsCl) structure, with both $[111]_{\text{B2}}$ and $[110]_{\text{B2}}$ orientations, thin foils have been slowly temperature-cycled in situ from below the completion of the martensitic transformation to above the completion of the reverse transformation back to the B2 structure. The forward and reverse reaction start and finish temperatures along with the corresponding hysteresis behavior are in close agreement with the bulk material values when observed in the thicker sections of the foil. The diffraction patterns obtained from the martensitic structure starting from both orientations of the B2 structure are also very similar to previous patterns taken with a precession X-ray camera on bulk single crystals of the B2 structure cooled to form martensite. The martensite/B2 transformation is observed to be athermal occurring as a burst after an interval of cooling or heating between the reaction start and finish temperatures. The martensite forms predominantly by the mutual advance of two variants in a well-defined orientation as a self-

accommodating pair. These pairs of variants are the same as ones found in specimens that are completely martensitic before thinning. However, the morphology of the variants formed in situ in the microscope is much finer, and boundaries between groups of variants are less straight, than in samples thinned from the bulk.

A set of five Laue zone patterns from a single B2 structure grain extending from $[100]_{B2}$ through $[111]_{B2}$ to $[110]_{B2}$ has been obtained, containing a more complete set of diffuse premartensitic diffraction spots than previously reported. These premartensitic spots are rationalized in terms of displacement waves. The morphology of this premartensitic effect has been determined by careful dark field imaging from a premartensitic spot. A quasi-random morphology is observed with a domain size between 160 and 500 Å. This is compared with the 15 to 100 Å domain size contrast apparent in dark field images from a B2 (austenite) reflection.

Typical microstructure images have been obtained from TiNi martensite cold rolled 10%, 20% and 30%. At 30% cold work the microstructure has been radically altered. The normally smooth, continuous martensite and prior austenite boundaries are ill-defined due to dislocation pile-ups. The observed boundary dislocations are speculated to provide the back stresses needed for the superelastic behavior observed in prestrained material.

Publications:

1. "Modulated Substitutional-Interstitial Solute-Atom Clustering in Nitrided Austenitic Fe-34 Ni-V Alloys," J. H. Driver, R. Sinclair and K. H. Jack, Proc. Roy. Soc. Lond. A367, 99-115 (1979).
2. "In situ Observations of Diffusionless Transformations in NiTi," G. M. Michal and R. Sinclair, ICOMAT 79, (1979) pp. 136-141.
3. "Origin of Stacking Faults in NiTi Martensite," R. Sinclair, Modulated Structures 1979, edited by J. M. Cowley, J. B. Cohen, M. B. Salamon and B. J. Wuensch, AIP Proc. #53 (1979) pp. 269-271.
4. "Lattice Fringe Imaging of Alloys," R. Sinclair, Proc. 37th Annual Conference EMSA, edited by G. W. Bailey (1979) pp. 404-407.

5. "Comments on 'The Early Stages of the Transformation in Dilute Alloys of Titanium in Nickel'," D. E. Laughlin, R. Sinclair and L. E. Tanner, *Scripta Met.*, 14, 373-376 (1980).
6. "A Quantitative Assessment of the Capabilities of 2¹/₂D Microscopy for Analyzing Crystalline Solids," G. M. Michal and R. Sinclair, *Phil. Mag.*, in press (1980).
7. "Metallurgical Applications of the 2¹/₂D TEM Technique," R. Sinclair, G. M. Michal and T. Yamashita, submitted for publication.
8. "Physical Properties of Ion-Implanted SEM-Annealed Silicon," J. L. Regolini, N. M. Johnson, R. Sinclair, T. W. Sigmon and J. F. Gibbons, Laser and Electron Beam Processing of Materials, edited by C. W. White and P. S. Peercey, Academic (New York), in press (1980).
9. "High Resolution Imaging of Cadmium Telluride," R. Sinclair, F. Ponce, T. Yamashita and P. Pirouz, *Proc. 7th European Congress on Electron Microscopy*, in press (1980).
10. "Structure Imaging of Defects in Cadmium Telluride," F. Ponce, T. Yamashita and R. Sinclair, *Proc. 38th Annual Conference EMSA* (1980) in press.
11. "A Transmission Electron Microscopical Investigation of Phase Transformations in TiNi," P. Moine, G. M. Michal and R. Sinclair, *ibid*, in press.
12. "Defect Structure of Deformed WC," M. K. Hibbs and R. Sinclair, *ibid*, in press.
13. "Analytical Electron Microscopy of Ferroelectric BaTiO₃," M. L. Mecartney and R. Sinclair, *ibid*, in press.
14. "Microstructural and Chemical Analyses of BaTiO₃ Dielectrics," M. L. Mecartney, R. Sinclair and G. J. Ewell, submitted for publication.
15. "Combined High Resolution and Analytical TEM Studies of Phase-Separated Alloys," C. K. Wu, A. F. Marshall, G. Thomas and R. Sinclair, *Proc. 38th Annual Conference EMSA* (1980) in press.

57. SURFACE, INTERFACE, AND ELECTRONIC STUDIES GROUP

W. E. Spicer, Professor, Electrical Engineering, Materials Science,
Stanford W. Ascherman Professor of Electrical Engineering
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Synchrotron Radiation Laboratory
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P. J. Jupiter	W. G. Petro**	R. O. Tatchyn
A. Landauer	J. W. Rouse	M. Taubenblatt
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D. T. Ling*	M. L. Shek	D. L. Weissman-Wenocur
J. Manni**	J. Silberman	

* Received Ph.D. during report period.

**Received MS during report period.

Agency Support:

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ONR N00014-75-C-0289	(Thrust Program on Alloy
ARPA MDA 903-79-C-0257	Catalytic Materials)
(Joint Project with IC Lab)	
IBM PO No. BK584372Z	NSF DMR 77-27489

Technical Objective:

To utilize and develop tools of electron spectroscopy and Auger sputter profiling to study the properties of surfaces and interfaces. Emphasis is placed on a balanced program for both metals and semiconductors in order to provide the students with a broad insight into current research activities in the field.

Approach:

Use capabilities of conventional laboratory sources and the Stanford Synchrotron Radiation Laboratory (SSRL) to obtain experimental results and to interpret these.

This group strongly, together with students, moves freely from one subgrouping to another. The faculty has strong links with other departments and laboratories at Stanford: the Departments of Electrical Engineering, Applied Physics, Materials Science and Engineering, and Chemical Engineering; the Stanford Electronics Laboratories; the Integrated Circuits Laboratory, the Stanford Synchrotron Radiation Laboratory, and the Joint Stanford-NASA Ames Institute for Surface and Microstructure Studies. The students come from Electrical Engineering, Applied Physics, Materials Science and Engineering, and Physics. They have undergraduate backgrounds in chemistry and chemical engineering as well as the departments listed above. The work is structured to maximize the interaction between different disciplines. This is an outgrowth of the interdisciplinary concept which characterizes CMR.

For convenience, this report will be broken into four parts. However, these divisions are for the convenience of the reader and do not represent strong segmentation within the group. The faculty most directly concerned will be listed before each section; however, it should be recognized that each faculty has interactions with all projects.

Research Report:

- (1) Studies of Semiconductor Surfaces and Interfaces in which Photoemission is a Principal Tool

Professors: W. Spicer and I. Lindau

- (A) A Unified Model for the Formation of Schottky Barriers (SB) and 3-5 Oxide Interface States

Making use of the data accumulated by this group at Stanford over the last six years, a unified model has been developed to explain the phenomena described in the title. Native defects are found to be produced by the added metal (SB) or oxide (interface states) [1-4]. These states pin the Fermi level, producing the Schottky-barrier pinning

(height). Detailed defect energy-level assignments have been worked out and can be found in the literature [2,3,4]. Good correlations are found with device characteristics [1-4].

This work was supported by ARPA and ONR.

Reference Publications:

1. W. E. Spicer
2. W. E. Spicer, P. W. Chye, P. R. Skeath, and I. Lindau, Inst. of Physics Phys. Conf., Ser. No. 50, Bristol, 1979, p. 216.
3. W. E. Spicer, I. Lindau, P. R. Skeath, C. Y. Su, and P. W. Chye, Phys. Rev. Lett. 44, 420 (1980).
4. W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, JVST, Sep-Oct 1980 Issue, in press.

(B) The Chemical Nature of the Cs-O Overlayer on GaAs (110) and Its Relation to NEA Photocathodes and to MOS Devices

Graduate Student: C. Y. Su

Photocathodes made of GaAs with its surface activated by coadsorption of Cs and oxygen is the single most-important element in the third generation low-light level photoelectron image intensifier technology. The same structure has also found extensive use as a source for spin-polarized electrons, which has important bearing on several areas of scientific research. However, to date, no fundamental understanding of either the chemical or the electronic nature of the Cs-O adlayer has been obtained. Several models based on yield measurement alone have been proposed. All these models assumed cesium oxides of simple composition covering an inert GaAs substrate. The cesium-oxygen system is known to exhibit a very complex phase diagram. Our earlier photoemission studies [1] of the cesium-oxygen system indeed revealed the complexity of the reaction of oxygen with cesium. Those results questioned the assumption of simple-composition cesium oxides. More importantly, we have found striking evidence for the interaction of the Cs-O adlayer with the GaAs substrate [2,3]: on a GaAs (110) surface covered with a monolayer of Cs, oxygen is found to bond to Ga and As with a rate 10^6 to 10^9 higher than

that of a good clean GaAs (110) surface. Such findings have led us to attempt an atom-by-atom understanding of this system. Such understanding will not only provide fundamental knowledge for the GaAs photocathode, which is currently moving into production, but will also contribute to the future development of other narrow band-gap (<1.2 eV) 3-5 semiconductor-based photocathodes. In addition, information on GaAs-oxygen interface reactions is important for MOS devices.

During this reporting period, two classes of investigations have been carried out: (1) Photoelectron spectroscopic measurements of oxygen adsorption on thick Cs films (condensed at 150°K) with high photon energy to include both core levels and valence-band region. This study not only facilitates better understanding of the interaction of Cs and oxygen but also provides important clues to the understanding of the very complex photoelectron spectra we have to deal with in the Cs-O-GaAs system and provides insight into the MOS interface. (2) Photoelectron spectroscopic measurements of activated GaAs (110) surfaces with results correlated to their white light sensitivity (expressed as microampere/lumen). This class of experiments allows direct determination of the nature of the Cs-O overlayer that gives the negative electron affinity (NEA) condition.

In the studies of oxygen adsorption on thick Cs films (condensed at 150°K), we found a shift of Cs core levels to lower binding energy with increasing coverage. A similar shift has also been found in our earlier studies of oxygen adsorption on monolayer Cs-covered GaAs (110) surfaces [2,3]. The O-2p emission in the thick Cs film studies revealed two distinct oxygen states. One state gives a peak with binding energy 2.7 eV (referred to the Fermi level), and the other gives two peaks with binding energies of 4.5 eV (strong) and 8.4 eV (weak). The first state appears at lower oxygen exposure and is interpreted as being due to O^- ions in formation of suboxides (e.g., $Cs_{11}O_3$, Cs_7O , and Cs_2O) after comparing with the combined structural and photoemission studies of Ref. 4. The second state appears at higher exposure and may be related to nondissociative O_2^{-2}/O_2^- ions in the formation of peroxide or higher oxides (Cs_2O_2 , CsO_2 , etc., referred to below as oxides in order to distinguish them from suboxides). In photoemission spectra obtained from adsorbing oxygen on Cs-covered GaAs (110) surfaces, no emission can be found at any oxygen

coverage in the energy region expected for the O-2p level of suboxides. The existence of cesium oxides in that case, however, is evidenced by the weak peak at 8.1 eV binding energy (referred to as valence-band maximum), which is absent in the spectra of oxygen on bare GaAs (110). The strong peak expected for cesium oxides, however, overlaps in energy with the O-2p level of oxygen bonded to GaAs. The failure to form cesium suboxides on GaAs surfaces can be understood as follows. Oxygen atoms formed from dissociation of molecular oxygen are readily bonded to Ga and/or As because more stable bonds can be formed between oxygen and Ga than that between a two-dimensional Cs layer and oxygen. However, no stable compounds can be formed between nondissociative oxygen species and Ga and/or As, while molecular oxygen can easily be incorporated into the Cs layer with a local $\text{Cs}^+-\text{O}_2^{-2}$ (or O_2^-) coordination close to that found in peroxide or higher oxides.

For GaAs surfaces subjected to cycles of (Cs,O) treatments, photoemission spectra have revealed that, in order to achieve and maintain stable activation (white light sensitivity $>350 \mu\text{A}/\ell$), the appearance of a small peak at 2.7 eV BE is necessary. However, this peak can never appear by itself; it always accompanies a much stronger peak at 4.5 eV BE. The appearance of the 2.7 eV peak is thus interpreted as the presence of O^- ions at the very top of the Cs-O adlayer which is separated from the GaAs surface by approximately $10 - 20 \text{ \AA}$.

From the above results, a simple scenario can be summed as follows.

- (1) O^- ion-containing cesium compounds are unstable in contact with GaAs surfaces. A buffer layer of cesium oxides and/or (GaAs)-oxides is necessary for their presence in the system.
- (2) The interface between GaAs and (Cs,O) adlayers is more appropriately described as a "heterojunction" between GaAs and amorphous cesium oxides containing varying concentration of O_2^{-2} ions; the transport of photoelectrons out from GaAs is controlled by the barrier set by this heterojunction.
- (3) The final escape of electrons into vacuum is controlled by a layer of O^- ion-containing Cs-O compound. Because an O^- ion can be oriented more effectively to produce a stronger

dipole, a lower work function of the composite surface and hence a higher yield can be achieved by such a layer than by a thick layer of O_2^{2-} -containing cesium oxides.

This work was supported by DARPA and ONR.

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2. W. E. Spicer, I. Lindau, C. Y. Su, P. W. Chye, and P. Pianetta, Appl. Phys. Lett. 33, 934 (1978).
3. C. Y. Su et al, to be written.
4. A. Simon, in Structure and Bonding, Vol. 36, Springer-Verlag,

(C) Column 3 and 5 Elements on GaAs (110): Bonding and Adatom-Adatom Interaction

Graduate Students: Perry Skeath and C. Y. Su

Column 5 elements adsorbed on GaAs (110) exhibit strikingly different behavior than adsorbed column 3 elements in terms of the overlayers bonding to the semiconductor, effect on the semiconductor surface lattice, and long-range order. A strong interaction between adatoms is found with submonolayer coverings of column 3 metals which leads to the formation of flat raftlike metallic patches. Unlike the column 3 metals, Sb adsorption produces large changes in the electronic states and atomic arrangement of the semiconductor surface lattice. An elementary view of the factors responsible for the different characteristics and effects of these overlayers on GaAs (110) is given, but its extension to other adatoms is shown to be limited.

These results have strong relevance to current theoretical models of Al and Ga overlayers on GaAs (110), as well as to molecular beam epitaxy and Schottky-barrier formation.

This work was supported by DARPA and ONR.

(D) Photoemission Investigation of the Temperature Effect on Si-Au Interfaces

Italian Associates: Dr. I. Abbati, Prof. L. Braicovich, and A. Franciosi

Graduate Students: P. R. Skeath and C. Y. Su

We report extensive photoemission measurements carried out with synchrotron radiation and with conventional light sources on Si (111)-Au interfaces. The coverage dependence has been studied in detail at room temperature (RT) with synchrotron radiation. We have found considerable intermixing at all coverages, and the photoemission spectrum characteristic for pure gold was not even observed at coverages of about 150 monolayers. A deeper insight into the intermixing mechanism is obtained from the temperature dependence of the spectra, which was studied for surfaces covered with ten monolayers. Considerable intermixing is observed for interfaces prepared and measured at liquid nitrogen temperatures (LNT). Several hours of annealing at RT are required for an interface prepared at LNT to obtain the equilibrium situation reached immediately after preparation at RT. These results indicate that the thermal energy of the sample is not the only energy responsible for intermixing during interface preparation. We propose that an important contribution comes from the condensation energy of gold. The photoemission spectra show that the intermixing increases with the temperature up to $\approx 350^\circ\text{C}$. At temperatures higher than $\approx 400^\circ\text{C}$, there are no changes in the interface photoemission spectra. The amount of intermixing at temperatures less than 400°C is much higher than that expected from bulk diffusion data and must be attributed to a chemical gradient effect.

(E) Si-Pd and Si-Pt Interfaces

Italian Associates: B. De Michelis, Dr. I. Abbati, and Prof. L. Braicovich

Graduate Students: J. N. Miller and S. A. Schwarz

Photoemission (PS) and Auger-electron spectroscopy were used to study the formation of Pd silicide in UHV on Si single crystals. The Pd depositions ranged from submonolayer coverages to hundreds of angstroms

thickness. AES sputter-depth profiles indicate that room temperature Pd-Si interdiffusion occurs over ~100 Å and that Pd reduces the native Si oxides, with oxygen appearing at the vacuum surface of the evaporated layer. We have been able to separate out the relative contributions of Si and Pd to the silicide valence band by using a wide range of photon energies in the PS studies. The Pd d-bands in the silicide are filled and, due to the strong Pd-Si interaction, are pulled down more than 2 eV relative to Pd metal. In addition, we suggest that the silicide formed at the surface may be more closely related to that of the glassy metals rather than the well-defined (although closely related) Pd₂Si compound. Similar results are also obtained for the system of Pt on Si.

(F) Systematics on the Electron States of Silicon d-Metal Interfaces

Italian Associates: Prof. L. Braicovich and Dr. I. Abbati

Graduate Students: J. N. Miller, S. Schwarz, and P. R. Skeath

We discuss the trends in photoemission spectra from some silicon d-metal interfaces: Si (111)-Au, Si (111)-Ag, Si (111)-Ni, Si (111)-Pd, Si (111)-Pt. In particular, we discuss the correlation between the chemical processes taking place at the interface and those in the formation of bulk silicon d-metal compounds. Although a general correlation is found, some important differences are seen; in particular, no evidence of the formation of strictly stoichiometric silicides in the interface is found even for the cases in which well-defined bulk silicides are known to be stable. We discuss also the role of the hybridization between d-electrons of the metal and (sp) electrons of silicon in the formation of intermixed interface phases. The considerations presented here can be useful as guidelines to interpret future results on other reactive silicon d-metal interfaces. (This is an abstract of a manuscript accepted in the JVST Sep/Oct Issue as part of the PCSI-7 Proceedings.)

(G) The Electronic Structure of the Diamond (111) 1×1 Surface: Valence-Band Structure, Band Bending, and Band-Gap States

Japanese Visitor: Prof. T. Ohta, Photon Factory

Graduate Student: B. B. Pate

Photoemission, LEED, and AES measurements were made on the mechanically polished (111) surface of a type IIa diamond. No emission from filled states in the fundamental gap was found over the photon energy range $13.3 \text{ eV} < \omega < 200 \text{ eV}$. This result, coupled with the sharp 1×1 LEED patterns which were obtained and the relative cleanliness (of elements which can be detected by AES) of the diamond (≤ 1 at.% oxygen, < 0.5 at.% Si) suggests hydrogen termination of the lattice. Photoelectric yield measurements demonstrate the photoelectric threshold to be at band-gap energy radiation. Investigation of the photoemission electron distribution curves (EDCs) show that, while the electron affinity at the surface is always positive, band bending is sufficient to result in an effective negative electron affinity under certain conditions. A variable surface dipole on the atomic scale, possibly due to the adsorption-desorption of a background gas, is reported. A study of the relative cross section of the upper (p-like) versus the lower (s-like) portion of the diamond valence band indicates comparable cross sections at a photon energy $\omega = 160 \text{ eV}$.

This work was supported by the Army Research Office.

(H) Interactions of Oxygen and Arsenic with GaAs (110)

Japanese Visitor: I. Hino

Graduate Student: W. G. Petro

During the past year, we have constructed and begun experimental work with an ultrahigh vacuum chamber and transfer mechanism for the treatment of single-crystal samples with As and other volatile gases which are incompatible with the main measurement chamber. This allows a sample to be prepared (by cleaving, for example) in the main chamber, transferred without breaking vacuum into the treatment chamber (which is then sealed off), and treated and returned to the main chamber where a wide variety of measurements (UPS, AES, LEED, etc.) can be performed.

Initial experiments with the chamber have been performed using a GaAs single crystal with an elemental As source and have demonstrated the feasibility of preparing As overlayers on GaAs. Work is presently under way to improve the cleanliness and controllability of the source. Photoemission measurements will then be made to determine the effect of

the As overlayer on core-level and valence-band spectra of the GaAs (110) surface.

Further experiments combining a high-power laser with the treatment chamber are also planned. The effect of laser radiation on the surface oxide of GaAs has already been investigated and it has been found that, above a threshold laser power density, the oxide layer is removed without seriously disturbing the relative concentration of Ga and As. Utilizing the treatment chamber, we will be able to perform similar experiments in an As-rich atmosphere and to investigate the possibility of laser annealing of GaAs.

(2) Studies of the Surfaces of Metallic Alloys with Practical Emphasis on Relationship to Catalysis

Professors: I. Lindau and W. E. Spicer

(A) The Electronic Structure of Pd-Au Alloys and the Water Reaction on Pd and Pd-Au

Graduate Students: D. L. Weissman-Wenocur, M. L. Shek, P. M. Stefan, and B. B. Pate

The study of single-crystal Pd and Pd-Au alloy surfaces was motivated by results obtained by Professor Boudart's group in the Chemical Engineering Department at Stanford. They found that, under atmospheric pressure conditions, the catalytic activity of the Pd for the reaction $2H_2 + O_2 \rightarrow 2H_2O$ increased by a factor of ~40 upon alloying the Pd with Au. Possible explanations were put forward, including the possibility that the addition of Au had a long-range (ligand) effect on the binding energy of oxygen atoms to Pd atoms. Another possible explanation was that, since oxygen does not adsorb on Au, the addition of Au to the Pd left spaces where hydrogen could adsorb in a mobile precursor state, giving it a higher probability of encountering an adsorbed oxygen atom.

Therefore, a major focus was first to examine the binding of oxygen to single-crystal Pd (111), as described in last year's CMR report. In the past year, we have "created" a Pd-Au alloy crystal in situ by evaporating Au on a pure Pd crystal and then heating the sample until the Au diffused into the bulk regions. (One attempt to buy a suitable Pd-Au single crystal was unsuccessful.) Using the synchrotron radiation

from the Stanford Synchrotron Radiation Laboratory (SSRL), we were able to use ultraviolet photoemission spectroscopy (UPS) to study the electronic structure during different stages of alloy formation, from sub-monolayer gold overlayers to small amounts of Au diffused in Pd to a thick layer of Pd-Au alloy which is stable up to temperatures of $\sim 800^\circ\text{C}$. We were able to tune the photon energy to the "Cooper minimum" of the photoionization cross section of the Pd 3d electrons (which occurs at $h\nu \approx 120$ eV) so as to enhance the structure of the Au 5d electrons.

The purpose of studying submonolayer evaporations and diffusions of Au was to determine the effect of alloying on the electronic structure of the Au, specifically on the Au 5d splitting and relative position. This would reflect the effect of Au-Au interaction as well as the number of Pd vs Au nearest neighbors on the Au d-bands. Evaporations were done of 0.1 monolayer, 0.3, 0.6, 1, and multimonolayers of Au. In each of these cases, before Au was diffused into the Pd, the Au 5d splitting at $h\nu = 120$ eV was $2.2 \text{ eV} \pm 0.1 \text{ eV}$. This compares to a splitting of 1.5 eV for atomic Au and 2.4 eV for a thick polycrystalline evaporated Au layer at $h\nu = 21.2$ eV. The fact that the splitting was the same for 0.1 monolayer as for 1 monolayer suggests that the Au-Pd interaction is the dominant one in determining the 5d splitting; a change in the number of Au nearest neighbors seemed to have no appreciable effect. The monotonic decrease of the Au d-band width indicated that the Au was not forming three-dimensional clumps or rafts.

When the sample was heated so that the Au diffused into the bulk, it was found that the Au 5d splitting decreased by 0.4 eV in every case; the 5d peak with larger binding energy shifted to 0.4 eV lower binding energy, and the other peak remained stationary. Again, this effect was essentially the same for each of the Au evaporations. Since nearly every Au atom would have only Pd nearest neighbors after diffusion, this result leads us to the conclusion that the Au-Pd interaction determines the splitting in the alloy. The splitting in the alloy is ~ 0.3 eV larger for Au in Pd than for atomic Au.

A region of Pd-Au alloy stable to $\sim 800^\circ\text{C}$ was formed by evaporating ~ 20 monolayers of Au, then annealing at 800°C until the composition became stable. The composition was determined by Auger spectroscopy

and UPS to be 30 to 35% Au. The UPS characteristics of this stable alloy were quite similar to those for the smaller amounts of Au diffused in Pd; the 5d splitting was 1.7 eV.

The stable Pd-Au alloy was used to perform surface chemistry experiments, specifically the adsorption of oxygen and the formation of H_2O from oxygen and hydrogen. Similar experiments were done with pure Pd. These experiments were performed quite recently, so a detailed analysis has not yet been made. One result which is quite apparent, however, is that oxygen adsorption on Pd-Au requires at least a twofold Pd site. The sample with 30 to 35% Au showed no evidence in photoemission, either through changes in the Pd d-bands or by appearance of O2s levels, of oxygen adsorption at room temperature.

The crystal was subsequently annealed at 900°C until the Au concentration decreased to 20 to 25%. In this case, very small amounts of oxygen did adsorb, estimated by thermal desorption spectroscopy to be 0.05 to 0.1 monolayer at saturation coverage.

Further data analysis should tell us the relative binding energies of oxygen on this 20 to 25% Au-Pd alloy vs on pure Pd. Also, the relative reactivities of hydrogen with adsorbed oxygen on these two crystals will be determined. This information should help clarify the mechanism causing increased catalytic activity of Pd for the H_2O reaction at atmospheric pressures due to alloying with Au.

This work was supported by Stanford University Gift Funds.

(B) The Electronic Structure of PtCu Alloys

Graduate Students: M. L. Shek, P. M. Stefan, D. L. Weissman-Wenocur, and B. B. Pate

Ultraviolet photoemission experiments have been performed at the Stanford Synchrotron Radiation Laboratory to investigate the valence structures of PtCu alloys. It is hoped that a knowledge of the electronic interactions between the constituents of an alloy will have implications for two other problems. The first is the problem of surface segregation which has traditionally been confined to the realm of thermodynamics or statistical thermodynamics, with major attempts to understand the effects of different crystal faces. The second is the question of how the

reactivity of Pt may be modified by the formation of Pt-Cu bonds. Our work in the past year may represent a first step towards the goal of seeing the underlying principles and relationships between the electronic structures and the surface segregation phenomenon in binary alloys.

Our approach so far is to concentrate on the Cu 3d-derived "surface density of states" in the PtCu valence band and to attempt to correlate its variations with different possibilities of Pt-Cu nearest neighbor interactions. This choice is based on these considerations. First, it is feasible to observe the Cu 3d valence structures unambiguously by utilizing the Cooper minimum of Pt 5d orbitals at a photon energy of 150 eV. An additional experimental advantage is the surface sensitivity due to the short escape depth (2 to 3 atomic layers) of photoelectrons near this energy. Second, the framework of nearest neighbor interactions is predominant in many electronic theories and hence a logical starting point. A necessary extension of our present approach is to examine the concurrent changes in the Pt valence states (at other photon energies). The role of the Cu 4s orbital must also be considered.

We have studied the following Pt-Cu systems:

- (1) Cu overlayer evaporated on Pt (111), from submonolayer coverages up to about 10 monolayers
- (2) model PtCu (111) surfaces formed by interdiffusion between Cu and a Pt (111) substrate, from 7% to 60%-75% Cu near the surface
- (3) Pt-1.3 at.% (bulk composition) Cu (111) single-crystal surface
- (4) Pt-2.3 at.% Cu (110) (bulk composition) surface

Some of the main results may be outlined as follows. (1) Small submonolayers of Cu (less than half a monolayer) on Pt (111) give rise to a resonance-like feature with a peak maximum at -2.5 eV below the Fermi level and a width of 1.7 eV at half maximum. (2) Cu incorporated into Pt (111) leads to a 3d structure which is broad and skewed, with a peak maximum at -2.5 eV and a shoulder around -0.9 eV. For the lower Cu concentrations (less than 30 to 38%), a shoulder around -3.4 eV is also apparent. (3) The PtCu (111) alloy surface shows a Cu 3d structure which also

peaks at -2.5 eV, in agreement with the model PtCu (111) surfaces. A preliminary estimate of the Cu near-surface concentration, using Auger electron spectroscopy (AES), is 1.5 to 1.9%. (The escape depth for the Cu 920 eV Auger electron is 5 to 6 atomic layers.) (4) The PtCu (110) alloy surface shows a Cu 3d peak with the the maximum at -2.2 eV and a peak shape similar to that of small amounts of Cu on Pt (111). The near-surface concentration of Cu is 6 to 7.5%. Thus, there is a striking difference between the (111) and (110) surface segregations, and this difference correlates well with the differences in the Cu resonances. It is to be noted that, at other photon energies (say 130 eV), the peak energies may be somewhat different from the values given above. But, the same trend exists with regard to the peak shapes.

For lack of a precise knowledge of the surface atomic arrangements, an in-depth understanding of our photoemission results is not yet feasible. Nevertheless, crude pictures may be visualized from the known crystal structure (fcc) and known surface orientations. The changes between chemisorbed Cu and embedded Cu, for the (111) face, suggest that the Cu 3d states hybridize strongly with the Pt 5d states as the number of Pt nearest neighbors increases, from a maximum of 3 on the surface to 9 in the first atomic layer and 12 in the subsequent layers. For PtCu (110), in spite of surface reconstruction indicated by a (1×3) low-energy electron diffraction (LEED) pattern, it is very likely that the surface atomic coordination remains smaller than that of the close-packed PtCu (111) surface. The narrow width of the Cu 3d peak for PtCu (110), indicating a weak Pt-Cu bonding interaction, is consistent with this contention. However, we note that a simple-minded counting of nearest neighbors cannot provide an adequate description. We have only shown how the Cu valence structures may depend, in a qualitative manner, on both the surface atomic coordination and interatomic potential.

The relevance of the above considerations to the surface segregation problem may be seen from a comparison between the near-surface Cu concentrations of PtCu (111) and PtCu (110). As our preliminary studies have shown, surface segregation of Cu occurs on PtCu (110), but no Cu enrichment is found for PtCu (111). Further experimentation is required to confirm this result. However, it is plausible that segregation of Cu is favored by the smaller atomic coordination and the weaker Pt-Cu

interaction on the (110) face. Strong bond formation between the unlike atoms should oppose any tendency towards the segregation of one of the components and thus a reduction in the number of strong bonds. Work will be pursued to understand more of how surface segregation correlates with surface atomic coordination and bond strengths.

This work was supported by NSF (Joint U.S.-Brazil Program) and Stanford Gift Funds.

(3) Studies of Si/SiO₂ Si-Metal Interface Using Principally Sputter Auger and the Study of Si Dopants on the Surface of Si

Professor: C. R. Helms

(A) Auger-Sputter Profiling Study of Schottky Barriers on Si

Graduate Student: Peter W. Lew

The electrical properties of Schottky barriers are very sensitive to the impurity content, interface chemistry, and interface morphology. These interfacial properties of the metal-semiconductor junction are, in turn, determined by processing parameters. To understand the relationship between the electrical properties and the interfacial microstructure, high-resolution Auger sputter profiling (ASP) has been performed on Schottky-barrier and related structures.

Work has been concentrated on four samples prepared at IBM (East Fishkill) by sputter deposition onto chemically cleaned n-type (100) Si substrates. The details of the sample preparation are described elsewhere [1]. The four samples consist of layers of tantalum and tantalum oxide on Si: (1) Ta₂O₅/Ta_xO_y/Si, (2) Ta₂O₅/Si, (3) Ta/Ta_xO_y (thin)/Si, and (4) Ta/Si.

The major findings concerning these samples are listed below.

- (1) The measured interface widths of Ta/Si or Ta_xO_y/Si interfaces are 70 ± 20 Å. Some additional experimental broadening is present in these studies, making this value an upper limit.
- (2) "Clean" Ta/Si interfaces contain appreciable amounts of oxygen for the sputter-deposited Ta films.
- (3) All the nonstoichiometric Ta oxides investigated contain sizeable amounts of carbon (up to 10 at.%).

- (4) Oxygen from the Ta_xO_y layer is dissolved into the Ta layer when the Ta/Ta_xO_y (thin)/Si sample is annealed in vacuum at 450°C for 1 hr.

Preliminary Auger sputter profiles of electron-beam deposited Ta layers show the presence of C at the Ta-Si interface. About 1-1/2 times more C is present when photoresist is used. Future work will compare interfacial and electrical properties of the sputter-deposited and electron-beam deposited samples.

This work was supported by a contract from IBM.

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(B) Segregation of Dopants at Si/SiO₂ Interfaces

Graduate Student: Roger Barton

Auger sputter profiling has been used to study the segregation of dopants in silicon at the silicon-SiO₂ interface. Annealing experiments have shown that the high interface phosphorus concentrations typically found in Auger sputter profiles exist in equilibrium with the "structural properties" characteristic of the interface. This segregation effect is expected to become an important consideration in the design of very small-scale integrated circuits. We have optimized the electron and ion-beam conditions in our Auger spectrometer so as to quantify our determination of impurity profiles. We have also studied segregation at interfaces in silicon samples that were subjected to various oxidation times, temperatures, and bulk doping levels. We find that simple thermodynamic models appropriately account for this data.

This work was supported by DARPA.

(C) Studies of HCl/O₂-Grown SiO₂

Graduate Student: J. W. Rouse
(Fairchild work in conjunction with Dr. Bruce Deal)

Researchers have recently found that the inclusion of HCl in an oxidizing ambient produces SiO_2 layers with desirable properties. The reproducibility of oxide breakdown voltage is increased, and there is a reduction of mobile alkali ions. The behavior of chlorine in growing the oxide may also provide insight into the kinetics of the oxidizing species since both Cl and oxygen are believed to enter the oxide as negative ions. Further study of this system is clearly necessary.

Work related to these HCl/O_2 -grown oxides has followed two tracks: (1) Auger sputter profiling (ASP) studies of the chlorine distribution; (2) effects of the Auger primary electron beam. Both of these will be briefly summarized.

Our studies have revealed, in agreement with other work [1,2], that chlorine in an HCl/O_2 -grown SiO_2 layer piles up on the oxide side of the SiO_2/Si interface. We have been using ASP to determine the total amount of interface chlorine in SiO_2/Si structures fabricated at Fairchild Semiconductor, Palo Alto. We have found and are studying Cl pileup at the Si/SiO_2 interface as a function of growth time, temperature, and HCl partial pressure. These studies have revealed a monotonic increase of interface chlorine as a function of growth time for fixed values of temperature and HCl partial pressure. We have developed a simple numerical program to model chlorine diffusion in the growing SiO_2 layer, and this will aid us in determining values for specific parameters such as the chlorine diffusion coefficient. Eventually, this will allow us to predict the chlorine pileup for a given set of conditions.

The second aspect of this work has been the study of the effect of the Auger primary electron beam on the chlorine distribution. We used thermally grown SiO_2 samples implanted with chlorine to determine to what extent the measured chlorine profile was subject to distortion by the electron beam. We compared these effects by sputtering or etching samples to various depths before turning on the primary electron beam. These studies revealed that the electron beam swept chlorine to the SiO_2/Si interface in an amount roughly proportional to the total electron beam exposure time. Quantitative analysis allowed us to predict the size of this effect, and we determined that the role of electron beam effects in producing chlorine pileup in the Fairchild samples was not a major one.

Future work will consist of completing studies of the Fairchild samples and correlating these with our numerical model to provide us with the ability to predict the amount of interface pileup.

This work was supported by DARPA.

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(D) The Interaction of As with Si (100) Surfaces

Graduate Student: S. C. Perino

In this program, we have been investigating the interaction of arsenic with the (100) surface of silicon. The goal of this program is to determine on an atom-by-atom basis the morphology, chemistry, and electronic structure of arsenic present in its various forms on the silicon surface. Results from this study will provide critical information concerning dopant (in this case, As) incorporation during chemical vapor deposition, the effects of dopant segregation to polycrystalline silicon grain boundaries, and related effects such as autodoping and Schottky-barrier formation.

Experimental techniques used to date in this study include thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). This is one of the first semiconductor TDS studies. A TDS experiment is typically conducted by adsorbing a species from the gas phase at a fixed temperature, heating the sample to higher temperatures linearly in time, and recording with a mass spectrometer the partial pressure versus temperature of the species desorbing from the surface. Since the partial pressure is proportional to the desorption rate, kinetic information is obtained from a TDS experiment. The arsenic adsorbate has been obtained by heating GaAs chips in a molybdenum evaporation source. In the preliminary study, no attempt

was made to reduce any of the constituents evaporated; therefore, As_2 , As_4 , as well as some Ga evolved from the source. In order to determine the extent to which coadsorbed Ga influenced the interaction of the arsenic with the silicon, experiments utilizing an elemental arsenic evaporation source are in progress. The disadvantages of an elemental arsenic source are the difficulty of controlling low evaporation rates and avoiding evaporation during vacuum bakeouts.

Several different arsenic species adsorbed on the Si surface have been observed by TDS. The least tightly bound species is obtained by adsorbing arsenic onto a room-temperature surface and monitoring the exposure with a mass spectrometer and timer. The desorption process appears first order at low exposures with a desorption temperature of about 335°C . At coverage greater than a monolayer as determined by Auger, the desorption peak temperature shifts upwards to a temperature of 400°C where a narrowing of the desorption peak is evident. This overall desorption behavior was observed for both As_4 and As_1 species detected by the mass spectrometer. Apparently, the As_1 species is only a cracking fragment (in the mass spectrometer) of the actual As_4 desorption species. In order to confirm this interpretation, the As_4 and As_1 signals were multiplexed in time so that both species could be examined for exactly the same exposure. The relative heights of the As_4 and As_1 peaks in the multiplexed spectra are the same as the corresponding relative flux intensities from the arsenic evaporator, supporting this conclusion.

A more tightly bound arsenic species with a desorption peak temperature of 650°C has been observed by adsorbing onto a heated surface. The amount adsorbed is at least ten times less than that amount adsorbed at room temperature. The more tightly bound species desorbs as a dimer and a tetramer species could not be observed. An Auger analysis indicated substantial amounts of gallium were present on the surface and suggested that this arsenic species may be influenced by the coadsorbed gallium. Preliminary experiments utilizing the elemental arsenic source support this conclusion since a dimer species is observed only at a higher desorption temperature of around 800°C .

A most tightly bound arsenic species remains on or within the surface after both the tetramer and dimer species have desorbed. Auger investigations indicate that accumulation into the most tightly bound

state is enhanced by adsorption at higher substrate temperatures. The most tightly bound species does not appear to smear out the Si p(2 × 1) LEED pattern in the same manner as occurs with the more loosely bound species. Further investigation of the most tightly bound species may yield information about its atomic nature and the extent to which it is incorporated into the bulk or outdiffuses. After the investigations into the kinetics of As adsorption/desorption have been completed, the effect of high As concentrations on the Si surface, on surface state densities, band bending, and Fermi-level position will be investigated using ultraviolet photoemission spectroscopy.

This work was supported by the Army, Air Force, and Navy through the Stanford Electronics Laboratories-Joint Services Program.

(4) Studies of Optical Excitation Cross Sections: Studies of Transmission Gratings and Their Use

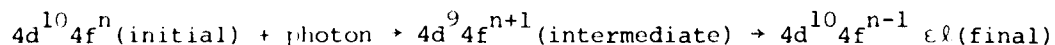
Professor: I. Lindau

(A) Theoretical Study of Line Shapes in Resonance Photoemission Spectra

(Professor Seb Doniach is strongly associated with this work)

Graduate Student: Se-Jung Oh

Photoemission on metals with an incomplete shell such as transition metals (3d-shell) and rare-earth metals (4f-shell) show a strong resonance enhancement as the photon energy is tuned through the energy corresponding to a transition from the initial ground state to the tightly bound intermediate state. For example, the photoemission of f-electrons from rare-earth metals and their compounds is strongly enhanced when the photon has enough energy to excite a 4d-electron to an unoccupied 4f level [1,2]. It is due to the process where the initial state 4d-electron is first excited to the tightly bound discrete-energy (4d-hole + 4f-electron) intermediate state and then autoionized into the final state by super-Coster-Kronig Auger decay. In atomic term values, we can write it as



Since this resonance process has the same initial and final states as the direct 4f photoemission, the constant initial state spectroscopy (CIS) shows a characteristic Fano profile.

In photoemission, the electrons of the system are relaxed to adjust to a suddenly-created core hole, and this relaxation shows up in the spectra in the form of a plasmon satellite or asymmetric line shape. We have studied the effects of electronic relaxations in both intermediate and final states on the line shape in the resonance photoemission process, as a function of final photoelectron energy, ϵ , and initial photon energy, ω , using Keldysh-Schwinger formalism.

We considered three types of relaxations.

- (1) Relaxations which have discrete energy (discrete type): Examples are plasmon excitations in metals, interband transitions or ligand-to-metal charge transfer in insulating compounds. We found that, if the relaxation coupling constant is different in intermediate and final states, this shows up as an ω -dependence of the plasmon satellite strength.
- (2) The singular adjustment of a conduction band to a core-hole formed by photoemission studied by Doniach and Sunjic [3] (continuous type). We found, in this case, that the Doniach-Sunjic asymmetry parameter on resonance is influenced by the intermediate state relaxation.
- (3) Kotani-Toyozawa model [4] for metals with an incomplete shell, where an unoccupied localized energy level (d- or f-state) is lowered down due to the potential of a core-hole and hopping of electrons between this state and conduction bands becomes possible.

In all cases, we found that the line shapes are influenced by the intermediate state relaxations as well as the final state relaxations when the system is at resonance, while the final state relaxations determine the line shapes off resonance. This is because, at resonance, the intermediate state has a long lifetime, so the electrons have enough time to adjust towards the fully relaxed intermediate state but, when the photon energy is far from resonance, the lifetime of the virtual intermediate state is short, and the system has no time to relax in the intermediate state.

This work was supported in part by NSF Grant DMR-7913102.

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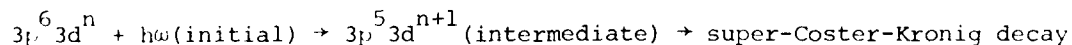
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(B) Resonant Photoemission of 3d States in Ni Compounds

Professional Associate: J. W. Allen (Xerox Palo Alto Research Center)

Graduate Student: Se-Jung Oh

Valence-band photoemission from nickel metal shows a satellite at about 6 eV below the Fermi level, which is resonantly enhanced with a Fano line shape for photon energy at the 3p→3d edge [1]. This has been an active subject of study, and several models have been proposed to explain the origin of this satellite and its resonant behavior. The resonant effect is probably similar to that observed for 4f emission from the rare earths at the 4d→4f absorption edge, i.e., due to the process



although it is not so simple and easily interpreted because the 3d states are not as localized as are the 4f states. The 3p core level excitation line shapes measured in Ni by photon absorption and electron energy-loss spectroscopy has been interpreted by this Fano-type interaction in which the excited configuration decays by super-Coster-Kronig process into the continuum of excitations of the 3d band [2], implying the possibility of resonant 3d-photoemission.

Among various models proposed for the origin of the 6 eV satellite structure [1,3,4,5], some are based on the atomic picture, while others are based on the band-like 3d states. Therefore, we proposed to

study the valence band of the nickel compounds for varying degrees of localization and numbers of the 3d electrons to test various models. Up to now, we have studied NiO, which has $(3d^8)Ni^{2+}(2p^6)O^{2-}$ configuration, and quite localized Ni 3d electrons.

Near the 3p edge (about 67 eV) of Ni^{2+} , the so-called "multi-electron satellite" [6], which is the structure at about 7 eV below the Ni^{2+} 3d main peak, is seen to show Fano-type resonant behavior similar to the Ni metal 6 eV satellite. Also, the Ni^{2+} 3d main peak shows resonant effects analogous to the 3d photoemission of Ni metal. Since these photon energy dependences of valence band photoemission of NiO are quite similar to those of Ni metal, it is hoped that the analysis of NiO data will help resolve the controversy concerning Ni valence-band photoemission.

The experiments were performed on the new 4° line of SSRL.

This work is supported in part by NSF Grant DMR-7913102.

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(C) Transmission Gratings and the Investigation of Bulk Optical Constants in the 100 to 1000 eV Energy Range

Graduate Student: R. Tatchyn

Recent developments in the analysis [1-4] of ultrafine planar transmission gratings indicate the feasibility of using such structures (composed of the suitable materials) in determining the bulk optical constants of the grating materials themselves. The method is based on

the measurement of the ratios of the zeroth- and first-order peaks of the diffracted intensity spectra transmitted through the gratings at the desired frequencies. The method is therefore naturally adaptable to the storage ring/monochromator systems of the soft x-ray beam lines at SSRL, and experiments designed to measure the above-mentioned order ratios are currently being planned.

Additional areas related to transmission gratings which have been theoretically examined by the investigators are:

- (1) blazed transmission grating structures [2,4]
- (2) optimized mirrors for synchrotron storage rings [5]
- (3) effects of the phase-space characteristics of synchrotron light on transmission grating resolution [6]

An ancillary experiment, utilizing transmission gratings, designed to characterize the spectral content of the Grasshopper Monochromator at the new SSRL soft x-ray beam line has also been performed, and the results are being held for collation and analysis [7].

This work was supported in part by NSF Grant DMR-77-27489.

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6. In preparation.
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(D) Resonance Photoemission studies

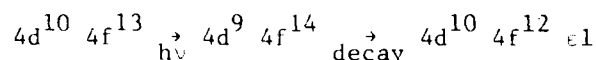
Professional Associates: J. W. Allen, L. I. Johansson

Graduate Students: M. Hecht, J. Manni and S. J. Oh

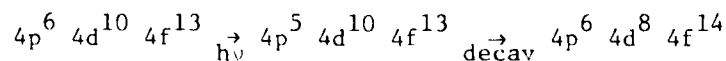
Yb and its compounds are of great interest because of the proximity of the 4f levels to the Fermi level and the fact that the 4f levels are filled in the metal but not in some of the compounds. This group reported previously on a Fano resonance at the 4d-4f threshold which could be turned on by oxidation of Yb to form the $4f^{13}$ ground state. Additional data on this subject including resonance behavior at the 4p threshold has been obtained. Secondly, we confirm the existence of a surface shift of the $4f^{14}$ derived levels of Yb metal.

In the earlier study, it was observed that oxidation of Yb results in a valence change from 2+ to 3+, i.e., a change from a full 4f shell to a $4f^{13}$ configuration with one vacancy. This is exhibited in the photoemission spectrum as a shift of about 3 eV to larger binding energy and a more complex multiplet splitting.

The creation of the vacancy in the 4f shell opens up the $4d \rightarrow 4f$ excitation channel, which results in enhanced 4f emission at the 4d threshold via the strong Coster-Kronig process,



Resonance behavior might also be expected at the 4p threshold involving the 4p, 4d, and 4f levels of Yb_2O_3 . We observed that the $4p_{1/2}$ photoemission line is suppressed due to the strong decay process



At the $4p_{3/2}$ edge, we also observed a resonant enhancement in the vicinity of the 4d levels. This data is presently being analyzed.

In the case of Yb metal we have observed a component of the $4f^{14}$ levels shifted by 0.6 eV to tighter binding energy. An increase of the $4f^{13}$ derived peaks were observed upon oxygen exposure but no change in the relative size of the shifted and unshifted $4f^{14}$ peaks. This lends support to the hypothesis that this shift represents a pure surface phenomenon.

(E) Measurement of Partial Photoionization Cross Sections

Professional Associate: L. I. Johansson

Graduate Student: M. Hecht

We are currently pursuing a program of measurements of subshell photoionization cross sections in a variety of elemental solids and simple compounds. The techniques for determining the energy dependence of partial photoionization cross sections obtained from measured peak areas in photoemission spectra obtained using synchrotron radiation have been refined during the last year.

The following factors have to be included when synchrotron radiation is used as the excitation source and a cylindrical mirror analyzer for the energy analysis. The first two are purely instrumental--the latter 3 assume a multi-step model of photoemission.

1. The usual practice of using a fixed analyzer pass energy while scanning electron kinetic energy results in a varying source area seen by the analyzer. This source area is on the order of the size of a typical synchrotron radiation beam, resulting in an unpredictable transmission function. We correct this problem by using a modified controller which allows us to select the ratio $E_{\text{pass}}/E_{\text{kinetic}}$. This results in uniform transmission as well as constant, but selectable, relative resolution ($\Delta E/E$).
2. Monochromatized light from high energy synchrotron radiation sources is always contaminated by harmonics and, to a lesser extent, scattered light. If the harmonics are more efficiently reflected by the optical elements or more efficiently converted by the photodiode, this results in large distortions of the measured monochromator transmission function below 100 eV. The same considerations apply to photoyield measurements or the measurement of photon-induced Auger electrons. We correct for harmonics by comparing secondary photoemission peaks induced by a harmonic to first order peaks measured with the monochromator set to the energy of that harmonic. A simple interaction technique converts a measured yield spectrum to the spectrum which would have been measured without harmonics. We correct for scattered light with a simple extrapolation technique to be supplemented by results of a recent monochromator characterization using a transmission grating.

3. Electron escape depth varies fairly rapidly below the escape depth minimum. We correct for this by combining available data with the so-called "universal curve" (2). We can check this and other electron energy dependent effects by measured photon-induced Auger yields, as discussed below.
4. The electrons are refracted by the surface of the material, resulting in a loss of intensity of the outgoing beam at low energy. This could result in a factor of 2 error at 30 eV. We correct for this using a jellium model. Accuracy is limited both by the model and by our knowledge of the inner potential.
5. It is not uncommon to use light incident on a sample at an angle of 75° or larger with respect to the normal, since this enhances the photoemission flux. However, reflection of light from the surface can reduce emission, and the bending of light towards the surface by refraction can significantly enhance it at these angles. We avoid this problem by working at angles less than 30° , which results in significantly reduced intensity.

The 4d, 5s and 5p subshell cross sections of Ba have been determined. With the inclusion of the correction factors discussed above we are now able to make a detailed comparison to theoretical many-body calculations.

(F) Photoelectron Branching Ratio in the 5d Subshell of Pt, Au and Pb

Professional Associates: L. I. Johansson, E. Kallne

Graduate Student: M. Hecht

It is known that the photoionization cross section of states split by spin orbit interactions can exhibit slightly different energy dependencies which may give rise to an energy dependent branching ratio. This effect has so far been studied mostly for the gas phase but investigations have recently also been carried out on solids. In most cases it has been found that the predictions of the current atomic calculations explain the branching ratio behavior fairly well also for the solids. In one case however, namely for the Au 5d subshell, a modulation in the energy range 100-150 eV has been observed which has not been given a satisfactory explanation. In order to further elucidate the seemingly anomalous Au 5d branching ratio behavior we have measured the $5d_{5/2}/5d_{3/2}$ photoelectron intensity ratio for Pt, Au and Pb over the energy range 50-250 eV.

The Pb 5d's are core like states with a binding energy of about twenty eV and appear as two well resolved peaks with a spin orbit splitting of 2.7 eV. In Au and Pt the 5d states comprise the valence band and have total widths of about six and eight eV and are centered about five and four eV below the Fermi level for respectively Au and Pt.

The branching ratio for Pt and Au exhibit a distinctly different behavior than for Pb. A relatively strong modulation is observed for photon energies between about 80-180 eV both for Pt and Au and the branching ratio behaves rather similar in these two cases. For Pb on the other hand the ratio also deviates from the statistical value of 1.5 and shows an energy dependence, but it is not modulated the way it is for Pt and Au. Very similar trends for the total 5d subshell cross section was obtained for all three materials for energies above 90 eV.

The observed behavior in branching ratio for the 5d shell of Pb can be explained by the atomic effects discussed by Walker and Waber. The atomic effects can not explain the modulation observed for Pt and Au, however, because the spin orbit splitting is only 2.5 eV and 2.7 eV respectively for Pt and Au and the 5d cross section exhibit a very similar energy dependence for all three metals.

While the Pb states are core like states and thus are expected to resemble atomic states, the 5d states in Pt and Au are definitely affected by the crystal potential. The photon energies used in the present investigation lie in the intermediate regime, between the UPS and XPS regimes, where "band structure effects" (final state plus transition matrix element effects) have been shown to be of importance in angular resolved photoemission measurements on valence bands. These findings can be directly translated to our results on Pt since we made the measurements on a Pt(111) single crystal and a complete angular averaging was not achieved. Also for the evaporated Au film the modulations can be understood if preferential orientation of the crystallites in sample occurred.

The comparisons of the branching ratio behavior of the spin orbit components in the 5d subshell for the metals Pt, Au and Pb allow us to draw the following conclusions. For the Pb 5d components the deviation in the branching ratio from the statistical value and the energy dependence can be understood from current atomic models. For Au and Pt on the other hand, strong modulations occur in the energy range 80-200 eV that most probably are due to "band structure effects".

Acknowledgment - This work was supported by NSF Contract DMR 77-02159

58. SOLID STATE PHYSICAL CHEMISTRY

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Agency Support:

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Office of Naval Research - N0014-67-A-0112-0083

NSF-MRL through CMR - Thrust Program on Noncrystalline Metals

(1) Thermodynamic & Kinetic Studies of Liquid Metal-Oxygen Systems Using Solid State Electrochemical Techniques.

Objective and Approach:

The present program concerns the use of solid electrolyte electrochemical cells to study thermodynamic and kinetic phenomena in liquid metal-oxygen systems. We employ solid oxide electrolytes to establish electrochemical cells, with one electrode comprised of oxygen dissolved in a liquid metal. Several techniques employing combinations of measurements of potentials and currents of these cells are used to measure the oxygen solubility, activity of oxygen, Gibbs free energy of formation of relevant oxides, and the diffusion coefficients of oxygen in liquid metals. We are presently investigating the degradation of commercially available solid oxide electrolytes, since their reliable performance is crucial to the present study. During the past year, major emphasis has been placed on this topic.

Research Report:

The a.c. electrical conductivity of yttria-stabilized zirconia solid electrolyte specimens, $\text{ZrO}_2 + 8 \text{ wt\% } \text{Y}_2\text{O}_3$, with porous Pt-paste electrodes has been studied over a temperature range of 400-1000°C in air. The complex admittance of these specimens was determined over a frequency range from 2HZ to 400KHZ. The true lattice (bulk) conductivity

is separated from grain boundary effects and from electrode polarization through the analysis of the complex admittance plots.

The decrease in conductivity during post-sinter annealing (aging) at temperatures of 800, 900, 1000°C is attributed to the following three trends: (1) segregation of an yttria-rich layer near the grain boundaries and triple points (this latter phase is believed to have an adverse influence on the electrical properties of zirconia); (2) formation of tetragonal ZrO_2 at temperatures above 600°C and retention of this metastable form along with stabilized fluorite phase upon cooling to lower temperatures; and (3) ordered domains formed within the disordered fluorite phase.

The analysis of complex admittance plots specifies a capacitive-resistive electrolyte polarization, corresponding to a partial blocking of oxygen ions at the electrolyte grain boundaries by a second phase there.

The microstructural changes upon annealing were investigated by employing scanning electron microscopy (SEM) and transmission electron microscopy (TEM) utilizing in both cases energy dispersion x-ray spectrometry (EDS). In TEM, the quantitative analysis of regions down to 200-500 Å has been obtained. The TEM micrographs in the bright field mode revealed contrast features in the grains of the specimens as well as isolated clear regions within the grain. Diffraction micrographs from specimens which were annealed at 1000°C for a week contained two distinct features in addition to the cubic fluorite substructure reflections. There were patterns of diffuse scattered intensity and "extra" reflections forbidden by the fluorite structure symmetry. The "extra" reflections are attributed to intragranular precipitates of tetragonal ZrO_2 solid solution within the cubic matrix. The presence of a yttria-rich glassy phase at the intergrains and triple points was demonstrated by EDS and a diffuse ring pattern characteristic in the diffraction mode.

The dark field image of a grain containing these contrast features formed with an "extra" reflection in the objective aperture shows

grosser features and supports the proposal that tetragonal intragranular phases are present.

(2) Analysis of Dynamic Reacting Systems Using Mass Spectrometric Techniques; Control of Impurities in the Epitaxial Growth of High Quality GaAs

Objective and Approach:

There is considerable practical interest in the accurate analysis of vapor species in high temperature chemical process environments. These environments typically contain reactive gaseous environment in typical crystal growth processes for semiconducting materials. We focus, in particular, on the liquid phase epitaxial (LPE) GaAs growth process. It has been established that Si, C and O are unintentional impurities in LPE GaAs crystals and their presence exerts a significant influence on the crystal properties. It has been suggested that these elements are present in the crystal as a result of specific impurities in the gaseous environment during crystal growth such as CO, H₂O and SiO, however, direct "in situ" analysis of the crystal growth ambient, has not been made.

In the use of mass spectrometry as an analytical tool, it is necessary to introduce a representative sample into a detection chamber which operates at a pressure of $\sim 10^{-6}$ torr. As a consequence, for a system at atmospheric pressure, it is necessary to meter the sample into the detector chamber with an appropriate device. Common techniques for accomplishing this include: a simple capillary; a selective membrane; and a chromatographic column. For high temperature systems, however, all of these systems may perturb the chemistry during sampling. A solution to this problem is the formation of a molecular beam by free jet expansion through a sampling orifice. Recently a conical nozzle has been adapted for use in molecular beam mass spectrometry (MBMS). Although there are extensive studies on the gas dynamics of the two other types of sampling orifices, relatively little work has been done to characterize the conical nozzle orifice. In the present work, we characterize the use of this type of nozzle for molecular beam sampling.

The relevance of this method for characterization of crystal growth environments is explored for the case of gallium arsenide liquid phase epitaxial growth. Our results of this study are used to modify existing crystal growth procedures to improve the resulting epitaxial layers.

Research Report:

Our past MBMS results have shown that carbon and silicon may be incorporated in GaAs as a result of the hydrogen annealing schedules that are conventionally used to purify the gallium solvent prior to liquid phase epitaxial (LPE) layer growth. We are presently exploring the use of chemical getters as a method of more rapidly and effectively removing impurities from the gallium liquid solvent prior to LPE growth. The use of titanium and zirconium as chemical getters normally produces p-type layers with remarkably high hole mobilities: $\mu_p \sim 200-400 \text{ cm}^2/\text{volt sec}$ at 300°K . Work is in progress to analyze the behavior of these getters when the processing variables are changed and to more thoroughly characterize the electronic properties of these GaAs layers.

The present MBMS activity concerns the measurement and control of water vapor in gaseous environments and the use of low concentrations of xenon as an internal standard for the MBMS technique. Results from the latter activity show promise for improved sensitivity and accuracy for the MBMS technique.

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59. PROCESS INDUCED DEFECTS IN SILICON

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*Received MS during report period.

Agency Support:

EPRI 790-2
Monsanto 19-21-179A

Technical Objective:

The objective of this program is to understand the mechanism behind the production of defects in silicon during device fabrication, to find methods for reducing defect production, and to characterize the effects of various defects on semiconductor devices.

Approach:

Various types of process induced defects are studied by means of, (a) conventional defect delineation etches, (b) carrier generation rate measurements, (c) device yield measurements, and (d) current transient spectroscopy.

Research Report: Current Transient Spectroscopy

An instrument has been constructed to characterize the energy levels and recombination parameters of atomic defects in semiconductors. The device detects the current transient from trapped electrons following reverse biasing of a p-n junction. A detection limit of less than 10^9 defects per cm^3 has been achieved permitting detection of defects even in the highest quality silicon.

Research Report: Inert Gas HCl Gettering

The intent of this research program is the development and characterization of a new gettering technique which is performed on polished silicon slices prior to any other processing. The research program includes investigation of pre-oxidation gettering by HCl in an argon ambient. The kinetics of the gettering process is studied by examining gettering effectiveness as a function of time and temperature by examination of the defect structure using conventional defect delineating etches and using p-n junction and depleted MOS generation rate measurements to determine junction leakage and yield distributions.

Preliminary results have shown that the oxidation induced stacking fault density can be reduced two orders of magnitude and the generation lifetime increased to 10 ms by proper gettering. Pregettered wafers are currently being tested to determine their yield advantages in integrated circuit fabrication.

60. THERMOPHOTOVOLTAIC SOLAR ENERGY CONVERSION

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Agency Support:

EPRI 790-2

Technical Objectives:

A thermophotovoltaic (TPV) converter is a direct conversion heat engine that converts incandescent radiation from a hot surface (2000°C) into electricity by means of a photovoltaic cell. The objective of this program is to obtain a realistic appraisal of the achievable energy conversion efficiency using silicon photovoltaic cells in a thermophotovoltaic energy converter. Efficiencies over 35 percent are hoped for. These high efficiencies are achieved by recycling the portion of the spectrum that the TPV cell cannot use (mostly at wavelengths greater than 1 μ m) back to the radiator.

Approach:

Based on results of numerical simulations of TPV conversion a preliminary TPV cell was designed. Because of the unique requirements in TPV conversion this cell differs considerably from a typical solar

cell. Current efforts involve bringing the cell fabrication to a sufficient level of sophistication to determine if there exists any reason why the expected high efficiencies cannot be achieved. The program strategy is to: (a) fabricate TPV cells, (b) measure their efficiency and other relevant parameters, (c) compare the results with the TPV modeling program to characterize the physical processes operative in the cells (our TPV cells operate with a broad spectrum incandescent radiant flux of 300 W/cm^2 , an intensity sufficient to produce effects not observed in normal silicon solar cells), (d) adjust the TPV model with new parameters as necessary, (e) redesign the cell fabrication to improve performance, and (f) iterate through the above steps.

Research Report:

(1) TPV Cell Fabrication

Twelve runs of TPV cells have been completed. Their energy conversion efficiency has improved from 6 percent in the first cell to a current 26 percent. All of the important parameters have been characterized. Current cells are limited by four mechanisms: (1) base region carrier recombination, (2) contact area surface recombination, (3) contact area infrared absorptance, and (4) scattering of infrared radiator to beyond the critical angle for escape by the top contact grid. Programs addressing each of these areas are underway. Preliminary results in reducing these loss mechanisms have been encouraging. While these results have not been incorporated into complete TPV cells, the TPV model predicts an efficiency of 35 percent when using these values. Presently we estimate that highly developed TPV cells could achieve efficiencies between 40 and 45 percent.

(2) Deposited SiO_2 -Si Interface

Surface recombination at the Si-SiO₂ interface is an important loss mechanism in TPV cells. Thus, the lowest possible interface state density is desired. At the same time the shallow junctions of TPV cells prohibit thermally growing the SiO₂. The kinetics of deposited SiO₂ interface state annealing has been studied with a goal of

producing the minimum interface state density consistent with acceptable junction motion. Procedures have been developed that give an interface state density of $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ and a junction diffusion of 200 Å.

(3) SIPOS Heterojunction Contacts

The thin diffused layers in today's microelectronic circuits are generally transparent to minority carriers. As a result, the properties of many devices, particularly bipolar transistors, are partially controlled by recombination at the metal semiconductor interface. Future projection of device geometries indicate that such recombination will force a severe compromise on performance. For example, an emitter cannot be made too shallow, or contact recombination will reduce its efficiency; making it deeper, however, reduces basewidth controllability and decreases speed because of emitter charge storage.

Reducing the minority carrier recombination velocity at the metal semiconductor interface would enhance device performance. Such an effect has been achieved [1] wherein current gain was greatly increased in polysilicon emitters when a thin SiO_2 layer was introduced. It appears that this gain was realized because of the differential tunneling probability between electrons and holes in thin SiO_2 layers and, therefore, is limited to npn transistors.

The initial literature search for materials suitable for incorporation into the heterojunction contact indicated that most interfaces were plagued by high interfacial state densities: the resulting recombination currents masked the effect of bulk diffusion currents rendering the heterojunction concept of utilizing a Boltzmann barrier to reflect the undesired minority carrier species irrelevant. Work done at SONY on SIPOS (Semi-Insulating Polycrystalline Silicon) doped with phosphorus and boron indicated this material, with suitable annealing, possessed acceptable interfacial properties [2] and its fabrication is compatible with conventional silicon technology. The ability of SIPOS to reduce undesired minority carrier currents in the SONY devices indicated that a study of the transport mechanisms involved would be of value in this field which is still largely dominated by empiricism.

The SIPOS films in the SONY study were deposited using CVD by decomposition of silane, nitrous oxide, and, in the SONY application, a dopant gas (phosphine). The existence of literature on the properties of films deposited using this method and the availability of suitable facilities in the IC Lab favored this method over alternative methods such as sputtering or glow discharge, at least for preliminary studies. The reactor used for all SIPOS depositions to date employs atmospheric pressure, cold walls, and an RF heated susceptor. Because no previous SIPOS depositions using this reactor had been performed, and because process parameters are sensitive to reactor geometry, the initial series of depositions was used to establish approximate values for gas flows and susceptor temperatures to yield films of uniformity sufficient for characterization.

There were initial difficulties with temperature control. For example, the susceptor temperature is monitored using optical pyrometry, and so questions arose as to the effect of depositions on the (cold) tube wall on the accuracy of such monitoring. However, exact reproducibility was not critical at this stage and the run to run variations encountered were not severe enough to warrant transfer to a hot wall reactor at that time; however, work is proceeding on a hot wall reactor which will eventually be required for device quality films.

Using the process settings as established for optimum uniformity of deposition, we next attempted to establish the feasibility of simple testing techniques to evaluate oxygen concentration in the films. These included etch rate studies, refractive index and thickness measurement via ellipsometry, mechanical step height measurement, and gravimetric studies. Each of these proved to be unsuitable for various reasons. For example, ellipsometry assumes homogeneous isotropic non-scattering and specularly reflecting films. Although the assumption of isotropy is probably valid, it is doubtful that the others are. Optical studies later indicated the laser frequency used for the ellipsometer may lie in a range of strong dispersion. This and the presence of inhomogeneities in the film compound the difficulty of interpreting of ellipsometric data.

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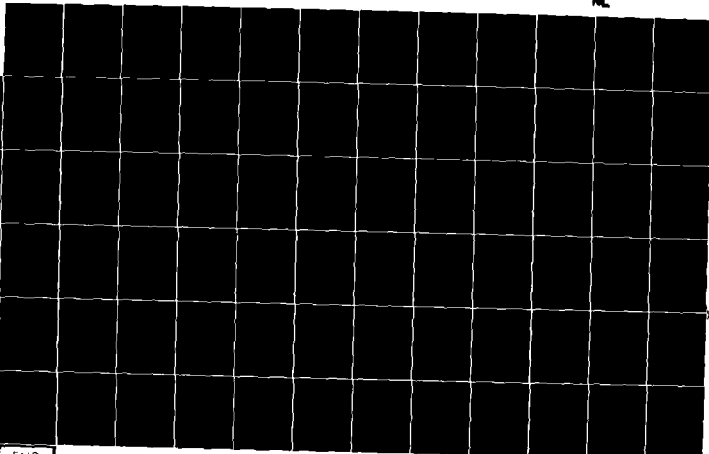
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Optical constants of the SIPOS films are being determined from reflection and transmission spectrophotometry. The results can yield a spectral plot of refractive index and the absorption constant. The frequency dependence of these quantities can give clues to the joint density of available states, and the type of absorption mechanisms involved. It may prove possible to extract an apparent "optical gap", and to note its dependence upon oxygen concentration. Furthermore, the refractive index obtained in regions of weak dispersion may prove to be a more reliable guide of oxygen concentration. The dependence of optical constants upon film thickness can also be investigated with this technique. A series of samples prepared using the range of anticipated N_2O flow rates and their spectrophotometric results will be analyzed using a series of computer programs being written to aid in thin film analysis.

The next phase of the investigation will turn to conventional techniques for measuring temperature dependence of conductivity, drift mobility, thermoelectric power, and Hall coefficient. These should shed some light on possible transport mechanisms.

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61. FUNDAMENTAL ASPECTS OF REACTIVITY IN INORGANIC SYSTEMS

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NSF CHE77-22722

Technical Objective:

A. Electronic Interactions between Metal Ions. One manifestation of such interactions is net electron transfer in oxidation-reduction reactions. Of interest are the rates as function of the properties of the ligands associated with the metal ions as well as of the matter separating them. The principles governing the processes are important as providing a basic understanding of one of the major classes of chemical change, but they also have some relevance to understanding electronic conduction on

a molecular level. The electronic interactions manifest themselves also in some special properties possessed by mixed-valence molecules. Such species often show a near infra red absorption which arises from metal-to-metal electron transfer, and provides a measure of the electronic coupling between the metal centers.

B. Basic Chemistry of Heavy Transition Elements. The special efficacy of some of the heavy transition metals as catalysts is well known, as is the fact that their chemistry can differ markedly from that of their congeners in the first transition period. A systematic exploration of the chemistry of selected members is in progress, with the goal of understanding their reactivity in basic terms.

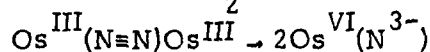
C. A research program, involving collaboration between industry (Hercules, Inc.), a group at Cal Tech (Anson) and three groups at Stanford (Boudart, Collman and Taube) is in progress with the goal of developing a catalyst for the oxygen cathode. It is supported jointly by the NSF and industry (Hercules absorbs its own research costs, which are the equivalent of 1-1/2 full time research workers). The general approach is to synthesize metal-containing species which make possible multicenter, and it is hoped, multivalent attack on O_2 by the reduced metal complex. The catalysts are to be adsorbed or otherwise attached to the electrode surface, so that the oxidized form resulting from the reaction of the reduced form with O_2 can readily absorb electrons from the electrode, completing the catalytic cycle.

Research Report:

A. Electronic Interactions between Metal Ions. The mixed valence species $[(NH_3)_5Ru \text{---} \bigcirc \text{---} NRu(NH_3)_5]^{5+}$ first synthesized in my laboratories continues to be the subject of investigation and speculation. At issue is the extent of electron delocalization in the ground state. This is complete enough so that the energy of the intervalence transition does

not depend on the dielectric properties of the solvent (.i.e., electron transfer between metal centers is rapid compared to rotation of solvent dipoles), yet the molecule retains many of the characteristics expected for Ru(II) and Ru(III) molecule. The molecule $[(\text{NH}_3)_5\text{RuN}\equiv\text{NRu}(\text{NH}_3)_5]^{5+}$ recently synthesized by David Richardson shows many of the anomalies of the μ -pyrazine species, but has the advantage of being simpler in composition, and, we expect, being simpler to understand. One significant observation is that the $\text{N}\equiv\text{N}$ stretch is inactive in the infra red, but active in the Raman. Were the molecule trapped in a particular Ru(II)...Ru(III) state for as long as 10^{-12} sec, the $\text{N}\equiv\text{N}$ stretch would be infra red active. This observation then sets a lower limit on the rate of internal electron transfer. ESCA measurements as well as studies of the chemistry are in progress. These will undoubtedly help us to understand the electronic structure of the species. The great interest in the μ -dinitrogen and μ -pyrazine species derives from the fact that they are neither deeply-trapped nor strongly delocalized. Different descriptions apply to the extremes, and neither is easily generalized to the intermediate case.

B. A remarkable reaction has been discovered by David Ware in studying the chemistry of Os(VI). When OsCl_5N^- (chloronitridoosmate(VI)) is brought into contact with pyridine, N_2 is evolved and a chloropyridineosmium(III) species is formed almost quantitatively. This is the reverse of the long sought reduction of N_2 by disproportionation



and proves that there is no unsurmountable kinetic barrier to this kind of reaction. In principle, it is possible to design a system in which a labile equilibrium is realized between a nitrido and a dinitrogen species.

C. The collaborative research on the oxygen electrode is making

excellent progress, owing chiefly to the contributions of the Collman and Anson groups. Our own research has been less successful in synthesis than in reaching a basic understanding of some reactions involving the reduction of dioxygen. Here, through the efforts of Dave Stanbury, we can claim to have completed a definitive study of the mechanism of reduction of dioxygen by a class of outer sphere reducing agents.

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62. SEMICONDUCTOR PROCESSING, GAS DISCHARGES, GROWTH-DISSOLUTION AND SURFACE BEHAVIOR OF CRYSTALS, BIOMATERIALS

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Technical Objectives:

(a) To gain an atomistic level of understanding that is quantitatively predictive concerning the key features of semiconductor processing; i.e., oxidation, film formation, diffusion, etc. To fully control and exploit these processes in integrated circuit technology using both a macroscopic and a microscopic level of understanding and a representation that is both atomistic and parametric.

(b) To understand the fundamental principles of gas discharges so that they may be utilized in various applications such as sputtering, environmental control, surface doping and information displays.

(c) To gain a complete and quantitative understanding of the crystallization process from any media. To investigate the various contributions which comprise the energy of either a stationary or a moving

interface plus how this energy changes with the detailed topography and state variables (C, T, P, ϕ) of the interface.

(d) to develop devices and techniques for non-invasively monitoring living systems. To investigate membrane properties and the growth of essential body materials; e.g., nerves.

Approach:

(a) Theoretical investigation of all the processes involved in the thermal oxidation of silicon, the reactive sputtering of silicon and beam deposition of films. Experimental studies on the enhancement of the oxidation velocity via corona charging and via U.V. radiation, on phosphorus redistribution during oxidation, on the reactive sputtering of SiO_x ($0 < x < 2$) and SiC and on the deposition of layered materials.

(b) Experimental and theoretical investigation of plasma bubbles developed during gas discharges with application to A.C. plasma display panels.

(c) Theoretical and experimental investigation of crystal growth and interface instability in the compound CsCdCl_3 and in the large band-gap semiconductor, GaN. Theoretical investigation of the dissolution of quartz and various silicates. Experimental and theoretical investigation of the mechanical and surface electrostatic behavior of copper single crystals in ultra-high vacuum.

(d) Theoretical and experimental development of techniques for monitoring various components of the electrical equivalent circuit of human skin (in vivo). Experimental investigation of the regrowth of nerves in rats (in vivo).

Research Report:

(a) 1. A new structural model of Si to SiO_2 transformation via thermal oxidation has been proposed, which leads to a low excess free energy storage in the SiO_2 . Silicon is postulated to transform to α -cristobalite plus interstitial Si ions. Subsequent oxidation of these interstitials produces distortion of the lattice and speedy transformation of the α -cristobalite to vitreous silica so that only a very thin

($\sim 5 \text{ \AA}$) layer of crystal exists at the interface as a buffer layer. The model allows a satisfactory qualitative explanation of both the orientation and temperature dependence of (1) oxidation-enhanced diffusion (OED) in the silicon, (2) oxidation-induced stacking fault (OISF) formation in the silicon, (3) interface state (N_{it}) formation, (4) fixed oxide charge (Q_f) in the SiO_2 , (5) silica stoichiometry variation (SiO_x) near the interface, (6) silicon interstitial partition coefficient (k_I), and (7) the oxidation velocity (V).

2. A corona discharge technique has been developed for altering both the electric field in the SiO_2 and the nature of the oxygen species in the SiO_2 environment during the thermal oxidation of silicon. Either negatively or positively charged oxygen species have been sprayed on the gas/oxide interface during oxidation at 900°C and any alteration in oxidation rate studied. Significant enhancement of oxidation rate occurred in both cases.

3. An approximate theoretical model for phosphorus redistribution in silicon during thermal oxidation at constant velocity in the presence of a square well interface field (potential has width d and depth U at the interface and is zero at larger distances) has been developed. Theory predicts that the interface region will be 90% saturated with P after 90 minutes of oxidation at 900°C and after 420 minutes at 800°C . At earlier times (10 minutes at 900°C), the theory predicts a small pile-up and, just outside of the interface on the Si side, a depletion of P. All of these results were confirmed by Auger concentration profile measurements. Within the limits set by the Auger technique, which tends to broaden the peak of the concentration profile, we find $25\text{\AA} < d < 47\text{\AA}$ and $0.2 \text{ eV} < U < 5.2 \text{ eV}$.

4. Using a constant oxygen partial pressure in a Si deposition chamber partially isolated from a magnetron sputtering source of silicon, films of amorphous SiO_x ($0 < x < 2$) were formed at various substrate temperatures by varying the Si deposition rate. Films over the complete range of x have been prepared at thickness ~ 0.1 to $1.0 \text{ }\mu\text{m}$. Electrical measurements of these films are underway.

(b) The physics of electric (plasma) bubbles; i.e., a close packed

array of cylindrical glow discharges formed in a submillimeter gap between plane parallel, dielectric-covered electrodes excited by an A.C. voltage, has been extended by investigations of waveshape, frequency and resistance. By varying the rise time of the square-wave excitation in the range 0.3 μ sec to 5.0 μ sec, the transition from bubble domains to no bubble domains was found to occur as the peak current was reduced (rise time reduced). Domains were observed to form for peak currents exceeding a certain critical value. The critical maximum gap length for domain formation was increased from 75 μ m to 125 μ m by increasing the rise time to 0.3 μ sec. The bubble diameter excursion ratio, $d_{\max}/d_{\min}$, was increased by increasing the total air equivalent thickness, X_T , of the cell. In addition, although a pure gas does not produce electric bubble domains, Penning mixtures (e.g., He + 0.5% Ar) do allow domain formation. All of these features will aid in the technological development of a shift-type plasma display device which is under construction.

(c) 1. Experiments on deformation-induced work function changes were performed on copper single crystals of various orientations in an ultra-high vacuum (10^{-10} Torr) environment after in-vacuo cleaning of the surfaces. Simultaneous load, displacement and contact potential difference measurements were made. The elastic deformation-induced work function change was found to be less than 25 MPa/% strain -- a result consistent with the experimental literature and with several theoretical models. The work function was found to vary linearly with plastic strain. The relative magnitude of the slope was predicted using a model based upon the patch and point effects of crystal facets which develop during slip plane egress. This result is in agreement with other experimental data.

2. The results of established crystal growth theory and silicate dissolution experiments were combined to develop a new model for mineral/water reactions controlled by surface processes. An analysis of the time dependence of interface reaction velocities indicates that linear rate laws apply when uniform detachment or layer source generation mechanisms control the dissolution rate. At low interface undersaturations, first-order, logarithmic rate laws prevail. A parabolic time

dependence develops if key surface detachment parameters vary as a function of $(\text{time})^{\frac{1}{2}}$.

Experimental rate data for quartz dissolution are used to define molecular activation mechanisms based on the kink-site detachment model. The quartz dissolution mechanism appears to involve the binding of ionic species to surface detachment sites. Surface binding reactions are controlled mainly by the sign and magnitude of the surface electrostatic potential. Because the interface electric field strength determines the activated kink-site density, the dissolution rate increases exponentially with ion concentrations in the bulk solution and rates are minimized for the solution pH at which the surface charge is zero (the isoelectric point).

The dissolution of silicates is more complex than quartz dissolution because most silicates dissolve incongruently. For silicates, both the interface electric field and variation in surface chemical composition control the dissolution rates. To characterize such a solid, a new thermodynamic intensive variable was defined for the surface. The results yield a method for determining the chemical configuration of a surface from changes in its surface tension and in the bulk liquid composition.

3. Using a liquid gallium/gaseous ammonia reaction, we have formed GaN under a variety of conditions. A brief summary of the various unique features observed in our experiments is as follows:

- (i) Solubility effect: liquid Ga exhibits a very small solubility of GaN ($\sim 10^{-5}$ gm GaN/gm Ga in the range $\sim 900^{\circ}\text{C} < T < 1000^{\circ}\text{C}$) and appears to have a retrograde solubility in the 900°C range.
- (ii) Creeping Fluid effect: above 750°C , the fluid creeps at increasing rates as T increases and as $P_{\text{NH}_3}/P_{\text{NH}_3}^*$ increases (P^* is the equilibrium-partial pressure); however, it doesn't always creep towards the hot end of the crucible.
- (iii) Carrier Gas effect: different carrier gases lead to different amounts of GaN formed in the same time at $T = \text{constant}$; however, H_2 produced more GaN than Ar, which is opposite to theoretical expectations, and the amount of GaN formed was not always the same

for the same set of input gas-temperature conditions.

- (iv) Nucleation effect: copious nucleation occurred and we have been unable to significantly reduce it.
- (v) Temperature effect: at low temperatures ($T < 800^{\circ}\text{C}$) a thin impermeable GaN film covers the melt, at high temperature ($T > 1000^{\circ}\text{C}$) significant evaporation of GaN occurs and at intermediate temperatures ($T \sim 950^{\circ}\text{C}$) the best crystals formed.
- (vi) Melt Convection effect: the system does not readily exhibit convective flow even with a large thermal driving force.
- (vii) Alloy Addition effect: for Ga-Bi alloys we found an increase in the nucleation frequency of GaN and thus a finer polycrystalline mass in opposition to the results of Logan and Thurmond.

A theoretical model based upon the electrical nature of GaN and upon the surface active nature of nitrogen was designed to qualitatively fit all of these observations.

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63. STATE-TO-STATE REACTION DYNAMICS

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NSF-MRL through CMR

Technical Objective:

To understand elementary bimolecular gas-phase reaction processes and gas-surface interactions by preparing well-defined quantum states of the reactants and determining the subsequent quantum states of the reaction products.

Approach:

We prepare specific quantum states of reagent molecules using a laser. The internal state distribution of products from the resulting reaction is then inferred by laser-induced fluorescence or from visible chemiluminescence.

Research Report:

- (1) The Reaction of Alkaline Earth Atoms (Ba, Sr, Ca) with Vibrationally and Rotationally Excited HF

To obtain detailed information about the effects of internal excitation on reaction dynamics, an optical parametric oscillator (OPO) has been used to prepare HF in selected vibration-rotation states. The OPO output is continuously tunable from 1.5 to 4 microns and can be

used to excite single rotational lines in the first vibrational level of HF (ground electronic state). For this purpose, the linewidth of the OPO has been narrowed by using a beam expanding prism, diffraction grating and etalon. Sufficient energy to drive the endothermic reaction $\text{HF} + \text{Sr} \rightarrow \text{SrF} + \text{H}$ has been provided by the internal excitation of the HF reactant. The SrF product is detected by laser-induced fluorescence. This provides information about the effect of rotation on the reaction rate and on the product internal state distribution.

By pumping the reagent molecules to $v=2$, detailed information about the effect of increased vibrational excitation in conjunction with rotational excitation may be obtained. Such experiments on DF + alkaline earth metals are planned. It is also possible to prepare oriented reagent molecules using polarized infrared radiation. This allows us to obtain information on the effect of reagent orientation on the reaction dynamics of $\text{M} + \text{HF}$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Ca}$).

(2) Laser Fluorescence Studies of Surface Dynamics

Our surface analysis and molecular beam scattering chamber has been completed although the molecular beam source itself remains unfinished. In the interim, however, we have used a capillary gas doser to deliver nitric oxide at an effective surface pressure of 1×10^{-5} Torr and a chamber ambient of 2×10^{-8} Torr. This has allowed us to obtain laser fluorescence spectra of NO scattered from a clean, ordered Pt(111) surface at various temperatures. Fluorescence was excited using 214 nm light produced from a YAG-pumped dye laser output which was anti-stokes shifted seven times in a high pressure H_2 cell. Although preliminary, these spectra suggest that NO rotational accommodation on this surface is complete. We calculate that the pulsed molecular beam source, when completed, will increase the current signal to noise ratio by at least a factor of 30.

In addition to the NO/Pt(111) system, we plan to construct a smaller, although similar, surface analysis and beam scattering chamber to study the dynamics of Group V diatom scattering from III-V compound semiconductor surfaces. The dynamics of As_2 scattering from GaAs($\bar{1}\bar{1}\bar{1}$)

is of particular interest since it is known that As_2 leaves this surface with a translational energy distribution characterized by a temperature which is significantly less than the surface temperature. The results of this study will be used to elucidate the dynamics of molecular beam epitaxial growth of III-V semiconductor films and heterostructure lasers.

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SECTION D

PUBLICATIONS

SECTION D

PUBLICATIONS SINCE LAST REPORT

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SECTION E

DOCTORAL DISSERTATIONS

SECTION E

DOCTORAL DISSERTATIONS

1. M. P. Bohrer, "Transport of Macromolecules Across the Glomerular Capillary Wall," Chemical Engineering (January 1980).
2. D. L. Bourell, "Large-Strain Deformation of a Mild Steel at Intermediate Temperatures," Materials Science and Engineering (September 1979).
3. N. W. Carlson, "Two-step Polarization Labeling of Na_2 ," Physics (June 1980).
4. W.-H. Chen, "Acoustic Imaging with Grating Acoustic Scanners," Electrical Engineering (April 1980).
5. R. Chow, "Mechanical and Surface Electrostatic Behavior of Copper Single Crystals in Ultra-High Vacuum," Materials Science and Engineering (June 1980).
6. D. E. Cooper, "Excited State Dynamical Processes in Molecular Crystals: Optical Coherence Experiments," Chemistry (April 1980).
7. B. R. Copeland, "I: A Theory for the Effect of Ion Binding on Phase Equilibria in Charged Membranes; II: A Freeze-Fracture Study of Lecithin/Cholesterol Membranes," Chemistry (January 1980).
8. F. G. Courreges, "Properties of Sputtered Ito/CdTe Solar Cells," Materials Science and Engineering (January 1980).
9. D. C. D'Avanzo, "Modeling and Characterization of Short-Channel Double-Diffused MOS Transistors," Electrical Engineering (April 1980).
10. W. F. J. Deeg, "The Analysis of Dislocation, Crack, and Inclusion Problems in Piezoelectric Solids," Materials Science and Engineering (June 1980).
11. P. Denisevich, Jr., "Synthesis of Beta-Linked 'Face-to-Face' Porphyrin Dimers and Their Application to the Electrocatalytic Reduction of Dioxygen," Chemistry (September 1979).
12. J. W. DeVilbiss, "Wave Dispersion and Absorption in Partially Saturated Rocks," Geophysics (April 1980).
13. R. Fuentes-Samaniego, "Theoretical Studies of Diffusional Processes in Solids Under Stress," Materials Science and Engineering (January 1980).

14. P. H. Fuoss, "Structural Studies of Amorphous Materials Using Anomalous Scattering," Materials Science and Engineering (June 1980).
15. L. Galan-Estella, "X-Ray Photoemission and Auger Electron Spectroscopy of Multialkali Antimonide Photocathodes," Materials Science and Engineering (April 1980).
16. N. A. Godshall, "Electrochemical and Thermodynamic Investigation of Ternary Lithium-Transition Metal-Oxygen Cathode Materials," Materials Science and Engineering (June 1980).
17. S. E. Groh, "'Mercaptain-Tail' Porphyrins: Synthetic Analogs for the Active Site of Cytochrome P-450," Chemistry (June 1980).
18. E. Herbolzheimer, "Enhanced Sedimentation in Settling Vessels Having Inclined Walls," Chemical Engineering (April 1980).
19. B. Heshmatpour, "Kinetic and Thermodynamic Studies of Liquid Metal-Oxygen Systems Using Solid State Electrochemical Techniques," Applied Earth Sciences (January 1980).
20. J. N. Hollenhorst, "I. Signals and Noise in the RF SQUID; II. Quantum Limits in Gravity Wave Detection," Physics (September 1979).
21. J.-R. Hwang, "Nitrogen-Nitride, Hydrogen-Hydride and Oxygen-Oxide Reactions in Liquid Reactive Metal-Tin Alloys, and Metallurgical Applications," Applied Earth Sciences (June 1980).
22. Z. S. Jan, "Localized States and Transport in Amorphous Silicon Prepared by Glow-Discharge Decomposition of Silane," Materials Science and Engineering (January 1980).
23. B. K. Janousek, "Electron Photodetachment from Gas-Phase Molecular Anions: An Investigation of the Thermochemistry and Energy Levels of Reactive Neutrals," Chemistry (January 1980).
24. S. W. Johnson, "Modification of Surface Reactions on Ni(100) by Adsorbed Sulfur," Chemical Engineering (June 1980).
25. E. Kjartansson, "Attenuation of Seismic Waves in Rocks and Applications in Energy Exploration," Geophysics (January 1980).
26. R. H. Klundt, "Subgrain Refinement Strengthening in Stainless Steel Alloys," Materials Science and Engineering (September 1979).
27. E. I. Ko, "Adlayer Effects on the Surface Reactivity of W(100) and Mo(100) Single Crystals," Chemical Engineering (April 1980).
28. S. Ladas, "The Adsorption and Catalytic Oxidation of Carbon Monoxide on Small Pd Particles," Chemical Engineering (April 1980).

29. D. T. Ling, "Angle-Integrated and Angle-Resolved Photoemission Studies of Chemisorption on Copper and Copper/Nickel," Electrical Engineering (January 1980).
30. V. Lubarda, "Elastic-Plastic Deformation at Finite Strain," Mechanical Engineering (January 1980).
31. M. L. Marrocco, III "'Face to Face' Porphyrin Catalysts for the Electroreduction of Oxygen: MCD, Electrochemistry and Electrocatalysis," Chemistry (June 1980).
32. G. M. Michal, "Diffusionless Transformations in TiNi," Materials Science and Engineering (January 1980).
33. P. F. Michelson, "Properties of Superconducting Weak-Links," Physics (April 1980).
34. T.-G. Nieh, "The Influence of Grain Boundary Segregation and Cavity Formation on High Temperature Fracture of Silver and Copper," Materials Science and Engineering (April 1980).
35. E. H. Rezayi, "The Effects of Phonon Dynamics on the Singular Behavior of a One-Dimensional Fermi Gas," Applied Physics (January 1980).
36. B. W. Scharf, "An Insulated-Gate Thyristor Structure: Principles of Operation and Design," Electrical Engineering (January 1980).
37. N. E. Schlotter, "I. Vibrational Spectroscopy of Tetraphenyl-Group IVB Molecular Crystals; II. Electronic Properties of Triatomic Rare Gas Halides, Rg_2X , Calculated by Diatomics-in-Molecules Methods," Chemistry (January 1980).
38. C. G. Schmidt, "A Unified Phenomenological Model for Solute Strengthening, Deformation Strengthening, and Their Interactions in Type 316 Stainless Steel," Materials Science and Engineering (January 1980).
39. S. A. Schwarz, "The Auger Sputter Profiling Technique and Its Application to Studies of the Si-SiO₂ Interface," Electrical Engineering (January 1980).
40. E. M. Silverman, "Alloy Factor on the Chemisorption and Surface Reactivity of Transition Metal Surfaces," Chemical Engineering (June 1980).
41. J. E. Sutton, "Metal-Metal Interactions in Weakly Coupled Binuclear Ruthenium Complexes," Chemistry (January 1980).
42. L. W. Swenson, Jr., "Mechanics of Human Articular Cartilage," Applied Mechanics (September 1979).

43. M. E. Thomas, "A Study of Carbon Monoxide Chemisorption on Mica Supported Microsurfaces of Palladium and Nickel Using the Thermal Desorption Spectroscopy (TDS)/Transmission Electron Microscopy (TEM)/Transmission Electron Diffraction (TED) Technique," Materials Science and Engineering (January 1980).
44. M.-J. Tsai, "Photovoltaic Properties of Indium Tin Oxide/Indium Phosphide Heterojunctions," Materials Science and Engineering (September 1979).
45. A. M. Vetter, Jr., "Regenerative Beam Breakup in Multi-Pass Electron Accelerators," Physics (April 1980).
46. D. D. Walker, "Saturated Tetraaza Macrocyclic Ligand Complexes of Ru(II) and (III)," Chemistry (June 1980).
47. C. A. Waters, "Microwave Surface Impedance Studies on Copper at Low Temperature," Physics (January 1980).
48. C. J. Wen, "Chemical Diffusion in Lithium Alloys," Chemical Engineering (June 1980).
49. R. L. White, "The Use of Mechanical Alloying in the Manufacture of Multifilimentary Superconductor Wire," Materials Science and Engineering (January 1980).
50. P. K. Wolber, "A Fluorometric Study of the Structure and Acyl Chain Dynamics of Pure Phosphatidylcholine Vesicles, and Vesicles Containing Cholesterol or the M13 Coat Protein," Chemistry (January 1980).
51. D. C. Wolfe, Jr., "On the Application of Optical Computed Tomography to Remote Air Pollution Monitoring," Applied Physics (June 1980).
52. S.-J. Yang, "X-Ray Photoemission Spectroscopy of the S-1 (Ag-O-C₅) Photocathode," Materials Science and Engineering (April 1980).

APPENDICES

APPENDIX - I

I. FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH

Name	Title	Department
A. Acrivos	Professor	Chemical Engineering
H. C. Andersen	Professor	Chemistry
B. A. Auld	Adjunct Professor	Hansen Laboratories
*D. M. Barnett	Professor	Materials Science & Engineering, Applied Mechanics (Mechanical Engineering)
C. W. Bates, Jr.	Professor	Materials Science & Engineering, Electrical Engineering
M. R. Beasley	Professor	Applied Physics, Electrical Engineering
A. I. Bienenstock	Professor	Materials Science & Engineering, Applied Physics
M. Boudart	Professor	Chemical Engineering, Chemistry
S. G. Boxer	Asst. Professor	Chemistry
J. I. Brauman	Professor	Chemistry
*G. E. Brown	Assoc. Professor	Geology
+R. H. Bube	Professor	Materials Science & Engineering, Electrical Engineering
*R. L. Byer	Professor	Applied Physics
D. L. Clark	Asst. Professor	Physics
J. P. Collman	Professor	Chemistry
+S. Doniach	Professor	Applied Physics
R. W. Dutton	Assoc. Professor	Electrical Engineering
R. H. Eustis	Professor	Mechanical Engineering
C. W. F. Everitt	Adjunct Professor	Hansen Laboratories
W. M. Fairbank	Professor	Physics
*M. D. Fayer	Assoc. Professor	Chemistry

*CMR Executive Committee Member

+On Leave During Academic Year

R. S. Feigelson	Adjunct Professor	Materials Science & Engineering, Center for Materials Research
R. J. Flory	J. G. Jackson-C. J. Wood Professor Emeritus	Chemistry
C. W. Frank	Assoc. Professor	Chemical Engineering
H. O. Fuchs	Professor Emeritus	Mechanical Engineering
G. G. Fuller	Asst. Professor	Chemical Engineering
*T. H. Geballe	Professor	Applied Physics, Materials Science & Engineering
J. F. Gibbons	Professor	Electrical Engineering
R. P. Giffard	Asst. Professor	Physics
S. S. Hanna	Professor	Physics
*T. W. Hänsch	Professor	Physics
W. A. Harrison	Professor	Applied Physics
K. Heinemann	Adjunct Professor	Materials Science & Engineering
C. R. Helms	Adjunct Professor	Electrical Engineering
W. C. Herring	Professor	Applied Physics
G. Herrmann	Professor	Civil Engineering, Applied Mechanics (Mechanical Engineering)
K. O. Hodgson	Assoc. Professor	Chemistry
*R. A. Huggins	Professor	Materials Science & Engineering
*G. S. Kino	Professor	Electrical Engineering, Applied Physics
H. T. King	Asst. Professor	Physics
C. H. Kruger	Professor	Mechanical Engineering
E. H. Lee	Professor	Applied Mechanics (Mechanical Engineering)
E. I. Lindau	Adjunct Professor	Electrical Engineering, Stanford Synchrotron Radiation Laboratory
J. G. Linvill	Professor	Electrical Engineering
W. A. Little	Professor	Physics
*R. J. Madix	Professor	Chemical Engineering

D. M. Mason	Professor	Chemical Engineering, Chemistry
H. M. McConnell	Robert Eckles Swain Professor	Chemistry
J. D. Meindl	Professor	Electrical Engineering
A. S. Michaels	Adjunct Professor	Chemical Engineering
A. K. Miller	Assoc. Professor	Materials Science & Engineering
+*W. D. Nix	Professor	Materials Science & Engineering
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A. M. Nur	Professor	Geophysics
R. H. Pantell	Professor	Electrical Engineering
G. A. Parks	Professor	Applied Earth Sciences, Civil Engineering
N. A. D. Parlee	Professor	Applied Earth Sciences
G. L. Pearson	Professor Emeritus	Electrical Engineering
R. F. W. Pease	Professor	Electrical Engineering
R. Pecora	Professor	Chemistry
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W. E. Spicer	Professor	Electrical Engineering, Materials Science & Engineering
C. R. Steele	Professor	Mechanical Engineering, Aeronautics and Astro- nautics
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L. Stryer	Professor	Structural Biology
R. M. Swanson	Asst. Professor	Chemical Engineering
H. Taube	Professor	Chemistry
W. A. Tiller	Professor	Materials Science & Engineering
M. Weissbluth	Professor	Applied Physics
*R. L. White	Professor	Electrical Engineering, Materials Science & Engineering
R. N. Zare	Professor	Chemistry

APPENDIX - II

II. RESEARCH ASSOCIATES AND PROFESSIONAL STAFF

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T. Adachi	Electrical Engineering
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R. N. Anderson	Applied Earth Sciences
R. Anton	Materials Science and Engineering
E. Arimondo	Physics
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I. Bass	Applied Physics
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T. Berclaz	Chemistry
F. Betts	Applied Physics
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B. A. Boukamp	Materials Science and Engineering
L. Braicovich	Electrical Engineering
P. Bruylants	Chemical Engineering
B. Cabrera	Physics
K. D. Challenger	Materials Science and Engineering
C. C. Chiang	Chemistry
C.-H. Chou	Hansen Laboratories
C. Chun	Hansen Laboratories
T. Claeson	Ginzton Laboratory
T. J. Collins	Chemistry
B. Couillaud	Physics
C. C. Cutler	Ginzton Laboratory
R. A. Dalla Betta	Chemical Engineering
D. H. Dameron	Electrical Engineering
D. A. Deacon	Hansen Laboratories
R. H. W. S. de Jong	Geology
R. C. DeMattei	Center for Materials Research
K. Dill	Chemistry
N. S. Dixon	Physics

L. Dosza	Chemistry
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E. R. Evitt	Chemistry
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W. S. Feng	Electrical Engineering
J. Fontana	Electrical Engineering
J. R. Fox	Chemistry
H. Gerhardt	Physics
L. Gerzberg	Electrical Engineering
J. C. Gibeling	Materials Science and Engineering
P. Giuliani	Applied Physics
L. Golmayo	Electrical Engineering
M. D. Golmayo	Materials Science and Engineering
H. R. Greenstein	Materials Science and Engineering
F. Guastavino	Materials Science and Engineering
T. M. Gur	Materials Science and Engineering
D. G. Hafeman	Chemistry
T. Halicioglu	Materials Science and Engineering
R. H. Hammond	Hansen Laboratories
S. Haroche	Physics
M. S. Hassan	Applied Earth Sciences
U. Hauser	Physics
J. E. Heiserman	Electrical Engineering
A. G. Herrmann	Mechanical Engineering
P. C. Hiberty	Chemistry
J. Higdon	Chemical Engineering
I. Hino	Electrical Engineering
C. P. Ho	Electrical Engineering
C. Horwitz	Electrical Engineering
B. Huberman	Applied Physics
G. M. K. Humphries	Chemistry
D. Ilic	Electrical Engineering
P. Irvine	Chemistry
S.-Y. Jen	Applied Physics
P. Jones	Chemistry
M. Kasuga	Materials Science and Engineering
S. M. Kay	Physics

P. Ketrush	Materials Science and Engineering
B. T. Khuri-Yakub	Hansen Laboratories
J. K. Koester	Mechanical Engineering
Y. Konai	Chemistry
T. A. Koogle	Mechanical Engineering
P. Kordos	Electrical Engineering
W. Kot	Materials Science and Engineering
G. S. LaRue	Physics
J. E. Lawler	Physics
D. D. Lee	Electrical Engineering
M. C. Y. Lee	Materials Science and Engineering
H. Lefevre	Ginzton Laboratory
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T. J. Lotz	Chemistry
C. M. Lyneis	Hansen Laboratories
J. M. Madey	Hansen Laboratories
A. Makinouchi	Mechanical Engineering
R. L. Mallett	Mechanical Engineering
C. Marsal	Chemistry
A. F. Marshall	Center for Materials Research
L. Martinez	Materials Science and Engineering
R. Matheson	Chemistry
S. Matsumoto	Electrical Engineering
M. S. McAshan	Hansen Laboratories
G. M. McClelland	Chemistry
M. A. McCloskey	Chemistry
K. Meier	Chemistry
F. K. Meyer	Chemistry
P. F. Michaelson	Hansen Laboratories
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J. N. Miller	Electrical Engineering
P. Moine	Materials Science and Engineering
K. Moro	Chemistry
M. R. Mrusik	Materials Science and Engineering
L. E. Nagel	Materials Science and Engineering
C. R. Natoli	Applied Physics
W. H. Nelson	Chemistry
P. Oesterlin	Applied Physics
B. G. Ong	Chemical Engineering
A. C. Ouano	Chemistry

T. Ozawa	Chemistry
R. B. Pettman	Chemistry
R. P. Phizackerley	Chemistry
M. A. Piestrup	Electrical Engineering
P. Pirouz	Materials Science and Engineering
S. J. Poon	Applied Physics
H. Poppa	Materials Science and Engineering
I. D. Raistrick	Materials Science and Engineering
D. Ramsey	Physics
G. M. Rao	Center for Materials Research
M. Raous	Mechanical Engineering
S.-Y. Ren	Applied Physics
D. Rice	Materials Science and Engineering
G. Rossi	Electrical Engineering
R. K. Route	Center for Materials Research
S. C. Rowland	Materials Science and Engineering
O. Ruano	Materials Science and Engineering
K. C. Saraswat	Electrical Engineering
T. Sasaki	Mechanical Engineering
R. Schindler	Materials Science and Engineering
N. S. Scott	Chemistry
R. A. Scott	Chemistry
G. W. Series	Physics
T. Shibata	Electrical Engineering
J. Shott	Electrical Engineering
A. Siegel	Physics
R. Singer	Materials Science and Engineering
J. D. Smith	Materials Science and Engineering
T. I. Smith	Hansen Laboratories
J. Smits	Hansen Laboratories
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L. W. Swenson	Mechanical Engineering
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L. Templeton	Chemistry
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G. von Eynatten	Physics
J. Wadsworth	Materials Science and Engineering
C.-C. Wang	Chemistry
C. F. Wang	Physics
Z.-Y. Wang	Physics
W. K. Warburton	Materials Science and Engineering
G. A. Waychunas	Center for Materials Research
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H. M. Wu	Materials Science and Engineering
M.-R. Xia	Physics
M. J. Yacamán	Materials Science and Engineering
G.-Y. Yan	Physics
C. Yang	Materials Science and Engineering
A. Yeh	Chemistry
T. Yoneda	Chemical Engineering
C. Yuan	Chemical Engineering
W. Zakowicz	Electrical Engineering
E. Zironi	Materials Science and Engineering
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APPENDIX - III

III. GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS

APPLIED EARTH SCIENCES

B. Heshmatpour	J.-R. Hwang	V. S. Tripathi
C.-H. Hua	S. H. Slivinsky	

APPLIED PHYSICS

S. J. Bending	G. A. Hayward	B. B. Pate
K. E. Bennett	M. H. Hecht	G. A. Pavlath
R. A. Bergh	F. Hellman	D. W. Pettibone
J. E. Bowers	M. A. Henesian	M. Riazat
D. A. Browne	J.-M. Heritier	D. Rugar
W. F. Carlsen	J. A. Hildebrand	S. T. Ruggiero
L. A. Christel	Y. W. Hu	M. Schilfgaarde
K. L. Conway	D. B. Kimhi	M.-L. Shek
M. J. F. Digonnet	J. O. Kramer	G. E. Sokol
M. D. Duncan	H. A. Kunkel	D. G. Stearns
W. D. Eades	J. Kwo	J. J. Talvacchio
S. R. Early	R. A. Lacy	R. L. Thornton
C. Eberspacher	K. F. Lee	J. J. Tien
J. A. Edighoffer	M. C. Leifer	F. P. Trebino
M. J. Endemann	A. Lietoila	R. B. van Dover
M. M. Fejer	R. C. Lye	A. J. Viescas
R. D. Feldman	J. G. Manni	Y.-F. Wang
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S. Froyen	F. G. Muennemann	D. G. Weinstein
J. B. Green	S. A. Newton	D. L. Weissman-Wenocur
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CHEMICAL ENGINEERING

N. M. Abbas	L.-T. Chen	M.-A. Gashgari
E. K. Austin-Lange	S.-C. Cheng	G. E. Gdowski
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CHEMICAL ENGINEERING (continued)

E. Iglesia	M. A. McDonald	W. J. Smith
D. S. Inloes	S. T. Oyama	E. M. Stuve
S. W. Johnson	J. Sanchez-Arrieta	J. W. Thomas
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K. E. Lange	S. N. Semerak	C. J. Wen
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C. S. Bencosme	K. M. Kosydar	D. E. Richardson
S. E. Bott	G. Kubiak	M. G. Roelofs
P. J. Brothers	A. Kuki	R. N. Rosenfeld
R. R. Bucks	F. W. Kutzler	C. M. Rynard
G. S. Cartwright	H. W. H. Lee	J. L. Sessler
C. E. Chidsey	P. E. Louis	S. C. Shatas
M. S. Co	D. R. Lutz	L. M. Smith
S. D. Conradson	A. M. Madonik	S. G. Stanton
D. E. Cooper	K. R. Maier	J. E. Sutton
L. C. BeDolt	M. L. Marrocco	D. C. Torney
P. S. Drzaic	E. F. McCord	D. D. Walker
M. D. Ediger	G. D. Meitzner	G. S. Wann
A. Flamberg	R. J. D. Miller	D. C. Ware
M. E. Foley	R. S. Moog	R. S. Weber
P. Frank	E. J. Moore	J. Wishart
D. A. Geselowitz	C. R. Moylan	L. K. Woo
C. R. Gochanour	K. A. Nelson	K. A. Wright
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ELECTRICAL ENGINEERING

T. C. Anthony	G. B. Bronner	S. J. Eglash
S. Ayter	A. N. Chu	P. M. Fauchet
J. A. Borsuk	P. D. Corl	P. F. Finman
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R. C. Bray	J. M. Eggleston, III	T. M. Hall

ELECTRICAL ENGINEERING (continued)

Y.-F. Jan	D. N. Modlin	P. R. Skeath
K. G. Jew	F. Mohammadi	F. E. Stanke
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G. K. G. Krieger	S. Y. Oh	C.-Y. Su
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L. K. Lam	D. K. Peterson	R. L. Swent
H. G. Lee	B. Rezvani	M. R. T. Tan
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K. K. Liang	S. A. Schwarz	M. A. Taubenblatt
D. T. Ling	A. R. Selfridge	C. Terwilliger
R.-Y. Liu	A. P. Shah	P. F. Titchener
K. J. Malloy	S. A. Shamma	C. C. Williams
D. Mandelkern	J. C. Sheppard	F. C. Wu
M. M. Mandurah	J. A. Silberman	E. M. Young

GEOLOGY

W. E. Dibble, Jr.	K. D. Keefer	J. E. Shigley
J. R. Dyer	D. C. Pohl	C. A. Tosaya
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T. Bourbie	R. J. Knight	D. A. Seeburger
J. W. DeVilbiss	D. Moos	J. E. Stein
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MATERIALS SCIENCE AND ENGINEERING

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R. T. Barclay	S. C. Chang	L. Galan-Estella
R. W. Barton	R. Chow	S. H. Garofalini
N. L. Baumrind	F. G. Courreges	N. A. Godshall
M. C. Bost	W. J. Deeg	L. A. Gore
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MATERIALS SCIENCE AND ENGINEERING (continued)

M. K. Hibbs	R. R. Mueller	M.-J. Tsai
C. Ho	J. C. Y. Ng	B. L. Vaandrager
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Y. Ito	J. E. Nielsen	F.-C. M. Wang
Y.-F. Jan	W. C. Oliver	J. C. Wei
Z. S. Jan	T. Oyama	J. G. Werthen
V. Jayaram	F. A. Ponce	K. E. Westphal
S.-K. Joo	J. Poris	S. L. Westphal
M. E. Kassner	S. A. Raza	R. L. White
D. W. Kisker	M. T. Resch	J. E. Wittig
D. W. Kum	D. M. Rickey	C. R. Wolfe
S. Laderman	M. Rivier	C.-C. Wong
A. Landauer	M. P. Scott	J. C. Wright
M. I. Landstrass	K. L. Seaward	H. M. Wu
G. C. Lesh	S. L. Shinde	M. Y. Wu
P. W. Lew	J. D. Smith	T. Yamashita
T. C. Lowe	B. C. Snyder	K.-S. Yu
R. Maltiel	G. B. Stephenson	S. J. Yang
K. J. Mark	T. Tanaka	A. A. Ziaai-Moayyed
G. M. Michal	A. Tasooji	
F. K. Moghadam	C. Thompson	

MECHANICAL ENGINEERING

(including Division of Applied Mechanics)

I. M. Al-Khattat	J. A. Gran	R. M. Nelson
P. C. Ariessohn	M. Hemami	V. Pannaganti
V. G. Baghdasarians	K. S. Kim	N. Shaikh
J. S. Chung	R. B. King	L. W. Swenson
R. Festini	S.-B. Lee	T. B. Wertheimer
G. A. Francfort	C. Levy	
Y. S. Garud	V. Lubarda	

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M. Bassan	N. S. Dixon	W. T. Hill, III
S. Benjamin	L. S. Fritz	R. F. Hollman
N. W. Carlson	J. M. Graybeal	D. J. Jackson
W. L. Carter	J. R. Hall	K. M. Jones
A. L. De Lozanne	J. R. Henderson	P. J. Jupiter

PHYSICS (continued)

K. E. Kihlstrom
L.-S. Lee
W. P. Lowe
D. R. Lyons
L. Madison

G. P. Morgan
B. J. Neuhauser
S.-J. Oh
T. P. Orlando
W. G. Petro

D. A. Rudman
A. J. Taylor
S. A. Trugman
J. C.-C. Tsai
A. M. Vetter, Jr.

E. R. Mapoles
P. F. Michelson

J. D. Phillips
K. E. Robinson

G. A. Westenskow
K.-P. Ziock

OTHER DEPARTMENTS

AERONAUTICS-ASTRONAUTICS

J. C. McDaniels

CIVIL ENGINEERING

M. D. Cohen

PHYSIOLOGY

K. V. Lemley

APPENDIX - IV

IV. GRADUATE DEGREES CONFERRED

Doctor of Philosophy

M. P. Bohrer	Chemical Engineering
D. L. Bourell	Materials Science and Engineering
N. W. Carlson	Physics
W.-H. Chen	Electrical Engineering
R. Chow	Materials Science and Engineering
D. E. Cooper	Chemistry
B. R. Copeland	Chemistry
F. G. Courreges	Materials Science and Engineering
D. C. D'Avanzo	Electrical Engineering
W. J. Deeg	Materials Science and Engineering
P. Denisevich, Jr.	Chemistry
J. W. DeVilbiss	Geophysics
R. Fuentes-Samaniego	Materials Science and Engineering
P. H. Fuoss	Materials Science and Engineering
L. Galan-Estella	Materials Science and Engineering
N. A. Godshall	Materials Science and Engineering
S. E. Groh	Chemistry
E. Herbolzheimer	Chemical Engineering
B. Heshmatpour	Applied Earth Sciences
J. N. Hollenhorst	Physics
J.-R. Hwang	Applied Earth Sciences
Z. S. Jan	Materials Science and Engineering
B. K. Janousek	Chemistry
S. W. Johnson	Chemical Engineering
E. Kjartansson	Geophysics
R. H. Klundt	Materials Science and Engineering
E. I. Ko	Chemical Engineering
S. Ladas	Chemical Engineering
D. T. Ling	Electrical Engineering
V. Lubarda	Mechanical Engineering
M. L. Marrocco	Chemistry
G. M. Michal	Materials Science and Engineering
P. F. Michelson	Physics
T. G. Nieh	Materials Science and Engineering
E. H. Rezayi	Applied Physics

GRADUATE DEGREES CONFERRED

Doctor of Philosophy

(continued)

B. W. Scharf	Electrical Engineering
N. E. Schlotter	Chemistry
C. G. Schmidt	Materials Science and Engineering
S. A. Schwartz	Electrical Engineering
E. M. Silverman	Chemical Engineering
J. E. Sutton	Chemistry
L. W. Swenson	Applied Mechanics
M. E. Thomas	Materials Science and Engineering
M.-J. Tsai	Materials Science and Engineering
A. M. Vetter, Jr.	Physics
D. D. Walker	Chemistry
C. A. Waters	Physics
C. J. Wen	Chemical Engineering
R. L. White	Materials Science and Engineering
P. K. Wolber	Chemistry
D. C. Wolfe, Jr.	Applied Physics
S. J. Yang	Materials Science and Engineering

Engineer

K. Furuta	Materials Science and Engineering
Y. Ito	Materials Science and Engineering
J. C. Wright	Chemical Engineering

GRADUATE DEGREES CONFERRED

Master of Science

K. S. Ahn	Materials Science and Engineering
R. C. Astrawinata	Materials Science and Engineering
K. B. Baker	Materials Science and Engineering
L. H. Banta	Materials Science and Engineering
R. T. Barclay	Materials Science and Engineering
R. A. Bergh	Applied Physics
M. C. Bost	Materials Science and Engineering
J. S.-C. Chang	Materials Science and Engineering
S. M. De Jesus III	Materials Science and Engineering
M. J. F. Digonnet	Applied Physics
R. Festini	Mechanical Engineering
M. Coniche	Materials Science and Engineering
J. K. Gregory	Materials Science and Engineering
D. T. Guidry	Materials Science and Engineering
T. M. Hall	Electrical Engineering
A. C. Holk	Materials Science and Engineering
D. A. Hughes	Materials Science and Engineering
Y.-F. Jan	Materials Science and Engineering
P. M. Kampf	Materials Science and Engineering
K. Kleespies	Materials Science and Engineering
D. W. Kum	Materials Science and Engineering
K.-Y. M. Kuo	Materials Science and Engineering
S.-H. Kwon	Materials Science and Engineering
D. R. Lyons	Physics
J.-G. M. Malcor	Materials Science and Engineering
K. J. Malloy	Electrical Engineering
J. G. Manni	Applied Physics
S. G. Marshall	Applied Earth Sciences
M. L. Mecartney	Materials Science and Engineering
E. J. Moore	Chemistry
G. P. Morgan	Physics
R. R. Mueller	Materials Science and Engineering
J. C. Y. Ng	Materials Science and Engineering
W. G. Petro	Physics
L. A. Poteat	Materials Science and Engineering
S. A. Ruffo-Appel	Materials Science and Engineering
J. Sanchez-Arrieta	Chemical Engineering
G. E. Sokol	Applied Physics
F. E. Stanke	Electrical Engineering
T. Tanaka	Materials Science and Engineering

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Master of Science

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P. F. Titchener	Electrical Engineering
C. P. Warren	Applied Physics
K. E. Westphal	Materials Science and Engineering
J. E. Wittig	Materials Science and Engineering
H.-M. Wu	Materials Science and Engineering
K.-S. Yu	Materials Science and Engineering

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