Center for Advanced Materials

CAM RESEARCH NOTES

Volume 2 Number 2 October 1988

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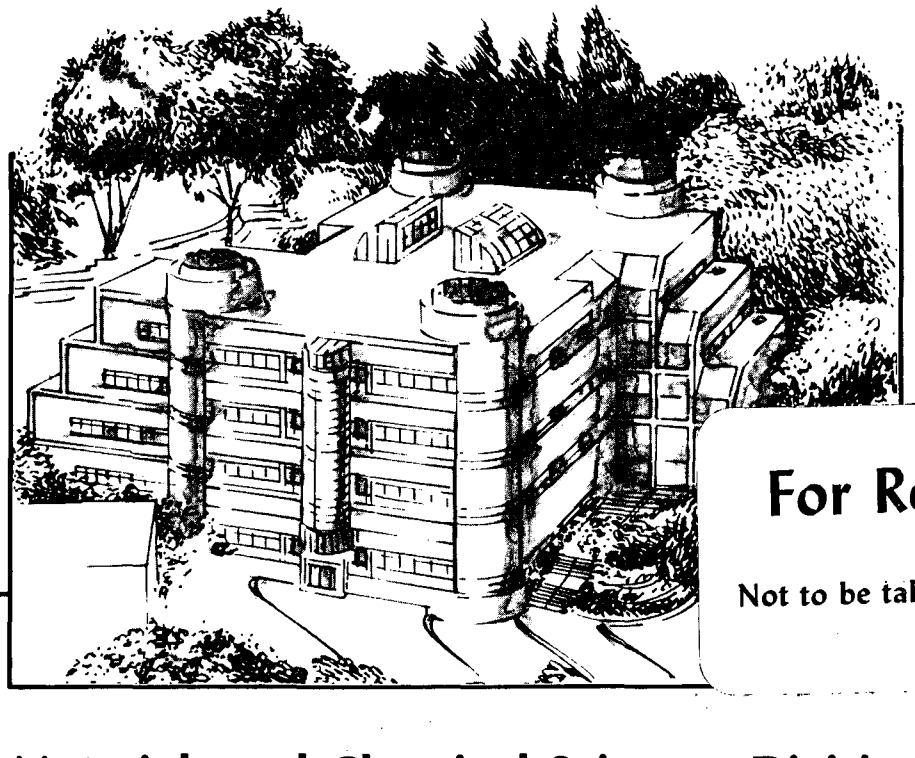

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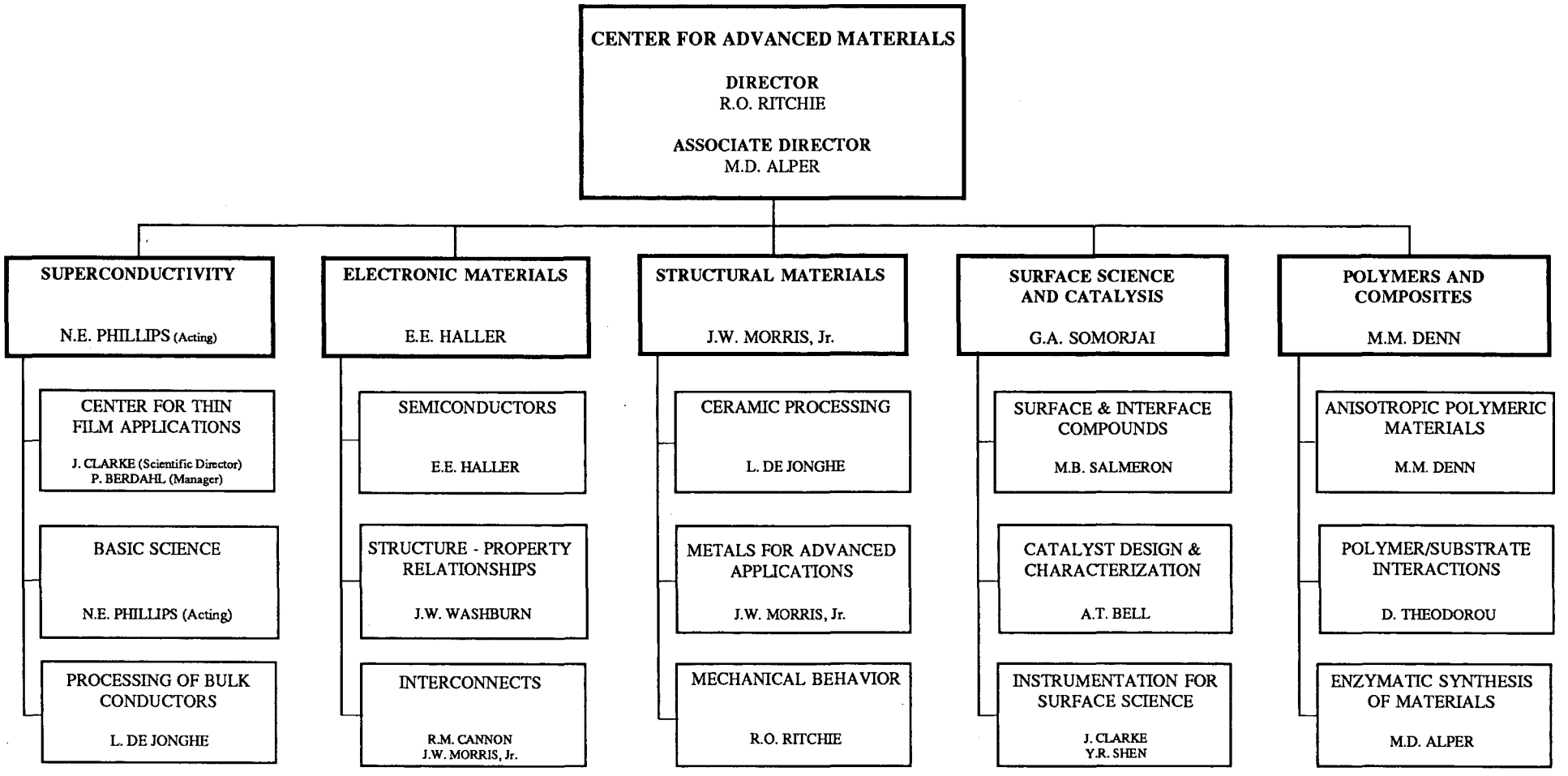
The Center for Advanced Materials was established in 1983 and receives major funding from the U.S. Department of Energy, Office of Basic Energy Science, Division of Material Sciences. Supplemental funding from other agencies is noted as appropriate. The mission of the Center is to perform basic research in areas of materials science of importance to U.S. industry. We welcome communication from any industrial research groups interested in collaborations or other interactions with the CAM programs.



October 26, 1988

Center for Advanced Materials

CAM *RESEARCH NOTE*

INDUSTRY PARTICIPATION

STRUCTURAL MATERIALS PROGRAM AWARDED GIFTS FROM FORD, LTV, ROUGE STEEL AND ALCOA

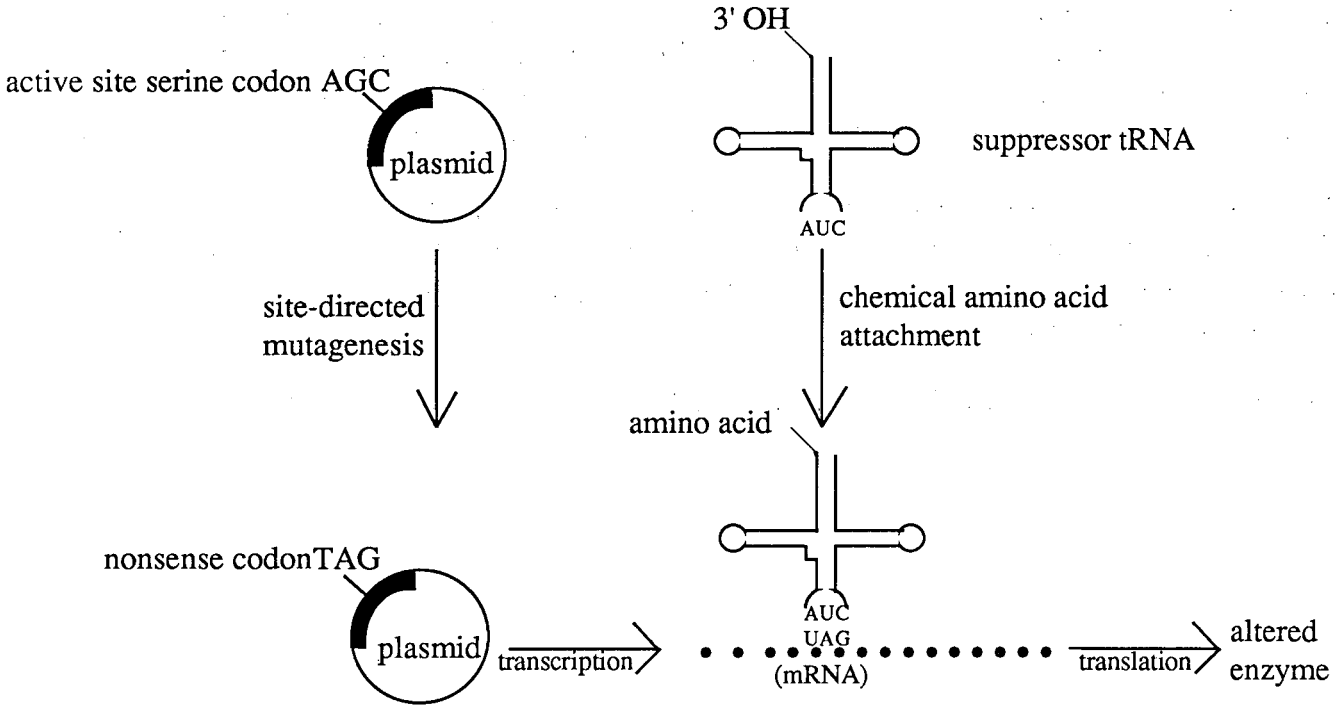
Unrestricted gifts totalling $177K were donated to the CAM Structural Materials Program during FY 1988 to support work on advanced metals. Ford Motor Company, LTV Steel Company, and Rouge Steel Company donated $102K as a group for both fundamental and application-oriented research on formability of sheet steels. Alcoa provided $75K for work on aluminum-lithium alloys.

Sheet steel formability is an important area of research for the automobile industry, where improved materials and processing techniques will permit the use of thinner sheet metal which can lead to material savings, lower manufacturing costs, and lighter, more fuel efficient vehicles. In addition, improved corrosion resistance will support the new emphasis that the industry is placing on longer lasting vehicles. According to program leader J.W. Morris, Jr., studies undertaken with the funds from Ford, LTV, and Rouge aim to simultaneously further the phenomenological and mechanistic understanding of deformation and to help solve industry-wide implementation problems with newly introduced products.

The gift from ALCOA is its second such grant to the program. It will be used to continue studies seeking to understand the basis of the exceptional low temperature properties of certain low density aluminum-lithium alloys that are good candidates for use in a variety of aerospace applications.

These awards bring the total of unrestricted gifts to CAM programs to $362,000.

CAM Industry Participation Office: Mark Alper (415) 486-6581



Substitution of unnatural amino acids in an enzyme active site. The codon for the target amino acid is altered via site-directed mutagenesis to a "nonsense codon" which codes not for an amino acid but for protein chain termination. A semisynthetic tRNA is then constructed that "reads" the nonsense codon and inserts into the protein chain the non-natural amino acid to which it has been chemically attached.

Center for Advanced Materials

CAM *RESEARCH NOTE*

POLYMERS AND COMPOSITES PROGRAM

DESIGNED PRODUCTION OF SEMISYNTHETIC ENZYMES ACHIEVED

The synthesis of novel materials through the use of enzymes depends, in many cases, on the ability to alter the active site of the enzyme, the cavity or cleft in which it binds and acts on its substrate. If this can be achieved in a rational and controlled manner, the enzyme can be made to act on the unusual, non-natural substrates that would be the precursors of the new materials.

Since the shape and chemical nature of the active site is determined by the linear sequence of amino acids that make up the enzyme, its alteration depends on changes in one of the enzyme's amino acids, usually one that actually lines the cavity that is the active site. Until now, this could be achieved only through a technique known as site directed mutagenesis, a powerful tool, but one that is severely limited by the fact that it can allow the substitution of one amino acid by only one of the other 19 naturally occurring amino acids.

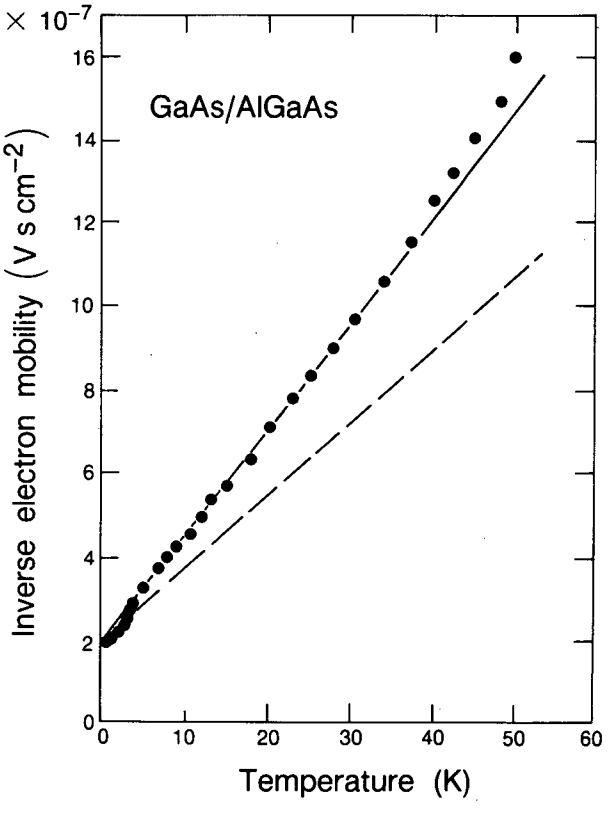
CAM scientists under the direction of Peter Schultz have now succeeded in devising a new technique that will allow the substitution of synthetic α-amino acids into a specific site in a protein chain. This is accomplished by altering the gene for an enzyme in a way that substitutes the coding sequence (codon) for the amino acid in question with a sequence that normally is not read at all (nonsense codon) and thus signals the end of the protein chain. A special "transfer RNA" is then constructed that can carry the synthetic amino acid, read the nonsense codon, and then insert that amino acid in the appropriate position in the enzyme.

This technique can be expected to have a significant impact—amino acids with a wide variety of sizes, shapes, charges, or functional groups can, for the first time, be introduced at specific locations in enzymes, vastly broadening their potential binding and catalytic capabilities.

This work was also sponsored by the Office of Naval Research and the Division of Energy Biosciences.

Schultz, P.G., et al., manuscript in preparation.

Enzymatic Synthesis of Materials, Mark Alper, Project Leader, (415) 486-6581; Peter Schultz, (415) 642-9277.



Experimental and calculated inverse electron mobility in GaAs/AlGaAs semiconductor material. Titanium and vanadium impurities were introduced into the GaAs crystals and used as a reference level for the pressure dependent measurement of the energy separation between energy levels introduced by those metals and the GaAs conduction band edge. Electron mobilities calculated from these values were shown to correlate with experimental values determined in GaAs/AlGaAs heterostructures. (XBL 8711-5943)

Center for Advanced Materials

CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

DIRECT MEASUREMENT OF SEMICONDUCTOR DEFORMATION POTENTIAL ACHIEVED

A major driving force in semiconductor research today is the need for faster devices based on faster transport of electrical current through the semiconductor crystal. There is, however a characteristic maximum transport rate for each material, limited by the lattice vibrations in the crystal (phonons) that can scatter charge carriers, thereby reducing their mobility. Although this phenomenon has been understood theoretically for over thirty years, the scattering amplitude (deformation potential) has remained an elusive and difficult parameter to determine, due primarily to the lack of an absolute reference standard upon which to base the measurement.

On the basis of recent indications that impurities, especially transition metals, in the semiconductor can provide this required absolute reference, CAM researchers, D. Nolte, W. Walukiewicz, and E. Haller have been able to devise a technique to make the first direct measurements of the deformation potentials in GaAs and InP. Specially fabricated samples of GaAs and InP with titanium and vanadium impurities were used to measure the pressure dependence of the energy separation between the titanium and vanadium and the conducting bands of GaAs and InP. From this data, values for the deformation potential and then the inverse carrier mobility of the GaAs and InP were determined. As shown in Figure 1, these values compare well to the best experimental data, demonstrating that the transition metal impurities do provide an accurate reference point for measuring deformation potential.

The importance of this discovery lies in its predictive value. Many technologically important semiconductors (InP is an example) are not available in sufficient quality to allow an estimation of their deformation potential. It is important, however, to be able to predict what the ultimate speed in the material would be if its quality could be improved. With this new technique, the maximum mobility of a material can be predicted long before that mobility could ever be achieved in practice.

D.D. Nolte, W. Walukiewicz, and E.E. Haller, *Phys. Rev. Lett. 49*, 501 (1987).

Semiconductors Processing and Characterization, E.E. Haller, Project Leader (415) 486-5294; W. Walukiewicz, (415) 486-5553.

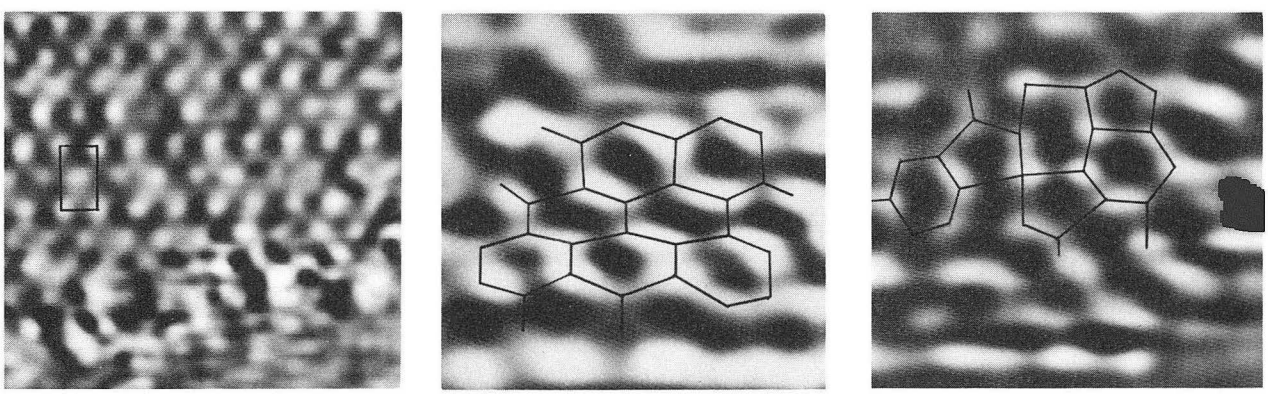


Figure 1. Periodic arrangement of S atoms (bright spots) on the Mo(001) as seen by the STM. The unit cell is shown by the solid lines and contains two atoms. Sulfur-sulfur distances are 3.14Å. (XBB 870-9763)

Figure 2. Small graphitic domain on the surface of an amorphous hard carbon film observed with the STM. The domain size is approximately 15Å. (XBB 884-2829A)

Figure 3. Disordered structure on the same hard carbon surface showing arrangements of atoms forming pentagons and hexagons. The C-C distances are typically around 1.5Å. (XBB 884-2831A)

Center for Advanced Materials

CAM *RESEARCH NOTE*

SURFACE SCIENCE AND CATALYSIS PROGRAM

DIRECT OBSERVATION OF MOLECULAR ADSORBATES WITH SCANNING TUNNELING MICROSCOPY

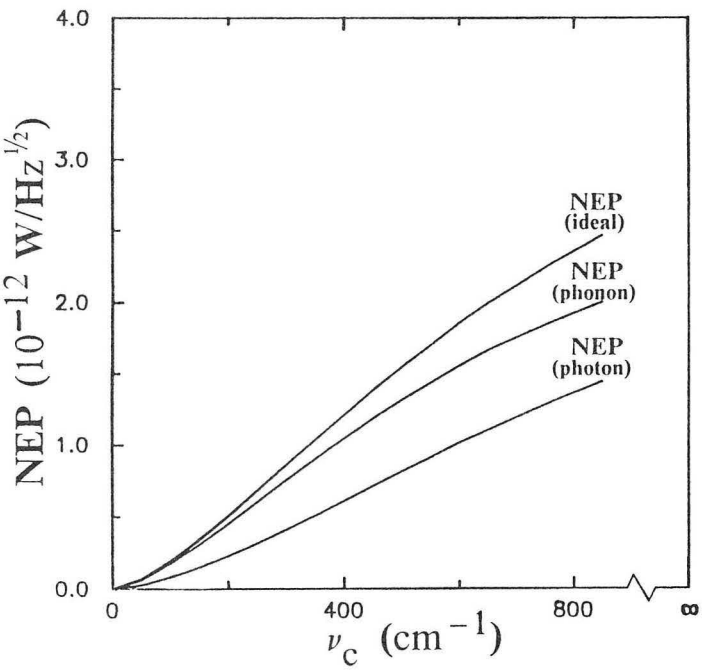
CAM scientists under the direction of M.B. Salmeron have developed a Scanning Tunneling Microscope (STM) that operates in air, in vacuum and in liquid environments to allow imaging of conductive surfaces at the atomic scale. It is being used to probe the structure of important catalytic surfaces and in particular the structure of adsorbate molecules. In this role, it represents a significant improvement over the crystalographic approach, based mainly on electron diffraction, which until now was the only tool available to study these structures. That technique was limited to periodic structures and studies in high vacuum; the STM on the other hand allows the observation of the surface atomic structure directly in real space in virtually any environment.

The CAM scientists have used the STM to image, for the first time, the surface of molybdenum and rhenium covered by a monoatomic layer of sulfur, in both vacuum and air. Imaging in air is made possible by the passivating nature of the sulfur overlayer that prevents the contamination of the surface. They have also used the new microscope to unravel the atomic structure of the surface of thin films of hard carbon coatings protecting the surfaces of computer hard discs. The amorphous nature of these films had prevented the study of their structure until now. With the STM it has been found that small domains (15Å) of graphitic carbon coexist with disordered arrangements of carbon atoms, sometimes forming pentagonal rings. Small regions having a diamond structure have also been detected.

Marchon, B., P. Bernhardt, M.E. Bussell, G.A. Somorjai, M. Salmeron, and W. Siekhaus, "Atomic Arrangement of Sulfur Adatoms on Mo(001) at Atmospheric Pressure: A Scanning Tunneling Microscopy Study", *Phys. Rev. Lett.*, vol. 60, p. 1166, March 1988. (W. Siekhaus, Lawrence Livermore National Laboratory.)

Marchon, B., M. Salmeron, and W. Siekhaus, "Observation of Graphitic, Amorphous and Diamond-like Structures on the Surface of Hard Carbon Films by Scanning Tunneling Microscopy", submitted to *Phys Rev. Lett.*, August, 1988.

Surface and Interface Compounds, Miquel Salmeron, Project Leader (415) 486-6230.



Ideal minimum noise levels for bolometers at 77K expressed as noise equivalent power. The use of high-T_c superconducting films currently available is predicted to allow construction of bolometers with NEP about 10 x 10^{-12} W/Hz$^{1/2}$, 1 to 2 orders of magnitude below the noise equivalent power of detectors currently available not requiring liquid helium temperatures. The NEP (ideal) is a function of phonon and photon noise. It can be thought of as the amount of light that would give the signal level actually given by noise in the absence of all light. (XBL 889-3427)

Center for Advanced Materials

CAM *RESEARCH NOTE*

SUPERCONDUCTIVITY PROGRAM

FEASIBILITY OF HIGH-T_c SUPERCONDUCTING BOLOMETER DEMONSTRATED

The noise mechanisms which limit the sensitivity of infrared detectors can generally be reduced by the effective use of low operating temperatures. For wavelengths shorter than 20 μm, liquid nitrogen temperature photovoltaic detectors such as HgCdTe and InSb are widely used and are very sensitive. At longer wavelengths, however, there is no satisfactory cooled detector technology above liquid helium temperatures, which are not acceptable in many applications.

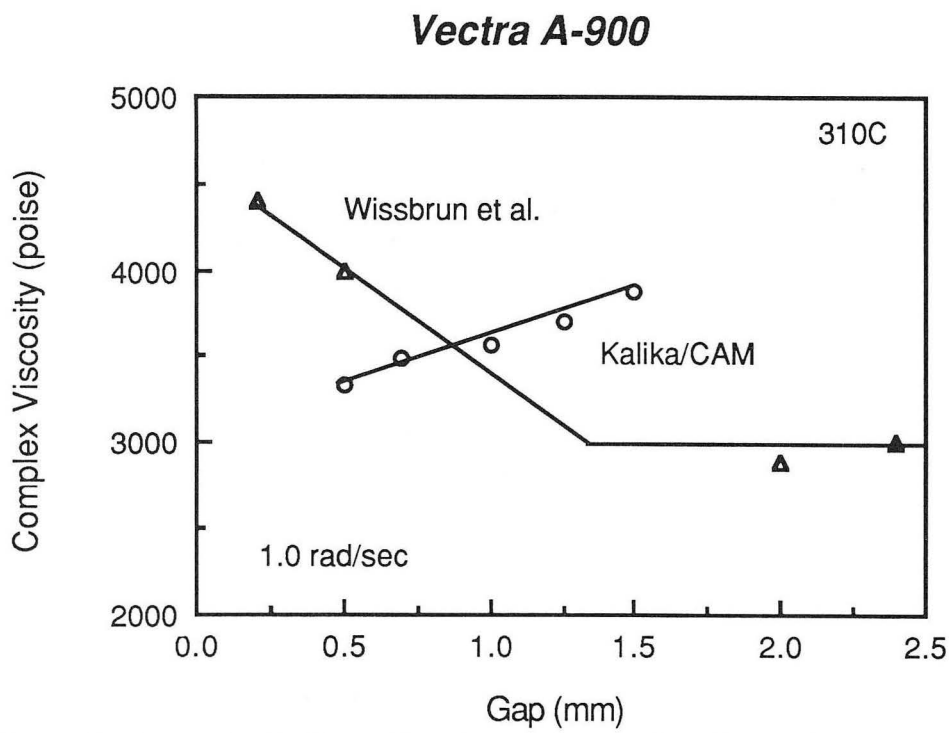
CAM scientists under the direction of P.L. Richards and J. Clarke, have performed a detailed theoretical analysis, along with experimental measurements of high-T_c superconducting films of $ErBa_2Cu_3O_7$ produced by a Stanford University group under the direction of M.R. Beasley and T.H. Geballe. They have demonstrated for the first time that a bolometric infrared detector with very useful properties can be made to operate at liquid nitrogen temperatures using high-T_c superconducting films. Unlike many proposed applications of high-T_c films, this high-T_c bolometer can be made with films that are currently available .

Measurements were made of the 1/f noise in films of the Stanford superconductors in order to predict the bolometer read-out noise. The observed noise in a high quality c-axis film deposited on $SrTiO_3$ was low enough that it would not limit performance of a liquid nitrogen cooled bolometer. It is predicted that the device will be one to two orders of magnitude more sensitive than currently available commercial infrared detectors which operate at room temperature.

Applications of this new technology include detectors for laboratory infrared spectrometers and for observations of bright sources such as the earth, from passively cooled spacecraft. These bolometers, now under construction, may represent the first practical devices constructed using the new high-T_c superconducting films.

Richards, P.L., S. Verghese, T.H. Geballe, and S.R. Spielman, "The High-T_c Superconducting Bolometer", Proceedings of the 1988 Applied Superconductivity Conference (to be published).
Richards, P.L., J. Clarke., R. Leoni, Ph. Lerch, S. Verghese, M.R. Beasley, T.H. Geballe, R.H. Hammond, P. Rosenthal, S.R. Spielman. "Feasibility of the High-T_c Superconducting Bolometer", to be submitted to *Appl. Phys Letters*. (M.R. Beasley, T.H. Geballe, R.H. Hammond, P. Rosenthal, and S.R. Spielman, Stanford University)

Center for Thin Films Applications, N.E. Phillips, Director, (415) 486-6062; Paul Richards, (415) 486-3027; John Clarke, (415) 486-3069; Simon Verghese, (415) 642-1247.



Magnitude of the complex viscosity of a liquid crystalline polymer, as measured in oscillatory shear between parallel plates at a frequency of 1 rad/sec, as a function of the spacing between the plates. The complex viscosity is expected to be gap-independent. The Hoechst-Celanese/ICI data of Wissbrun and coworkers show a surprising increase in viscosity for small gaps, as do their data in capillary flow. The CAM data on a Hoechst-Celanese polymer of the same composition, in contrast, show a decrease; CAM capillary data also show a decrease, though of smaller magnitude. Since the chemical composition of these materials is identical, synthesis or processing effects are apparently quite significant in determining properties. (XBL 889-3394)

Center for Advanced Materials

CAM *RESEARCH NOTE*

POLYMERS AND COMPOSITES PROGRAM

GAP GEOMETRY AFFECTS VISCOSITY IN LIQUID CRYSTALLINE POLYMERS USED IN ELECTRONIC INTERCONNECTS

Injection molding of small, complex parts for electronic interconnects has been the major use to date for melt-processible liquid crystalline polymers. This application exploits the unusually high degree of viscosity reduction that accompanies the shearing of these rigid-backbone polymers as they pass through the narrow opening in a mold. As a result of this decreased viscosity, the mold can be filled without excessive injection pressure.

CAM researchers, in experiments using two types of rheometers, have found that in addition to showing a decrease in viscosity with shear, the commercial copolymer Vectra A-900 (73% p-hydroxybenzoic acid / 27% 2,6-hydroxynaphthoic acid), made by Hoechst-Celanese, exhibits a further decrease in viscosity as the size of the gap decreases. This result has important implications: liquid crystalline polymers like Vectra may in fact be even more advantageous than previously thought for applications involving small spacings.

Somewhat surprisingly, researchers at Hoechst-Celanese working with colleagues at Imperial Chemicals Industries recently reported that in their hands the viscosity of a polymer of the same chemical composition increases markedly as the spacing in which flow occurs is decreased below 2 mm. This result would suggest that the processing advantage of liquid crystalline polymers may be lost, not improved, in very small channels, where major applications have been anticipated.

These results, although inconsistent, are reproducible and are unlikely to result from experimental error. Instead, this apparent contradiction supports earlier CAM studies demonstrating that large qualitative effects in liquid crystalline polymer properties can follow from subtle changes induced by synthesis or processing, mandates further research in this area.

Kalika, D.S., L. Nuel, and M.M. Denn, "Gap-Dependent Viscosity of Vectra A-900", submitted to *J. Rheology*.
Amundson, K.R., D.S. Kalika, M.R. Shen, X.M. Yu, M.M. Denn and J.A. Reimer "Influence of Degree of Polymerization on Phase Separation and Rheology of a Thermotropic Liquid Crystal Polymer", *Mol. Cryst. Liq. Cryst.*, 153, 271, (1987).

Anisotropic Polymeric Materials, M.M. Denn, Project Leader, (415) 642-0176; D. Kalika, (415) 486-4162.

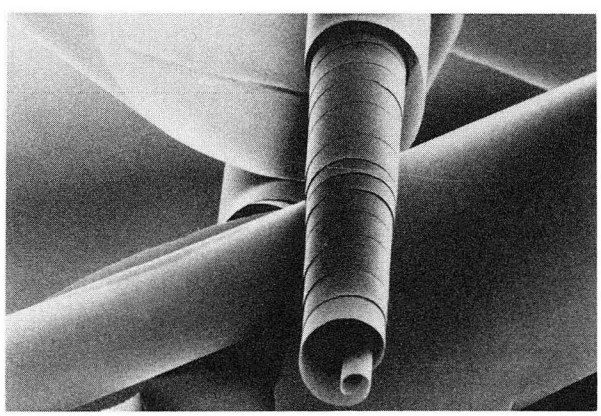


Figure 1
Examination of delaminated chromium-copper films on glass in the scanning electron microscope reveals that they curl into very tight rolls, a result of the presence of a step through-thickness strain gradient in the films. (XBB 887-6978)

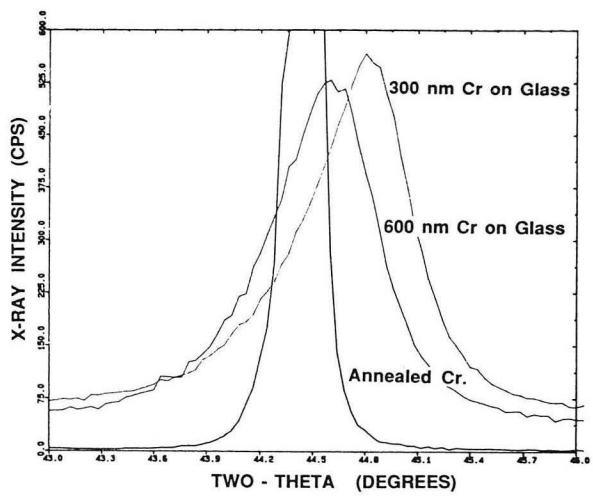


Figure 2
X-ray diffraction analysis showing a large peak shift and assymmetrical line broadening confirms the existence of the substrate to surface tensile strain gradient. (XBL 8710-4302A)

Center for Advanced Materials

CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

INTERNAL STRESSES THAT CAUSE DECOHESION SHOWN TO BE UNEVENLY DISTRIBUTED IN THIN FILMS

Adequate adhesion of thin metal or ceramic films to substrates is a key requirement for ensuring the reliability of integrated circuit devices. Film delamination during processing or in the course of operation can degrade or even destroy the performance of the IC. These failures generally result from internal stresses that are created during film formation, the origin and behavior of which must be understood in order to control them and increase film and therefore chip reliability.

CAM researchers under the direction of R.M. Fisher have studied chromium films and found that these internal stresses exhibit two unexpected characteristics that can lead to failure. One is the occurrence of a large in-plane anisotropy that develops when deposition is at an oblique angle to the substrate surface. This has been shown to lead to a premature onset of crack formation and spalling, effects that intensify with increasing film thickness.

The observation of a pronounced curling of delaminated films suggested the existence of another film anomaly: steep through-thickness stress gradients. These results suggest that the peak internal stress in the film is much larger than the apparent stress, which represents the average value across its entire thickness. The shear component of the stress at the interface is thus less than would otherwise be determined, adding to the difficulty of defining a "safe" operating regime in terms of optimum film thickness and surface preparation methods.

The presence of this stress gradient has been confirmed by X-ray diffraction and has been shown to result from differential stress relaxation during film formation. Continuing work is directed at quantifying the relationship between film deposition parameters and stress state resulting in the film with the objective of prescribing preferred preparation procedures.

R.M. Fisher, Jian-zhong Duan and C. Hetherington, "Nanograins and Boundaries in Evaporated Chromium Films", *Proc. 9th European Congress on Electron Microscopy*, Institute of Physics, York, UK, Vol. 2, page 356-360, July 1988.
R.M. Fisher, Jian-zhong Duan and G.G. Fox, "Structures and Stresses in Nanograin Thin Metal Films", submitted to *Journal of Materials Science and Engineering*, September 1988.

Interconnects Project, Rowland Cannon, Project Leader, (415) 642-9338; R.M. Fisher, (415) 486-4760.

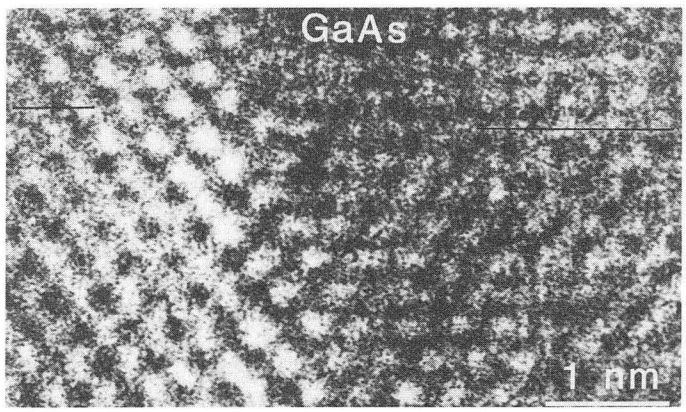


Figure 1
High resolution micrograph of APB in (110) projection. The shift of the lattice image is visible across the boundary. The observed broadening of the boundary image is probably due to strain caused by different bond length of As-As and Ga-Ga compared to As-Ga. (XBB 888-7334)

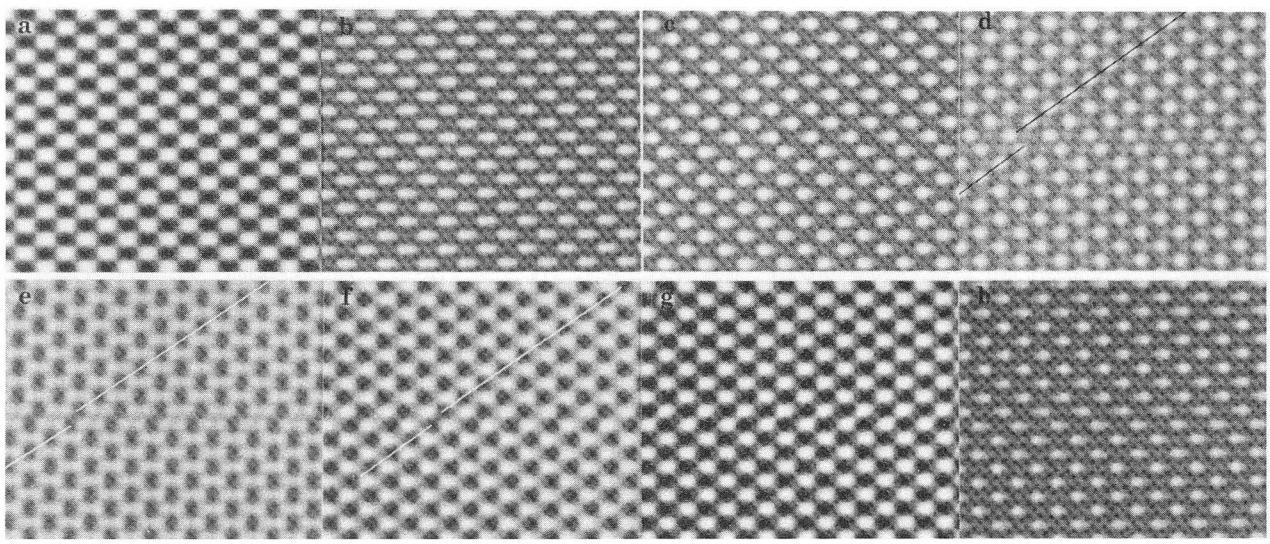


Figure 2
Simulated images of edge-on atomic resolution micrograph (110) of inversion boundary in GaAs on silicon. Sample thicknesses are a) 8 nm, b) 16 nm, c) 20 nm, d) 22 nm, e) 24 nm, f) 26 nm, g) 32 nm, h) 40 nm. As can be seen, the calculations predict that the effect can be imaged only when the sample thickness is greater than 20 nm and less than 32 nm. (XBB 888-7410)

Center for Advanced Materials

CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

INVERSION BOUNDARIES IN GALLIUM ARSENIDE GROWN ON SILICON IMAGED BY ELECTRON MICROSCOPY

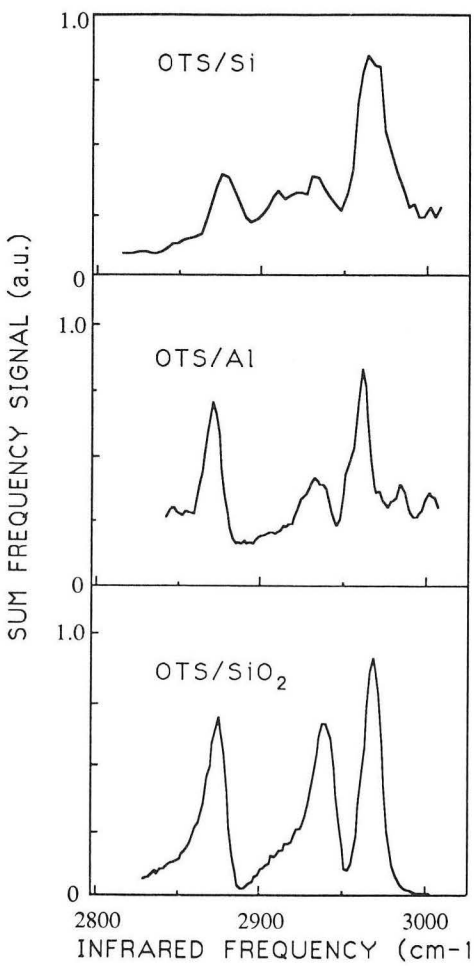
The growth of GaAs on silicon has been recognized as a highly desirable goal for a number of years. However, the large lattice misfit between these two semiconductors and the problems attendant with the growth of any polar crystal on a nonpolar substrate can result in a high density of lattice defects limiting the value of these heterostructures.

One such defect, antiphase disorder involves the replacement of the GaAs bonds of an ideal GaAs crystal by As-As and Ga-Ga bonds. These antiphase boundaries (APB's) affect the properties of the structure because they can be highly charged, and as a result collect charged impurities unless As-As and Ga-Ga bonds are close enough to neutralize each other. Much is known about these APB's and their causes, however, they have not until now been directly imaged.

CAM researchers Jack Washburn and Zuzanna Liliental-Weber, working with Michael O'Keefe of LBL's National Center for Electron Microscopy, have now succeeded in directly imaging these inversion boundaries. APB's were identified in samples by Convergent Beam Electron Diffraction (CBED) patterns and in high resolution micrographs taken on the Atomic Resolution Microscope (1 MeV). Multislice calculations for ARM conditions using the SEMPER program for the model structures of GaAs confirm the experimental observations that visibility of the image shift is dependent on sample thickness. It can be seen only in samples 21-27 nm in thickness with the strongest effect visible in those that are 24 nm.

Z. Liliental-Weber, E.R. Weber, L. Parechanian-Allen, and J. Washburn, *Ultramicroscopy*, in press.
Z. Liliental-Weber, M.A. O'Keefe, and J. Washburn, *Ultramicroscopy*, in press.

Structure-Property Relationships in Semiconductors, J. Washburn, Project Leader, (415) 642-0446, Z. Liliental-Weber, (415) 486-6276; M. O'Keefe, (415) 486-4610.



Sum-frequency spectra of the hydrocarbon octadecyltrichlorosilane (OTS), on silicon, freshly evaporated aluminum, and glass. Laser fluences for studies on the semiconductor and metal were reduced by 10 and 100 fold respectively to minimize substrate damage but the resonant vibrational features of the spectra are still clearly distinguishable. (XBL 889-3390)

Center for Advanced Materials

CAM *RESEARCH NOTE*

SURFACE SCIENCE AND CATALYSIS PROGRAM

MOLECULAR ADSORBATES ON METALS AND SEMICONDUCTORS ANALYZED WITH SUM-FREQUENCY GENERATION

CAM researchers led by Y.R. Shen have reported another new, versatile surface spectroscopic tool, infrared-visible sum-frequency generation (SFG). It is highly surface specific, applicable to all interfaces accessible to light, and has the potential to monitor in-situ dynamics, surface reactions, and intermediate surface species with picosecond time resolution.

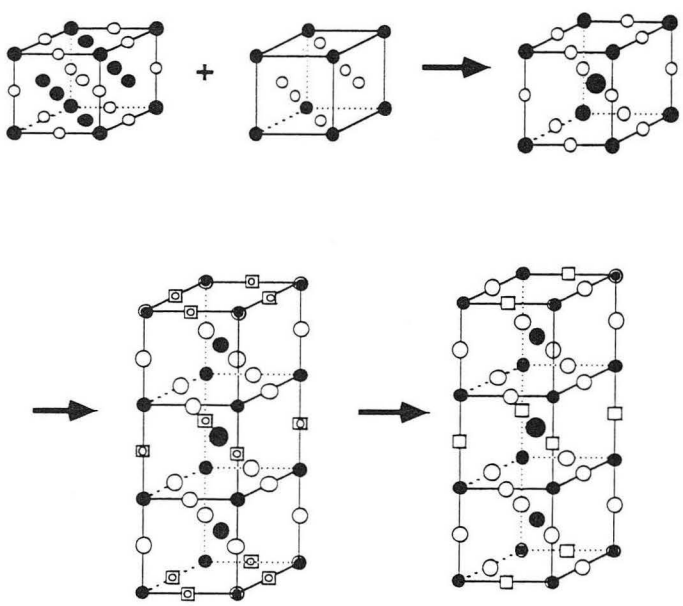
SFG has been used by the CAM group to analyze vibrational spectra of molecular monolayers of materials such as surfactants adsorbed at air/liquid, air/glass and liquid/glass interfaces. Recent research has been devoted to adapting the technique to studies of molecules adsorbed on metals and semiconductors, substrates of great interest because of their relevance to surface catalysis and surface preparation of electronic devices.

Two factors complicate the application of nonlinear optical techniques such as SFG to metals and semiconductors. First, since these materials absorb significant fractions of the incident optical pulses, laser fluences must be kept low enough to prevent damage to the experimental surface. Second, since metals and semiconductors have relatively large susceptibilities which will generate a non-resonant signal, this interference with the resonant signal of the monolayer must be minimized.

Both of these obstacles have been overcome. Spectra of the hydrocarbon chain of octadecyltrichlorosilane (OTS) adsorbed on silicon and freshly evaporated aluminum substrates were easily obtained with pulse energies 10% and 1% of those commonly used at dielectric interfaces. Even at these levels, the resonant vibrational features of the spectra are clearly distinguishable above the non-resonant background and are consistent with spectra of OTS at the air/glass interface. Spectra of ethylidyne coadsorbed with NO on Rh(111) were also successfully obtained.

Superfine, R., P. Guyot-Sionnest, J.H. Hunt, C.T. Kao, and Y.R. Shen, "Surface Vibrational Spectroscopy of Molecular Adsorbates on Metals and Semiconductors by Infrared-Visible Sum-Frequency Generation", submitted to *Surface Science Letters*.

Instrumentation for Surface Science, J. Clarke, Project Leader, (415) 642-3069; Y.R. Shen, (415) 642-4856.



Sequence of ordering reactions that create the tetragonal structure of $YB_{a2}Cu_3O_{7-x}$. (XBL 889-3392)

Center for Advanced Materials

CAM *RESEARCH NOTE*

STRUCTURAL MATERIALS PROGRAM

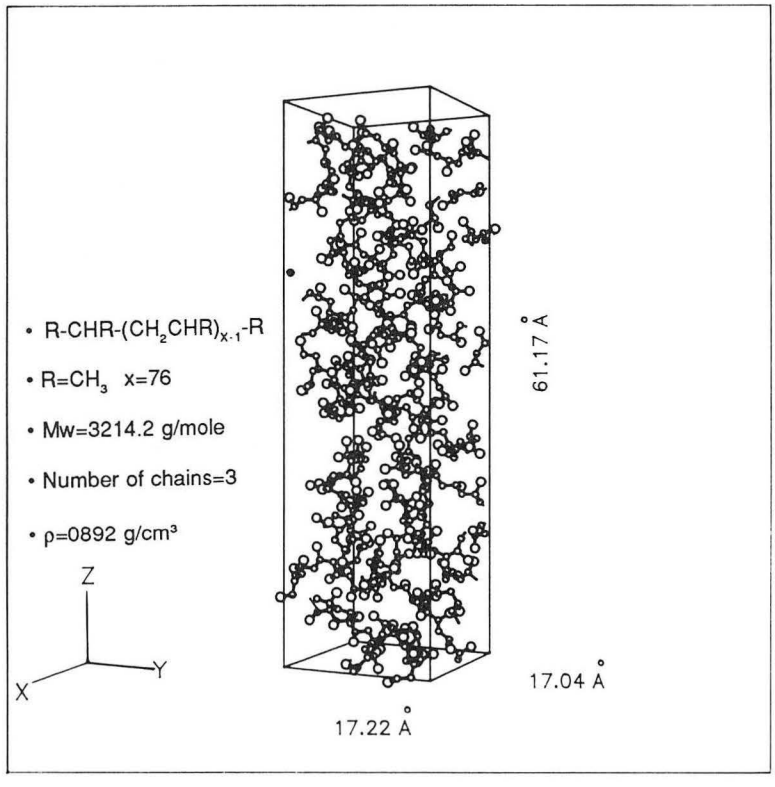
NEW THEORY CLARIFIES COMMON CRYSTAL STRUCTURES OF MULTICOMPONENT INTERMETALLICS AND OXIDES

Many of the advanced materials of greatest current engineering interest are multicomponent systems with complex crystal structures. Examples include oxide compounds that are superconductors at high temperature, intermetallic compounds for high temperature structures, and permanent magnets. To advance the materials science of these compounds it is critically important to understand and visualize their complex structures and the relationships among them.

Recent theoretical studies by CAM researchers T. Lindsey, A.G. Khachaturyan and J.W. Morris, Jr., have led to a new and more complete description of the most common crystal structures of intermetallic and oxide compounds. The theory is based on the observation that the crystal structures of many multicomponent compounds can be described in terms of simple crystal lattices that are divided into sublattices for each component by "composition waves". The theory identifies symmetry restrictions on these composition waves that guarantee that the structural energy of the compound has an extremal value with respect to small changes in the distribution of the chemical species. Structures that provide energy extrema can then be systematically drawn by selecting combinations of composition waves that satisfy the symmetry restrictions set by the theory. Since the preferred structures of ordered intermetallics and oxides have minimum structural energy, the theory readily identifies a large number of the preferred structures. It therefore provides a powerful tool that reveals the underlying simplicity of many complex structures. It has already been used, for example, at CAM to successfully predict new ordered phases in the high temperature superconducting compound $YBa_2Cu_3O_{7-x}$.

A.G. Khachaturyan and J.W. Morris, Jr., *Phys. Rev. Lett. 61*, 215, (1988).

Metals for Advanced Applications, J.W. Morris, Jr., Project Leader, (415) 486-4831.



An atomistic model has been used to explore the free surface of an amorphous glassy polymer. By translating the model box along the x- and y- directions, one obtains an infinite film of glassy atactic polypropylene, whose two faces perpendicular to the z- axis are exposed to vacuum. The film is 61.2Å thick, and consists of chains of molecular weight 3214. Ensembles of model structures such as this one are used to predict surface thermodynamic properties and to analyze molecular organization and conformation as a function of position within the film. (XBL 889-3391)

Center for Advanced Materials

CAM RESEARCH NOTE

POLYMERS AND COMPOSITES PROGRAM

SURFACE STRUCTURE AND SURFACE ENERGY OF GLASSY POLYMERS PREDICTED BY COMPUTER SIMULATION

Polymer scientists have long sought to control the interfacial properties of polymeric materials through the appropriate selection of the chemical constitution and architecture of the individual polymer chains. The asymmetry of cohesive interactions, as well as entropic constraints on chain conformation that arise at a surface, however, cause the molecular organization of polymers at interfaces to depart from what it is in the bulk. They thus require independent analysis.

CAM researchers under the direction of Doros Theodorou have developed a simulation approach for the prediction of surface thermodynamic properties of glassy amorphous polymers from the geometry and energetics of their individual chains. An ensemble of realistic multichain model structures, representative of a thin film of polymer exposed to vacuum on both sides, was generated on a Cray X-MP/48 via a combination of Monte Carlo and energy minimization techniques.

Initial results of the calculations have been encouraging. The internal energy contribution to surface tension, predicted directly from interatomic forces and distances in the model film, is within 15% of the experimental value. In addition, the simulation yields a wealth of detailed information on microscopic structure that is inaccessible experimentally. Results indicate that segment density follows a sigmoidal profile, dropping from its bulk value to zero over a region that is roughly 10 Å thick. In the surface region, the chemical bonds of the polymer backbone were shown to exhibit some tendency to orient parallel to the surface and the distribution of bond rotation angles is significantly perturbed relative to the bulk. Further, the model predicts that the chains assume flattened shapes, with their long axes parallel to the surface. Currently, this atomistic approach is being extended to graphite/polymer interfaces, to study aspects of structure and thermodynamics that are relevant to the performance of composites.

Mansfield, K.F., and D.N. Theodorou, "Molecular Simulation of Glassy Polymer Surfaces", *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 29 (2), 402, (1988).

Polymer-Substrate Interactions, D.N. Theodorou, Project Leader, (415) 643-8523; K. Mansfield, (415) 5927.

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