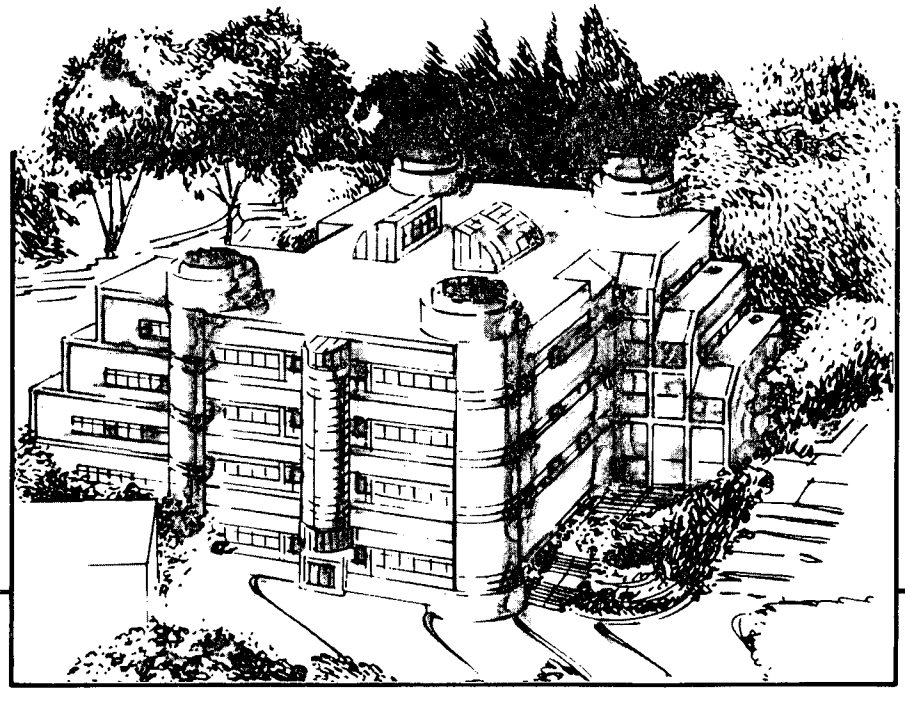
Center for Advanced Materials

CAM RESEARCH NOTES

Volume 2 Number 1 May 1988

INSIDE ...



Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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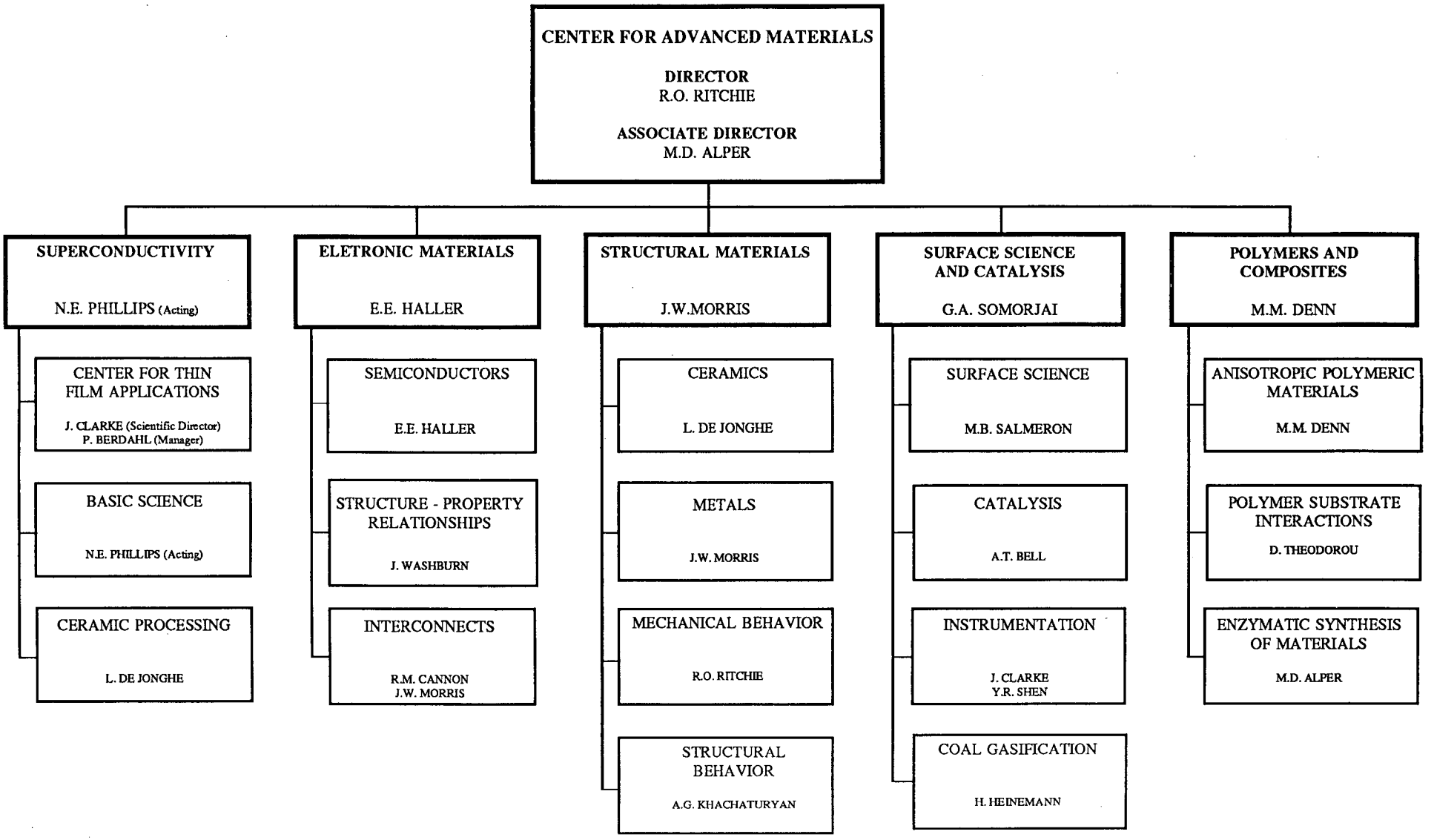
The Center for Advanced Materials was established in 1983 and receives major funding from the U.S. Department of Energy, Office of Basic Energy Sciences. Its mission is to perform basic research in areas of materials science of importance to U.S. industry. We welcome communication from any industrial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

CAM *RESEARCH NOTE*

INDUSTRY PARTICIPATION

SURFACE SCIENCE AND CATALYSIS PROGRAM RENEWS THREE INDUSTRIAL CONTRACTS

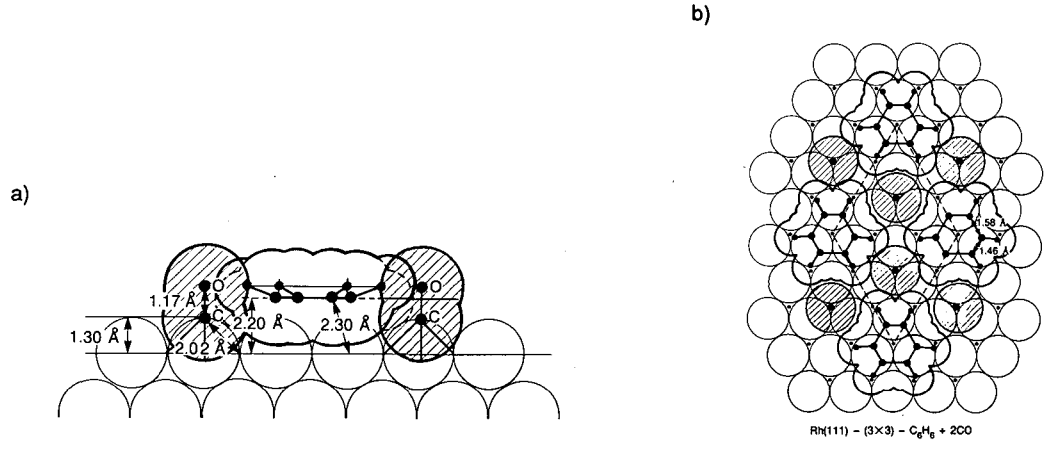
W.R. Grace has renewed its support of research in the CAM Surface Science and Catalysis Program bringing its total funding of the work to $108,000. The research, under the direction of Alexis T. Bell involves studies of the silicate and aluminosilicate species involved in zeolite synthesis. Its objective is to establish an understanding of the effect of base composition, silica concentration and solvent composition on the structure and concentration of secondary building units from which zeolites are formed.

The Harshaw/Filtrol Partnership has also renewed its funding to the program, in this case to a total of $96,000. This work, also performed under Bell's direction, involves nuclear magnetic resonance spectroscopy studies of NaY zeolite synthesis for the purpose of identifying the silicate species present in recycled NaY zeolite synthesis liquors, and determining which of these species optimizes NaY synthesis. The goal of the work is to find ways to enhance those species.

3M Corporation has renewed its contract with the program, supporting work which focuses on nonlinear optical studies of surfaces and adsorbates. This brings the total of its support of the CAM project to $68,000. Under the direction of Y. Ron Shen, the research involves studies of adsorbed organic molecules at interfaces using the surface second harmonic generation technique developed by Shen.

Research contracts between U.S. industrial concerns and CAM have been granted waivers of the Department of Energy's 25-30% "full cost recovery" charge. The waivers have been granted on the basis of CAM's stated mission to provide the basic research underpinnings for U.S. industrial research needs, and the fact that all work done at CAM is published in the open scientific literature. Companies supporting research at CAM can be given title to patents that arise from the work, subject to a non-exclusive, royalty free license retained by the government.

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



XBL 863-10701

An ordered layer forms when benzene and carbon monoxide are mixed on a Rh(111) metal surface; side view (a) and from the top (b). The dashed outline represents the periodically repeating unit cell. CO molecules are shown shaded: they stand perpendicularly to the surface between flat-lying benzene molecules (hexagonal rings of carbon and hydrogen drawn with Van der Waals contours). This arrangement ensures closest approach of the donor molecules (benzene) to the acceptor molecules (CO).

Center for Advanced Materials

CAM *RESEARCH NOTE*

SURFACE SCIENCE AND CATALYSIS PROGRAM

Gabor A. Somorjai, Program Leader

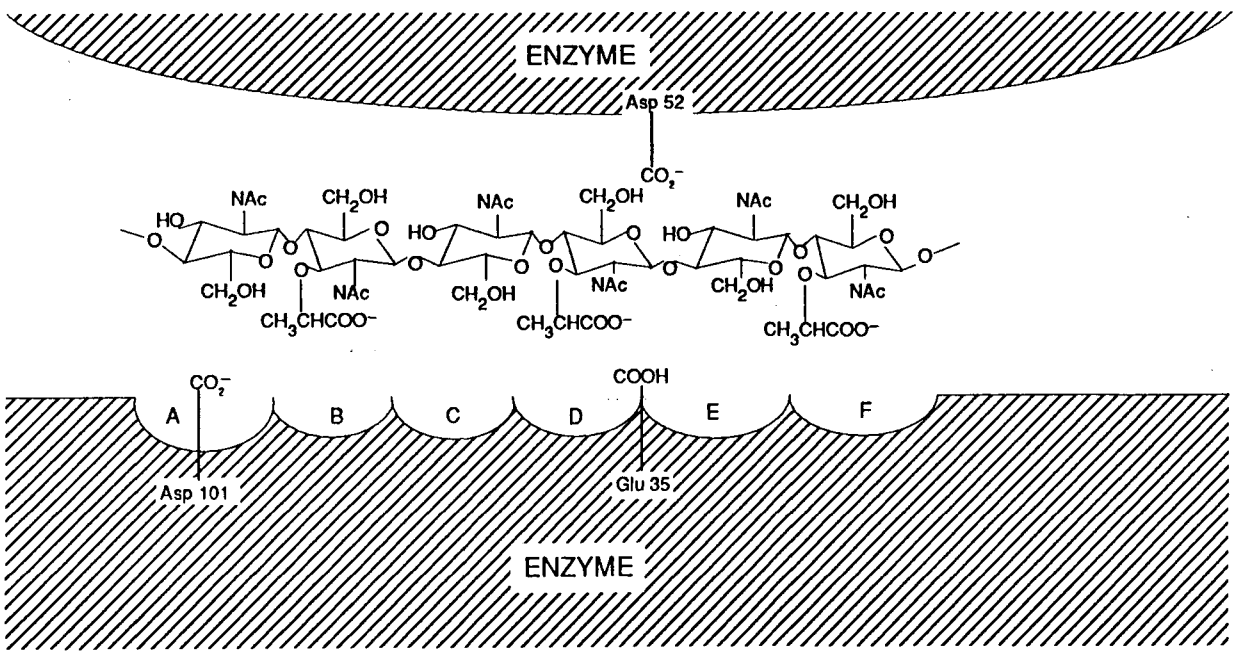
ADSORBATE-ADSORBATE INTERACTIONS REVEAL DETAILS OF CHEMICAL REACTIONS AT SURFACES

Surface science studies under ultra-high vacuum have been undertaken at CAM to elucidate the atomic-scale properties of submonolayers of molecules adsorbed at metallic and metal oxide surfaces. These studies will greatly increase our understanding and therefore control of the interactions between reactants and catalysts in a wide variety of important catalytic reactions.

In recent experiments performed under the direction of Michel Van Hove, mixtures of two different kinds of molecules were adsorbed on the same single-crystal metal surface; for instance, benzene and carbon monoxide were mixed on a Rh(111) single-crystal surface (see figure). Observations made using low-energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS) showed that these mixed layers exhibited both a unique ordering behavior and strong mutually-induced structural modifications.

The periodic ordering of the adsorbed molecules (see figure) occurs only when molecules of one of the molecular species donate charge to the metal substrate, while molecules of the other accept charge from it. The donor-acceptor combination therefore creates attractive interactions. This charge transfer can also strongly affect the structure of the molecules themselves. This is strikingly demonstrated in the carbon monoxide (acceptor)/benzene (donor) system: the C-O bond shows unmistakable signs of weakening.

Surface Science Project, M. Salmeron Project Leader, (415) 486-6230; M. Van Hove, (415) 486-6160



The lysozyme active site binds six sugars in a long polysaccharide chain that extends beyond the enzyme to both the right and left. Cleavage or synthesis occurs between sites D and E. Amino acids aspartate (Asp 52) and glutamate (Glu 35) point directly at that bond and participate in the chemistry of making or breaking it. Another aspartate (Asp 101) binds to the sugar in the A site, helping to hold the substrate in correct position for the reactions.

Center for Advanced Materials

CAM *RESEARCH NOTE*

POLYMERS AND COMPOSITES PROGRAM

Morton Denn, Program Leader

ENZYME FOR MATERIALS SYNTHESIS ALTERED THROUGH MANIPULATION OF ITS GENE

CAM scientists, under the direction of J.F. Kirsch have succeeded in using genetic and protein engineering techniques to specifically alter the active site of the enzyme lysozyme for use in materials synthesis.

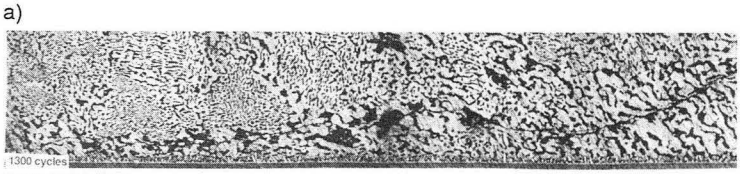
Lysozyme normally binds and catalyzes the degradation of polysaccharides such as the derivatives of cellulose found in bacterial cell walls. To use the enzyme for materials synthesis, its active, or substrate binding site must be altered so that it can bind synthetic sugars and polymerize them to make novel polymers. In order to perform this modification rationally, the mechanism by which the enzyme binds its substrate must be well understood. To elucidate this interaction, the gene for lysozyme, which had earlier been cloned and expressed by the CAM group, (Research Notes Vol. 1, No. 2) was altered in three ways. First, the two amino acids which participate in the enzyme's catalytic activity, aspartate 52 and glutamate 35, were replaced to allow isolated study of substrate binding in the absence of catalysis. Using the technique of site-directed mutagenesis, the 35th and 52nd codons of the gene were altered, leading to the replacement of the aspartate and glutamate with other amino acids that are not active in catalysis. As expected, activity was reduced 20-100 fold in each case; the mutant containing both changes has now been constructed and will be tested.

The third alteration involves aspartate 101 which binds the substrate and positions it for catalysis. It was replaced by a series of six other amino acids. The resulting enzymes were then studied for substrate binding. Binding energies have been calculated and the effect of amino acid size and charge, and solution pH evaluated. Continuing work is focused on using this information to select alterations that are best suited for binding the specific synthetic sugars selected as monomers for novel polymer synthesis.

Malcolm, B.A., S. Rosenberg, J.S. Allen, M.J. Corey, and J.F. Kirsch, "Expression and Site-directed Mutagenesis of Chicken Egg-white Lysozyme: The Catalytic Residues Asp-52 and Glu-35". Submitted to *Proc. Nat. Acad. Soc.*
Zhang, L., B.A. Malcolm, and J.F. Kirsch, "A Site-directed Mutagenesis Probe of the Role of Asparate-101 in Lysozyme Binding and Catalysis". To be submitted to *Biochemistry*.

Enzymatic Synthesis of Materials, M. Alper Project Leader, (415) 486-6581, J.F. Kirsch, (415) 642-6368

a)



XBB 860-10351

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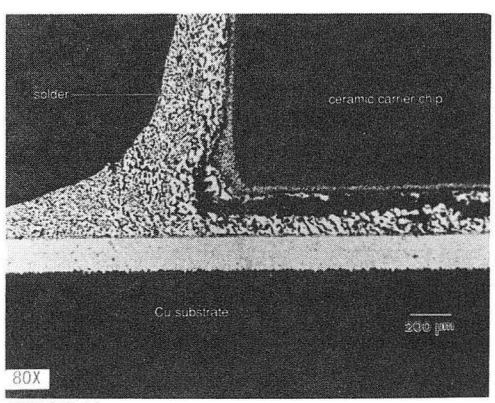

CBB 881-14

a) Thermal fatigue in a test specimen of 60Sn-40Pb solder on copper, showing grain growth in a shear band. The light constituent is Sn, the darker phase is Pb, and the dark band along the bottom is the copper. Note the coarsened structure in the band parallel to the interface between the copper and the solder. The fatigue crack, which is particularly noticeable at the right, propagates through this coarsened band.

b) Thermal fatigue in a simulated electrical contact tested at Texas Instruments (by M. Wolverton) under simulated operating conditions. 60Sn-40Pb solder joins a coated ceramic chip carrier to a copper substrate. The solder has coarsened in a band between the carrier and the substrate and has separated in fatigue.

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CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

Eugene Haller, Program Leader

GRAIN COARSENING ASSOCIATED WITH THERMAL FATIGUE IN SOLDER CONTACTS

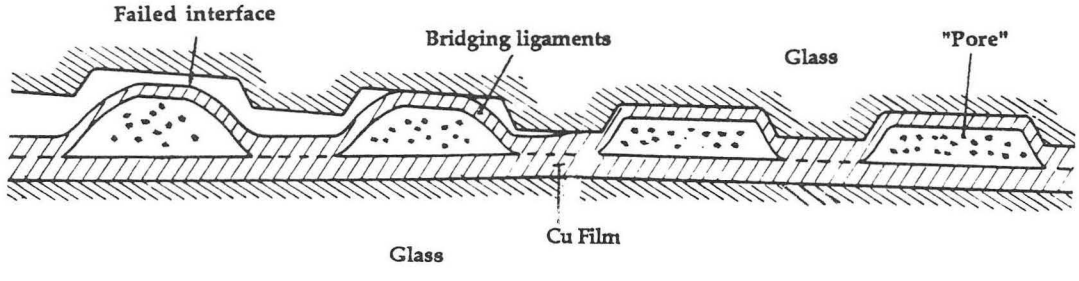
Thermal fatigue of soldered electrical contacts can be caused by the differential thermal expansion of the materials joined by the solder. As the device containing the contact is repeatedly turned on and off, this fatigue can result in breakage of the contact. Solder failure, therefore is a major problem confronting the microelectronics industry. The solution to the problem, and the resulting achievement of greater device reliability requires both the development of rapid tests to predict contact life and also the design of solders with improved resistance to thermal fatigue. Both require the development of a fundamental understanding of the mechanisms that lead to solder fatigue.

CAM researchers under the direction of J.W. Morris, Jr. have recently shown that thermal fatigue failure of typical Pb-Sn solder contacts is due to strain-induced grain growth in the solder.

The work involved the design and fabrication of a new test specimen, a "club sandwich" of Cu/solder/Cu-coated aluminum/solder/Cu that permits controlled experimental thermal fatigue of the eutectic solder in shear. Microscopic analyses of Pb-Sn solders subjected to this treatment have revealed that the mechanical shear is localized in bands, and that the temperature cycling results in rapid growth of the solder grains within the bands. This grain growth further concentrates the strain, and leads to rapid failure along the grain boundaries. The proposed mechanism has been confirmed independently by analyses of solder failures performed by collaborators at Texas Instruments, Inc. Continuing work involves application of these results to the design of more probative tests and more fatigue-resistant solders.

Interconnects Project, R. M. Cannon (415) 642-9338, and J. W. Morris, Jr. (415) 486-4832 Project Leaders

a)



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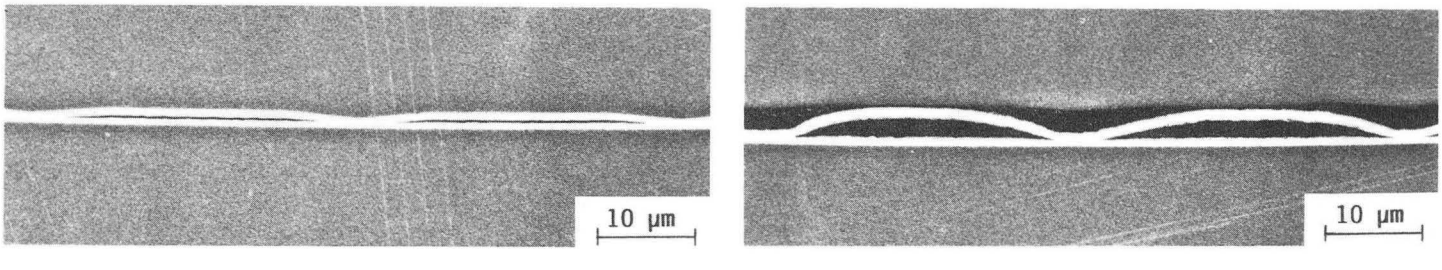

a) Schematic representation of the growth of a crack (l-r) in an interface toughened through the implantation of microcrack-like voids (pores) in the copper. The pores are formed by etching channels in the glass substrates prior to its bonding with the copper. As an interfacial crack grows, the presence of the pores leads to the production of ligaments that bridge the crack and strengthen the interface.

b) Scanning electron micrograph of interface before (l) and after failure.

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CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

Eugene Haller, Program Leader

INTERFACIAL ENGINEERING TOUGHENS CERAMIC/METAL INTERFACES

The continuing increase in the number of circuits placed on single VLSI chips has made the failure of the ceramic/metal interfaces a critical issue limiting the reliability of modern electronic devices.

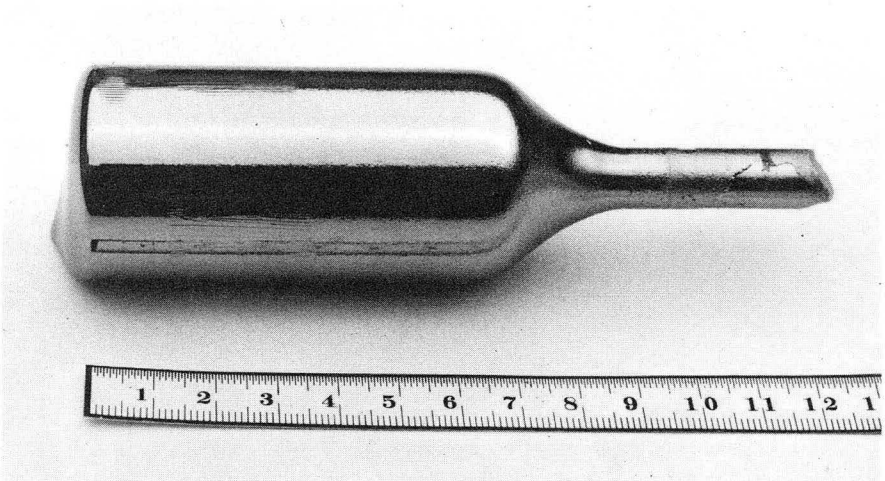
CAM researchers led by R.M. Cannon and R.O. Ritchie have developed a technique that can increase the resistance that these interfaces show to fracture by up to a factor of 80. The use of the technique can also reduce by orders of magnitude, the very high rate of crack growth seen in moist environments.

The technique, based on earlier research at LBL on the mechanical properties of glass/copper interfaces, involves implanting patterned arrays of microcrack-like "pores" by means of photolithography combined with evaporation and diffusion-bonding. These pores, resembling tiny channels within the copper, lie parallel to the interface. When a growing interfacial crack passes near the pores, their presence leads to the separation of the Cu from the glass in some but not all places. Thus "ligaments" of copper remain, bridging the gap created by the crack and holding the interface together (see figure). Continuing research is focused on achieving an expected additional order of magnitude increase in fracture resistance of these joints by adjusting the metal-film thickness, the deformation behavior of the metal, and the size and spacing of the "pores".

Cannon, R.M., T.S. Oh, J. Rodel, A.M. Glaeser, and R.O. Ritchie, "Toughening Ceramic-Metal Interfaces Using Patterned Arrays of Near-Interfacial Pores", LBL Report No. 24407, Dec. 1987, submitted to *J. Am. Ceram. Soc.*

Oh, T.S., J. Rodel, R.M. Cannon, and R.O. Ritchie, "Ceramic/Metal Interfacial Crack Growth: Toughening by Controlled Microcracks and Interfacial Geometries", LBL Report No. 24285, Dec. 1987; *Acta Metallurgica*, in press.

Interconnects Project, R. M. Cannon (415) 642-9338, and J. W. Morris, Jr. (415) 486-4832 Project Leaders; R.O. Ritchie (415) 486-5798



XBB 883-2258

GaAs single crystal grown using an advanced vertical gradient freeze technique. The first crystals produced at CAM were 1.5" in diameter. Facilities to grow crystals 3" in diameter are now under construction.

Center for Advanced Materials

CAM *RESEARCH NOTE*

ELECTRONIC MATERIALS PROGRAM

Eugene Haller, Program Leader

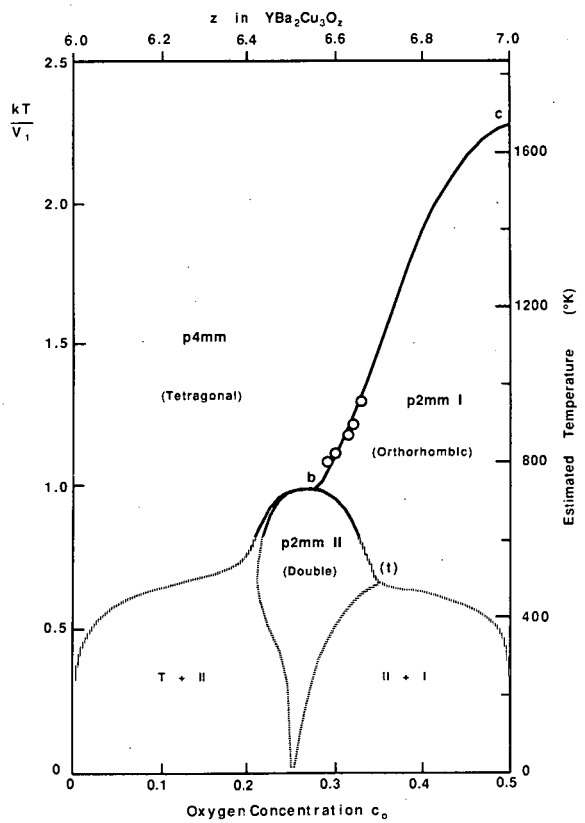
LOW DISLOCATION DENSITY GaAs CRYSTALS GROWN USING ADVANCED VERTICAL GRADIENT FREEZE TECHNIQUE

GaAs single crystals have been grown for the first time using an advanced vertical gradient freeze technique. The technique is unique in its use of a micro-processor controlled multi-heating zone furnace that allows precise and reproducible control of parameters including temperature gradients and crystal growth rate. In addition, the vessel is completely sealed, allowing the crystal growth to proceed in an arsenic atmosphere that can be controlled to achieve any desired stoichiometry of the GaAs melt and of the crystals. (Stoichiometry control has been shown to be of primary importance in reducing the density of structural defects in these crystals.)

Crystals grown using this technique by CAM researchers Edith Bourret and Joe Guitron have been shown to have a very low density of structural defects; more than half the area of wafers cut through them shows a dislocation density below 1,000/cm^2, increasing slightly towards the edges. This is to be compared with the average figure of 50,000-100,000/cm^2 in wafers from crystals produced by the Czochralski technique. Electronic characterization has shown that the electrical resistivity and the doping distribution in these wafers are very uniform, representing another significant improvement over those from crystals grown by traditional techniques. These characteristics are critical to the successful processing of gallium arsenide crystals for both opto-electronic devices and large-scale integrated circuits.

The crystals are produced in the shape of a cylinder of constant diameter and the periphery is smooth and free of voids or cracks. This geometry is optimum for subsequent, economical fabrication of devices.

Semiconductor Project, E.E. Haller Project Leader, (415) 486-5294; E. Bourret, (415) 486-5553; J. Guitron (415) 486-5555



XBL 881-49

Calculated phase diagram for superconducting compound $YBa_2Cu_3O_x$ showing cell doubling or orthorhombic phase proposed to have a superconducting transition temperature of about 60K. The open circles indicate tetragonal —> orthorhombic transitions as independently determined experimentally by Specht et al., at ORNL. The tetragonal phase is nonsuperconducting, the orthorhomic phase has a superconducting transition temperature of 90K

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CAM *RESEARCH NOTE*

SUPERCONDUCTIVITY PROGRAM

Norman E. Phillips, Program Leader

PREDICTION OF A CELL - DOUBLING ORDERED PHASE IN $YBa_2Cu_3O_x$

Calculations performed using ground state analysis have suggested the possible existence of a cell doubling orthorhombic phase in the high-T_c compound $YBa_2Cu_3O_x$. This same structure was independently deduced by H. Zandbergen and co-workers from high resolution transmission electron microscopy and diffraction performed at LBL's National Center for Electron Microscopy and also appears to be that identified independently by scientists at AT&T Bell Labs as having a superconducting transition temperature of about 60K.

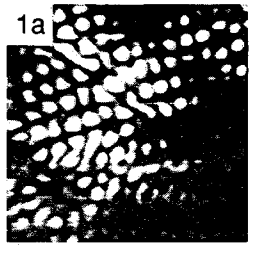
Under the direction of D. de Fontaine, the group calculated temperature-oxygen content phase diagrams featuring tetragonal (non-superconducting), orthorhombic (90K superconducting), and double orthorhombic (60K superconducting) phases. The predicted double orthorhombic phase region is situated below a bicritical point in the diagram (see figure). Subsequent determination of tetragonal —> orthorhombic transitions at various partial pressures of oxygen by scientists at the ORNL were found to agree with the predictions of the phase diagram after adjustment of the temperature scale.[1]

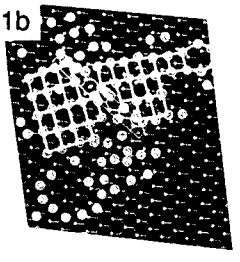
The calculated phase diagram constitutes the first experimentally supported diagram obtained for the $YBa_2Cu_3O_x$ ($6 \leq x \leq 7$) system. Phase diagrams are crucial for further progress in the field of high-temperature superconductors; these theoretical results complement experimental work aimed at elucidating phase equilibria in this system and should provide guidance for processing the material to obtain optimal properties.

1. Personal Communication, E. D. Specht, C. J. Sparks and F. Young, Oak Ridge National Laboratory.

D. de Fontaine, L.T. Wille, and S.C. Moss, *Phys. Rev. B.*, 36, 5709, 1987.
L.T. Wille and D. de Fontaine, *Phys. Rev. B., Brief Reports*, 37, 2227, 1988.
A. Berera, L.T. Wille and D. de Fontaine, *J. Stat. Phys.*, 50, 1988.
L.T. Wille, A. Berera and D. de Fontaine, *Phys. Rev. Lett.*, 60, 1065, 1988.

Basic Science of High-T_c Superconductivity, N.E. Phillips Acting Project Leader, (415) 486-6062; D. deFontaine, (415) 642-8177; L.T. Wille, (415) 642-8484; A. Berera, (415) 642-8484





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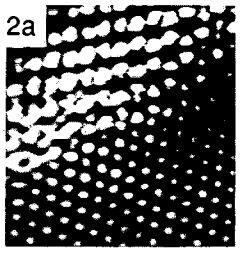
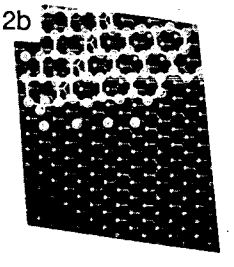




XBB 879-8306

Figure 1 a) 35Åx 35Å image of part of an island of silver atoms (white spots) deposited on a graphite surface. The island is clearly a monolayer. The underlying graphite honeycomb lattice is visible at the lower right of the image. 1b) Computer enhanced model reconstructed from 1a showing the positions of the adatoms (filled circles) on the honeycomb graphite lattice. Two ordered regions that are incommensurate with the substrate are observed in the interior of the island. The "wall" of disordered atoms between them is indicated by the shaded bar. At the edge of the island the silver atoms are disordered. This is probably because at the edge their interactions with the substrate atoms overwhelm their interaction with other silver atoms.

Figure 2 a) 35Å x 35Å image of a section of a monolayer gold island; 2b) Computer model. At the left of the shaded bar the atoms are in an almost perfect straight chain structure, while on the right the chains are more buckled but not quite in the honeycomb characteristic of the underlying graphite.

In both cases the metal films are prepared *in situ* in ultra high vacuum by evaporation to produce an average coverage of 0.1% of a monolayer. The STM is operated in the current imaging mode in which the tip scans the surface at a constant height and the variations in tunnel current are recorded. Metal adatoms appear as spots of enhanced current. The observed graphite lattice is adjusted onto its known perfect honeycomb lattice, and the adatoms are placed on the model image after undergoing the same transformation.

Center for Advanced Materials

CAM *RESEARCH NOTE*

SURFACE SCIENCE AND CATALYSIS PROGRAM

Gabor Somorjai, Program Leader

STM IMAGES EXPOSE UNEXPECTED ATOMIC STRUCTURES OF ULTRATHIN FILMS

The CAM scanning tunneling microscope (STM), which can directly image individual atoms, has been used to study the distribution and morphology of submonolayer metal films on graphite. Since both the substrate and the overlayer are imaged atom by atom, it is possible to measure with great precision the positions of the adatoms relative to the substrate, as well as the lattice parameters of the overlayer.

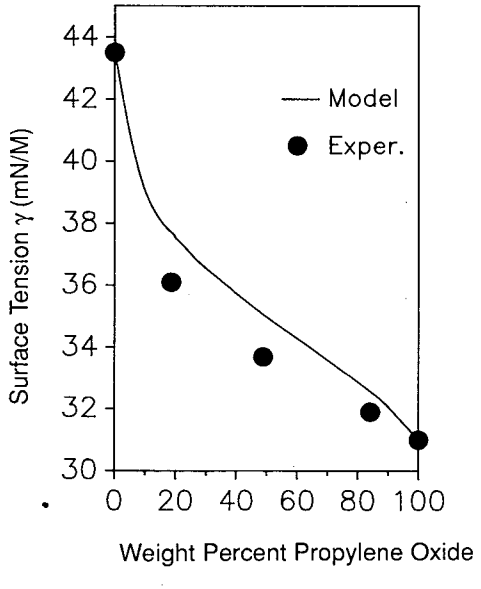
Images obtained by CAM investigators John Clarke, Eric Ganz, and Klaus Sattler have revealed a rich variety of unexpected phenomena that illustrate the complexity of deposition and morphology of submonolayer thin films and clusters. The metal atoms were shown for example, to form both small (~40Å diameter) two-dimensional islands and occasional small isolated clusters. The islands show commensurate (adatom lattice aligned in some manner with the lattice of the graphite substrate) and incommensurate phases; breaking of the adatom layer into several locally ordered domains separated by "walls" of disordered atoms (Figure 1); lattice buckling (displacement of atoms above or below their expected linear alignment, Figure 2); rotation of the overlayer relative to the substrate; and surface roughness at the edge of the island where the adatoms stray from the rigorous lattice structure found in the island's interior. Grain boundaries, defects and distortions are also visible.

The lattice structures observed are often quite unexpected and many are as yet unexplained; thus the microscope has opened a new and exciting window to the atomic structure of ultrathin films. Continuing studies are employing the STM to study the morphology, kinetics, nucleation, and growth of these films.

Ganz, E., K. Sattler, and J. Clarke, "Scanning Tunneling Microscopy of the Local Atomic Structure of Two-Dimensional Gold and Silver Islands on Graphite", *Phys. Rev. Lett.* 60, 1856, 1988.
Ganz, E., K. Sattler, and J. Clarke, "Scanning Tunneling Microscopy of Silver, Gold, and Aluminum Monomers and Small Clusters on Graphite", *J. Vac. Sci. Tech.* A6, 418, 1988.

Instrumentation Project, J. Clarke Project Leader, (415) 642-3069; E. Ganz, (415) 642-3634; K. Sattler, (415) 642-3634

(a)



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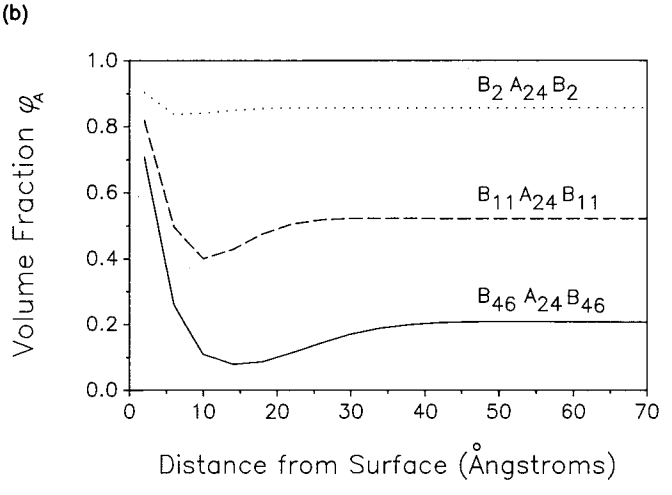


(a) Theoretical and experimental plots of the variation of surface tension with composition in triblock copolymers of propylene oxide and ethylene oxide.

(b) Surface composition of propylene oxide (A) /ethylene oxide (B) copolymers. Calculations predict that while the two monomer units in the copolymer segregate randomly in the bulk, composition of the material near the surface reflects the fact that the monomer with the lower surface tension tends to selectively gravitate towards the surface, while still covalently bound in the polymer.

Center for Advanced Materials

CAM *RESEARCH NOTE*

POLYMERS AND COMPOSITES PROGRAM

Morton Denn, Program Leader

SURFACE PROPERTIES OF POLYMERS PREDICTED BY MOLECULAR MODELING

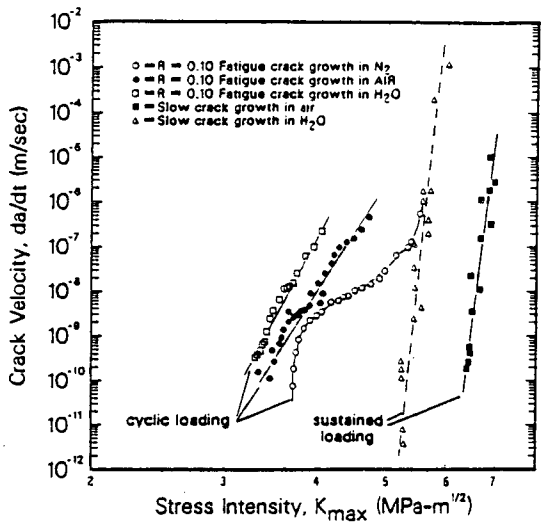
Understanding how the molecular constitution and architecture of polymers affect their interfacial behavior is a prerequisite for efficient materials design in areas such as adhesion, lubrication, industrial melt processing and surface modification to control wetting characteristics.

Polymer researchers at CAM have developed a statistical mechanical model that can predict surface and adhesion tension, and at the same time elucidate local structure at polymer melt surfaces and melt/solid interfaces. Molecular weight and the chemical identity of the monomer units making up a polymer chain are the sole inputs to the model. No adjustable parameters are involved. For homopolymers such as polyethylene and poly(dimethyl siloxane), the chain length and temperature dependence of surface tension are accurately predicted. Moreover, a detailed picture of local density, bond orientation and chain conformation is obtained and used to explain observable surface behavior.

The dependence of surface tension on chain architecture in copolymers is also captured successfully. It is shown that the strongly nonlinear variation of surface tension with composition in block copolymers is due to a preferential migration of one of the monomer types to the surface, which is impossible in random copolymers. Predictions of bond orientation in liquids consisting of surface active chains are consistent with NMR data in lipid bilayer membranes. In continuing work, the model is being used to explain intriguing recent experimental evidence on the forces exerted by ultrathin polymer films confined between solid surfaces.

Theodorou, D.N., "Structure and Thermodynamics of Bulk Homopolymer/Solid Interfaces: A Site Lattice Model Approach", *Macromolecules*, in press (1988).
Theodorou, D.N. "Microscopic Structure and Thermodynamic Properties of Bulk Copolymers and Surface Active Polymers at Interfaces", *Macromolecules*, in press (1988).

Polymer Substrate/Interactions Project, D. N. Theodorou Project Leader, (415) 643-8523



Subcritical crack growth behavior in the toughened ceramic, partially stabilized zirconia showing a comparison of cyclic crack velocities (fatigue), from the present study with sustained-load crack velocities (environmentally assisted fracture) from data of Becher, for nitrogen, 55% relative humidity air, and distilled water. Fatigue-induced crack growth is much faster than even environmentally assisted fracture under sustained loading conditions, although it too is increased in the presence of moisture. This marked sensitivity to fatigue threatens the use of ceramics in cyclic load applications such as turbine blades.

Center for Advanced Materials

CAM *RESEARCH NOTE*

STRUCTURAL MATERIALS PROGRAM

J. W. Morris, Jr., Program Leader

TOUGHENED CERAMICS SHOWN TO EXHIBIT SENSITIVTY TO FATIGUE

Efforts to capitalize on the high strength and fatigue insensitivity of ceramics for use in structural applications have been hindered by the extreme brittleness of these materials. A significant research effort in many laboratories has therefore been directed towards toughening ceramics, and thus increasing their resistance to fracture. CAM researchers under the direction of R.O. Ritchie report however, that methods now used to achieve this toughening can make the ceramic material dangerously susceptible to fatigue under cyclic loading conditions, significantly reducing their value in applications such as turbine blades which are exposed to vibrations and repeated on-off cycles.

Studies were performed on the toughened ceramic PSZ (partially stabilized zirconia), a material that is specially heat treated to decrease brittleness. They demonstrated, for the first time, the crack-growth rate behavior of fatigue cracks in this ceramic resulting from its cyclic loading under tension-tension conditions. Crack growth velocities were shown to be up to eight orders of magnitude greater than reported rates for the same material under sustained, rather than cyclic loads. Measured threshold stress intensities are also 40% lower under these cyclic conditions. In fact, the sensitivity of crack growth in these materials to environmental conditions and the dependence of the growth rate on stress intensity are analogous to that seen in fatigue of metals. Continuing research at CAM is focused on understanding the mechanism of this increase in fatigue sensitivity and assessing the extent to which it appears in other toughened ceramics.

Dauskardt, R.H. ,W. Yu, and R.O. Ritchie, "Fatigue Crack Propagation in Transformation-Toughened Zirconia Ceramic", *J. Am. Cer. Soc.*, 70 C-248-52, 1987.

Mechanical Behavior Project, R. O. Ritchie Project Leader, (415) 486-5798; R.H. Dauskardt, (415) 486-5544

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720

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