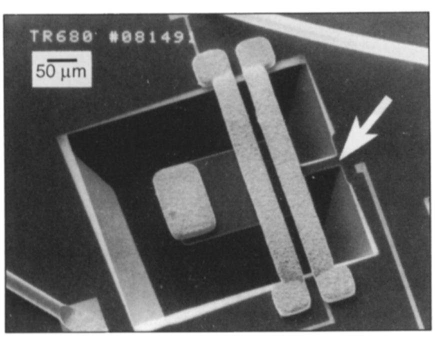
Nanosystem Measures Ultraslow Crack Growth

Massachusetts Institute of Technology (MIT) researchers are developing ultrasensitive, minuscule test systems to measure crack growth in silicon and other materials. Led by Stuart B. Brown, Department of Materials Science and Engineering, the researchers have created a system that can measure crack growth in single-crystal silicon with a resolution of nanometers. This resolution allows crack-growth detection at rates as slow as 10^{-15} m/sec, corresponding to a rate of one atomic spacing every two days—three orders of magnitude better than any other known technique, Brown said.

"There are many questions about how cracks start and grow in brittle materials," he said, and even minute cracks can cause a micromachine to fail. Micromachines, an emerging technology of microscopic mechanical devices, are already used as pressure and chemical-vapor sensors. A critical step in the design of such devices is determining whether their construction material—usually silicon—would crack and cause breakdowns. Even the tiniest fracture in a micromechanical device could disable it. After a group effort that included MIT researchers in electronics, materials science, solid mechanics, and electronic fabrication, Brown's team built the tiny crack-growth detector. The critical parts of the system cover about 400 microns.



Scanning electron micrograph of a micromechanical sample of silicon. The arrow shows where the crack is introduced.

Last year, Brown and co-worker John Connally reported in *Science* that their system had detected crack growth in single-crystal silicon exposed to moisture. The conclusion was that engineers should design sensors (and other micromachines) so that they're sealed hermetically, Brown said. The crack-growth rate measured was as slow as 3×10^{-13} m/sec. The results, Brown said, "indicate how these devices may fail, and what the operating limits are." He also noted that there may exist yet-to-be-discovered modes of failure unique to these devices. The system is composed of a 75-micron paddle-shaped cantilever beam extended over a square cavity, etched away using semiconductor fabrication technology. The beam consists of single-crystal silicon, like the surrounding material, and its unsupported end is tipped with gold for weight. The attached base of the paddle was given a small notch. Above the paddle and cavity are two thin gold electrodes, which are used to vibrate the paddle and create stresses at its base. The researchers put the system under conditions more severe than most micromachines would necessarily encounter in use.

As the crack in the base of the paddle grew, its resonant frequency changed. To determine crack growth, the researchers used a mathematical model of the structure with different crack lengths and their corresponding frequencies. "So we measure the resonant frequency of the actual specimen [at a given point in time], then use the model to tell us, given that frequency, how long the crack is," Brown said.

Biocompatible Zr-Pd-Ru Alloy Shows Resistance to Wear, Fracture

Preliminary tests of a new biocompatible alloy of zirconium, palladium, and ruthenium show that the material has extraordinary resistance to fracture and wear. Invented by Richard M. Waterstrat, physical metallurgist with the National Institute of Standards and Technology (NIST), the alloy is strong enough for dental and medical devices, and also holds potential as an industrial coating where high-performance materials are required for bearing surfaces and mechanical joints. Waterstrat's material shows strong resistance to wear, corrosion, and crack propagation, and none of the elements are known to cause toxic reactions in the body. As a hip or knee implant, the metal could meet a need for high wear resistance and wear-debris reduction. Reduction of wear debris is important because even inert debris can degrade surrounding tissues and cause failure of the replacement joint.

NIST scientists have shown that under applied stress, the alloy undergoes internal changes that increase its ability to resist further deformation and fracture. Cracks produced experimentally in alloy samples are apparently prevented from propagating by internal stress-induced transformations that occur near the crack tip.

The researchers conducted wear tests by sliding contact with a pin of polymethyl methacrylate (PMMA), a material used for bone cement in orthopedic replacement joints. Unexpectedly, results from a one-million-cycle wear test showed no net volume loss of material. Wear on the opposing PMMA pin was also low. Moreover, a five-million-cycle wear test showed no net loss of alloy material.

The metal, however, cannot easily be machined on a lathe, because cutting tools produce transformations on the surface that further harden the metal. However, the alloy can be readily shaped by grinding. Richard Waterstrat can be contacted at: B148 Polymer Building, NIST, Gaithersburg, MD 20899; telephone (301) 975-6831.

Molecular-Sized Water-Cleaning Microreactors Created

Chemists at Cornell University have created molecular-sized microreactors that remove organic substances from water. The microreactors are composed of giant spherical, hollow molecules that could serve as sites for performing highly controlled chemistry, according to Jean Frechet, professor of chemistry at Cornell.

The microreactors are "dendritic polymers" in which polymeric chains branch in all directions, instead of forming a more typical straight chain molecule. "The molecule adopts a treelike structure and as it grows, its branches fill space until the overall structure is spherical," Frechet said. Controlling the structure of the branch tips as the molecule grows is, however, a formidable problem, so Frechet and his colleagues have taken a new approach to synthesizing dendritic spheres by creating wedges and then assembling them into a sphere.

The advantage of the process is that the researchers are able to precisely control the composition of the surface of the sphere as well as the interior. To test this approach, they constructed a dendritic sphere that was water-attracting on the exterior and water-repelling on the interior. This structure is known as a micelle and is the same structure utilized by soap, enabling it to solubilize grease molecules, which seek out the interior of the micelle. The researchers found that an organic substance (pyrene), which is hardly soluble in water, migrated from water to the interior of the dendritic sphere. Their success in clearing pyrene suggests that the technology could be used to remove organics such as polychlorinated biphenyls from water, but Frechet expects the technique will be best utilized for microreactions.

For instance, his team has built the prototype of a sphere that is half hydrophilic and half hydrophobic. Such a sphere floats between the boundary of an oily organic liquid and water, coaxing a molecule from each layer to come into the interior. Once inside, the two molecules that normally would not interact could, in theory, be made to form a new product.

Dubbing the spheres "microreactors," Frechet predicts that they will be used to conduct organic chemistry in water, that now often can be done only in toxic and hard-to-dispose-of organic solvents.

The team also has built a spherical molecule in which the opposite halves of the spheres have opposite electrical charges. These giant dipoles orient themselves in an electrical field and may form the basis of new optical switches or data-storage systems, he said. Other spheres with alternating charged sectors could become molecular-size motors.

Met-Cars Produced in Quantities Large Enough for Research

Pennsylvania State University chemists have developed a method for producing metallo-carbohedrene molecules (met-cars) in quantities satisfactory enough for characterization tests. Last year, the researchers, headed by A. Welford Castleman Jr., announced their discovery of the hollow metal-and-carbon molecular cages. But their technique produced such small numbers of the molecules that they could only be studied as a gas.

The chemical properties of met-cars have interested both theoretical and corporate researchers, whose calculations predict that the electronic properties of these molecules should make them good catalysts, semiconductors and, possibly, superconductors. "But it was impossible to know for sure until we could make enough of the material to test its bulk physical properties," Castleman said.

Met-cars are produced by arcing electrode rods in a reactor. The Penn State researchers have come up with a mixture of carbon and metal powders (they had tried titanium and vanadium) pressed and baked into rods that can, with the right voltages, create larger met-car amounts. "Soot" results from the arcing, but earlier analytical techniques could not single out the met-cars within it. Castleman said that laser desorption allowed met-car detection. After its implementation, experimentation "was a long, tedious procedure," he said. "One day we would see a big peak in the data that would make us think we had really done it, then we would get no results at all after we had tried to fine-tune the recipe." The group can now make powders that contain 1% of the molecule.

Having established reproducible results, the group must address met-car isolation. "What we are looking for now is a good solvent for met-cars," Castleman said. The solvent would extract the met-cars from the soot much like water extracts salt from a mixture with sand. "You can pour off the water to separate the salt from the sand. Once we have met-cars in solution, they will be a lot easier to analyze," he said. "If we can get it out of the mixture, we will have enough to test it with techniques such as x-ray diffraction and nuclear magnetic resonance, which could confirm its structure and give us more clues about whether it has important scientific and technical applications," he said.

Electron-Assisted Etching May Reduce Surface Damage of Electronic Devices

An electron-assisted etching technique under development at the Georgia Institute of Technology may permit routine fabrication of nanometer-scale microelectronic devices without the surface damage caused by current etching systems. Conventional ion-beam etching processes used for fabricating the structures can damage their surfaces, altering optical and electronic properties. The Georgia Tech process, however, uses low-energy electrons (10–500 eV) in combination with reactive hydrogen gas (H_2) to etch features. The lighter electrons do not produce the same types of damage to the semiconductor surface.

"We can deliver simultaneously a beam of low-energy electrons and a beam of reactive molecules," said H.P. Gillis, Georgia Tech associate professor of chemistry. "These two species come together at the surface and the electrons stimulate the chemistry between the reactive beam and the surface. The reaction happens only at locations where both the electron beam and the reactive gas arrive."

The group successfully transferred patterns to a silicon substrate by guiding the beams carefully through a rudimentary mask. The researchers are progressing well with etching rates and pattern transfer, Gillis said. Also, an examination of surface structure before and after the etching shows little damage.

The group must still make a working electronic device and analyze its performance. The potential surface effects of the reactive hydrogen must also be studied but, Gillis said, "Hydrogen is attractive because the chemistry is simple compared to the species used in the conventional technique."

Gillis says the electron-assisted etching technique would be an alternative, not a replacement, to conventional etching for the current generation of VLSI semiconductor devices, and an alternative to the ion-assisted plasma techniques for the future generation of nanometer-scale devices.

Piezoelectrics' Displacement and Load Capacity Increased Tenfold over Standard

Research Corporation Technologies (RCT) reports a new process that transforms standard piezoelectric wafers into domed structures that exhibit a tenfold increase in displacement and load capacity over conventional piezoelectrics. Called RAINBOWs (reduced and internally biased oxide wafers), they support moderate loads while achieving large displacements with modest applied voltages.

Monolithic RAINBOWs are structurally similar to standard piezoelectric unimorphs. However, the new process yields structures capable of supporting loads of up to 20 pounds while still achieving large displacements (1–50 mils, depending on load). Performance can be augmented by stacking multiple RAINBOWs.

RAINBOWs are produced by a simple process that yields a stress-biased electrically conducting layer on one surface in about an hour. This process is similar to existing methods for making piezoelectrics. Characterization is available for resistance of the electrode layer, materials constants, load capacity versus thickness, and displacement versus diameter and thickness. Optimization continues on properties such as linearity, hysteresis, lifetime, frequency response, mechanical efficiency, and treating conditions. Multiwafer motors and pumps have been successfully tested.

RCT has filed patents on behalf of Clemson University and inventor Gene Haertling, and solicits partners to develop the technology in exchange for intellectual property rights. For more information, contact Eugene Cochran, telephone (602) 296-6400, or fax (602) 296-8157.

Sensors Unlimited Is Awarded Two SBIR Contracts for Infrared Research

Sensors Unlimited, Inc. has been awarded two Phase II Small Business Innovation Research (SBIR) contracts for the development of infrared technologies. The first contract is from NASA's Jet Propulsion Lab for the development of an optical "integrated circuit" photodetector array used in infrared cameras for night vision, satellite imaging, and pollution monitoring. The half-million-dollar contract will also involve facilities at Princeton University. The second contract—worth almost three-quarters of a million dollars, from Kirtland Air Force Base—is to develop high-power mid-infrared lasers for detecting polluting gases such as methane and carbon dioxide at part-per-billion levels.

Company president Greg Olsen said both contracts will result in commercial products that fit in with New Jersey's expanded effort to monitor and control environmental pollutants. Sensors Unlimited, a one-year-old firm, was assisted during its startup and contract proposal preparation by the New Jersey Commission on Science and Technology.

Scientists Move Atoms with Photons

A scientific team from AT&T Bell Laboratories and Harvard University is using light beams to position individual atoms, deflecting the atoms with the force exerted by photons as they deposit these atoms onto a substrate, according to Gregory Timp, a researcher in AT&T's Microstructure Physics Research Department.

Physics demonstrates that a photon

carries momentum, and this force is sufficient to move an atom if the atom is moving slowly enough. A large number of photons—a standing wave—can act like a lens to focus atoms, raising the possibility of developing a fundamentally new type of lithography for microelectronics. Progress in lithography means ever-finer lines and patterns. In the past several decades, minimum line widths have decreased from 25 microns to 0.5 microns.

"It has long been recognized that we will run into trouble below a tenth of a micron," Timp said. "In devices that small, the position of every atom matters. We're taking the first small steps in this direction." Horst Stormer, director of AT&T's Physical Research Laboratory, said that while the new technique changes the way people think of doing submicron lithography, "We're a long way from developing and manufacturing products with it—but it's exciting research."

In March, Timp delivered a paper, "Using Light as a Lens for Atom Optics," at a meeting of the American Physical Society in Seattle. His co-authors were Robert E. Behringer of the Optoelectronics Research Department at AT&T Bell Labs and Karl Berggren and Mara Prentiss of the Physics Department, Harvard.

Sensitivity of Smart Materials Doubled

Nancy Sottos, professor of theoretical and applied mechanics at the University of Illinois, reports doubling the sensitivity of smart materials used by the U.S. Navy to detect sonar-generated sound waves traveling through water. The smart materials detect sonar waves and respond by sending back additional sound waves designed to confuse the sonar.

Sottos works with small ceramic rods embedded in epoxy resin that respond to sonar or other pressure waves by causing a voltage drop proportional to an incoming signal's intensity and frequency. This piezoelectric effect is used to detect the characteristics of an incoming signal. The more sensitive the smart-rod composite, the more precisely it can respond. To make the sensors more sensitive, Sottos inserts a rubbery material between the ceramic sensor rods and the rigid block that contains them. The less rigid material permits the rods to expand along their vertical axes without cracking or being hindered by the rigid epoxy that surrounds them. The more the rod expands, the tinier the signals it can identify.

Rigid epoxy resin was chosen because the matrix discourages an undesirable rod response—contraction, or shortening and thickening—when the soundwaves are detected. A polymer composed solely of soft epoxy resin would allow the rods to lengthen without hindrance, but would not prevent their swelling as they shorten. Since rods lengthen by a factor of 100 times greater than they contract, scientists discourage contraction by providing a stiff matrix that resists intrusion. Sotto's compromise mediates between extremes of hardness and softness. The more sensitive the sensor, the fewer rods that need to be used, saving weight, electricity, and materials cost.

Synthesis of Fullerene Derivative Supports Theoretical Prediction

Researchers at Sandia National Laboratories used both theoretical modeling and organoborane chemistry to create a fullerene dihydride, a compound composed of a 60-atom cage with two hydrogen atoms attached. The resulting molecule was found to occur in only one of 23 possible configurations, confirming the researchers' ability to accurately forecast reaction products, and raising the possibility of similarly engineering other derivatives of fullerenes.

Chemist Paul Cahill said, "This is the first demonstration of using organoborane chemistry to attach another functional group selectively to buckyballs. We've opened the door to making a lot of other compounds, as well as controlling the reaction." An article describing the work of Cahill and chemist Craig Henderson was published in the March 26 issue of *Science*.

The fullerene dihydride synthesized by Cahill and Henderson represents the simplest hydrocarbon derivative of C_{60}. Using organoborane chemistry, a versatile synthesis method, the researchers reacted C_{60} to create an intermediate product. When hydrolyzed, $C_{60}H_2$ resulted. Prior calculations performed by the researchers predicted that one of 23 possible isomers of the molecule would predominate. The experimental results demonstrated that the predicted isomer did occur.

Cahill and Henderson are now applying their theoretical model to the synthesis of "rugby ball" dihydride, a 70-atom carbon ball with two hydrogen atoms attached. Henderson said the work is a step toward "molecular surgery," in which a single carbon atom of the fullerene "cage" would be replaced by another element to imbue the molecule with desired properties.

Artificial Heart-Valve Defects Studied with Ion Microtomography

A technique that grew out of research on weapons materials is now being applied to the study of defects in artificial heart valves. Researchers at Sandia National Laboratories are using ion microtomography (IMT), a nondestructive inspection technique, to produce detailed images of the interior of the valve materials, allowing researchers to "see" features or flaws as small as one micron.

The lab began a collaboration with Carbon Implants, Inc. after the Texas company's vice president, John Ely, read about Sandia's IMT work in an industry journal. Ely contacted the researchers to see if the technique could help his company study tiny cracks in their 1-mm-thick mechanical replacement valves, which are made of carbon that is coated with a carbon and silicon carbide alloy. IMT is 1,000 times more detailed than computer-aided tomography (CAT) scanning.

The Sandia team is examining samples sent by Carbon Implants—some with and some without flaws. The inspections are conducted in a vacuum chamber at Lawrence Livermore's multiuser tandem ion accelerator under a joint agreement between the two labs. The technique uses a highly focused proton beam with energies in the mega-electron-volts range. Magnetic lenses focus the beam down to two microns, and the beam is scanned across the specimen at various angles. Energy loss information accumulated in a computer for each slice is used to calculate approximate densities of materials within that cross section. The computer uses data from repeated slices to map out spatial variations in electron density and produce a rendition of a three-dimensional object on a screen.

So far, the researchers have identified a few common types of flaws in the firm's valves. For example, the valves may experience delamination under pressure, or a flaw in one part of a sample may cause residual flaws elsewhere. The goal is not only to detect flaws but to find out what effect they have on the rest of the sample by examining what lies above and below the flaws. While the work may eventually provide clues about how to improve the valves structurally, Ely said, he doubts that the IMT technique could be used for large-scale inspection of manufactured parts. "This method is primarily a research tool, not a quality-assurance tool," he said.

Joint Federal Lab Agreement Targets U.S. Competition

Under a joint agreement, the National Institute of Standards and Technology (NIST) and Sandia National Laboratories will link resources to boost U.S. competitiveness in world markets in the areas of microelectronics, advanced manufacturing, materials, and standards. The agreement will bring together federal and industrial researchers, and will build on existing programs at the two laboratories.

The labs will first concentrate on improving U.S. semiconductor products, guided by a "roadmap" of semiconductor research needs for industry produced by the Semiconductor Industry Association (SIA). NIST acting director Raymond Kammer said, "Our job now is to combine the strengths of NIST and Sandia in the areas identified and to respond to industry's requests."

The first joint projects under the agreement will be in semiconductor packaging and process control. The two labs will also jointly study control of chip production processes and ways to assure semiconductor reliability at the time of manufacture. NIST and Sandia plan to collaborate on other semiconductor research, including characterization of lithography tools, techniques for verifying information in computer models used to design semiconductors, and accreditation of laboratories that test semiconductors.

Oak Ridge/Ogden CRADA Studies Wastewater Cleanup

Researchers at Oak Ridge National Laboratory, under a cooperative research and development agreement, will work with Ogden Environmental and Energy Services Company to develop a technology for using microorganisms to remove uranium, arsenic, and other heavy metals from waste streams. Ogden will test the technique on an eastern German pond contaminated with uranium mill tailings. In the United States, the Department of Energy also has numerous sites where this environmental remediation technology may be deployed. The estimated cost of the three-year project is $2 million, to be shared equally by Ogden and DOE's Office of Technology Development.

Brendlyn Faison, team leader of the ORNL project, said the researchers would first identify the best medium for heavy-metal removal under the German site conditions, focusing on "gel beads" invented by ORNL. Each bead, about the size of a pinhead, contains millions of immobilized bacteria. In operation, a packed or fluidized bed bioreactor is filled with beads. Contaminated water is passed through the device and the dissolved metals in the solution are adsorbed on the bacteria. Water leaving the bioreactor may not have to be handled as waste, meaning that the residual waste materials would be only a fraction of the volume of the original waste stream. Since the microorganism and the gel material in the beads are mostly water, the discarded materials could be dried, reducing the mass by more than 80 percent, or incinerated, leaving only the metal compounds.