Self-Assembled Inorganic Film Fights Corrosion, Holds Catalysts

Andrew Gewirth and Walter Klemperer, professors of chemistry at the University of Illinois, devised a way of modifying metal surfaces with self-assembled monolayers of an inorganic compound called a silicotungstate, which is part of a class of molecules called polyoxometallates. These molecules are known to function as superacids, corrosion inhibitors, catalysts, and photochemical oxidants. The scientists grew this compound on silver surfaces.

"The silicotungstate anion contains a central silicon core surrounded by a series of tungsten-oxygen clusters," Klemperer said. "The molecule presents oxygen atoms to the silver surface, and it is the affinity of silver for these atoms that drives the self-assembly process."

Recent studies by the researchers, the latest published in the June 19 issue of the *Journal of the American Chemical Society*, have shown that the silicotungstate monolayer also will self-assemble on other oxophillic surfaces (such as copper and aluminum) once the native oxide layer is removed. Because the monolayer can accommodate a wide range of organic, organometallic, and inorganic functional groups, the films can hold catalysts for various kinds of electrochemical processes. The films also can be used as effective corrosion inhibitors.

"One of the problems with typical monolayer films is that they are easily oxidized, a property that makes them unsuitable as corrosion inhibitors," Gewirth said. "But, because the bond we are making between the metal surface and the silicotungstate anion is with oxygen, the molecule already is highly oxidized. Therefore, the film is very stable and prevents corrosion from occurring."

Because the silicotungstate anions will orient themselves to maximize the bonding that occurs between the oxygen atoms and the metal surface, the structure and functionality of the monolayer can be changed by changing the shape of the molecule.

"This imparts a kind of 'tunability' to the film," Klemperer said. "Our concept is to predesign these molecules to incorporate different functional groups in them and then bind them to the surface. It's almost like having a tool box where you have different building blocks that you can put down to form a variety of shapes and patterns, and then continue to build on top of them."

Aerosols Improve Inhalation Therapies

A type of dry aerosol mist, designed by a Pennsylvania State University and Massachusetts Institute of Technology-led international team and described in the June 20 issue of *Science*, has been shown in tests on rats to deliver medication significantly longer and more efficiently than currently used inhalation aerosols. According to the scientists, the aerosols now most commonly available often provide only a few hours of relief and the inhalation therapy has to be repeated frequently.

The aerosols are composed of tiny, near invisible particles that are three to ten times larger than those used currently but weigh up to 90% less. The scientists describe the particles as a whiffle ball with medication inside. When the whiffle ball-like porous particles are inhaled, the medicine slowly seeps out in the lungs and either acts directly on the lung tissue or enters the blood stream through the lung wall as inhaled oxygen does.

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According to David A. Edwards, associate professor of chemical engineering at Penn State, the larger, lighter particles remained longer in the lungs and were tolerated better with less inflammation in tests with rats. Large porous insulin particles, for example, stayed active in the rats' lungs for 96 hours which is about 15 times longer than the longest-acting aerosol currently known. Testosterone in porous particles produced higher blood hormone levels for 12–24 hours. Other medications, including albuterol, the leading fast-acting asthma reliever, are currently being tested in this aerosol formulation.

DNA Computer Logic Gates Mimic Those in Electronic Computers

Animesh Ray and Mitsu Ogihara of the University of Rochester announced at the First International Conference on Computational Molecular Biology in Santa Fe that they have built some hardware of logic gates made of DNA using biological laboratory techniques such as DNA ligation and gel electrophoresis. The logic gates rely on DNA codes.

These gates detect specific fragments of the genetic blueprint as input, then splice together the fragments to form a single output. For instance, a genetic AND gate links two DNA inputs by chemically binding them so they are locked in an end-to-end orientation. An enzyme called DNA ligase seals the gap between the ends of the two input strands, yielding a single new strand.

Using regular gel electrophoresis, the length of this new strand can be precisely measured, providing the DNA computer's output to the two input strands. For example, with the DNA AND gate, a final DNA sequence that is as long as the input strands linked together indicates that an AND operation has occurred. A similar system of two short DNA strands work together in Ray and Ogihara's OR gate, in which the output is likewise read in the length of the resulting DNA strands.

Ogihara recently showed mathematically that a computer consisting of a series of DNA-filled test tubes can work more efficiently than a digital computer in analyzing the information cascading in from a tangled web of logic gates. According to Ray, DNA microchips could make DNA computation even faster by speeding the tally of the DNA strands that serve as answers to computations. Rather than running the DNA through a slow gel electrophoresis, researchers could add labeled strands to a DNA chip, which consists of hundreds of squares containing different known strands of DNA. The added DNA would quickly bind to the strands in the square containing its complementary DNA sequence, and scientists could use the labels to detect the DNA answers.

Currently, logic gates used for computing have been electronic structures that detect signals coming from transistors. A growing group of scientists believe that DNA could serve as a very compact, efficient, and accurate form of memory in computers just as it does in the cells of the human body, with the capacity to store more information than electronic computers.

Interaction of Hydrogen Molecules Critically Dependent Upon Kinetic Energy and Orientation

Scientists from IBM's Almaden Research Center in San Jose and the University of California—Santa Barbara

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have found that molecules that spin parallel to a surface like helicopters can be up to three times more likely to react with that surface than molecules that approach the surface in an end-over-end rotation like cartwheels. Furthermore, the researchers found that this disparity is critically dependent on the incident kinetic energy of the molecules. This finding, reported in the July 4 issue of *Science*, is an important experimental contribution to the basic understanding of how reactions occur at surfaces.

The scientists studied the reaction of hydrogen molecules with a copper surface. By studying how the molecules form and leave a copper surface, the researchers obtained insight into the opposite, time-reversed process of adsorption. Molecules that are adsorbed onto the surface break apart into two hydrogen atoms bound to the surface, a process that is inhibited at low energies by a reaction barrier. The researchers learned that at kinetic energies just above that needed to overcome this barrier, molecules rotating parallel to the surface were up to three times more successful in reacting with the copper than those tumbling end-over-end.

These findings support the idea that the barrier to reaction should be smallest if both the atoms in the incident molecule can form chemical bonds to the surface at the same time. The energy required to break the molecular bond between the atoms would then be immediately offset by the energy released as both the new bonds with the copper atoms are formed. The scientists also found that the sensitivity of the reaction to alignment falls dramatically as the speed of the incoming molecule rises, most likely because the extra kinetic energy reduces the need for both atoms to form bonds at the same time.

Charles T. Rettner, research staff member at IBM-Almaden, said "By probing the nature and dynamics of the transition state between reagents and products, we are advancing the understanding of surface chemistry toward the ultimate goal of understanding such reactions in terms of the detailed motions of individual atoms."

Polarized Signatures in Ellipsometry Allow Detection of Nanoscale Contaminants

Optical scattering is used by the semiconductor industry to measure the microroughness of a silicon wafer as well as detect particulate contaminants and subsurface defects. However, the ability of optical scattering instruments to do the job is limited by problems with sensitivity. Light scattering due to microroughness can obscure or overwhelm the scattering caused by particles. Researchers at the National Institute of Technology (NIST) have discovered a way to cleanly distinguish the scattering caused by microroughness from that of particulate contamination or subsurface defects. Using a technique called bidirectional ellipsometry, scientists in the Optical technology Division of NIST's Physics Laboratory found that light scattered by microroughness has a characteristic, well-defined, polarization "signature." They also learned that other sources of scatter, such as particulate contaminants and subsurface defects, scatter light with unique polarizations different than those exhibited by microroughness. With this knowledge, the researchers designed an instrument that is blind to the microroughness optical scattering pattern. Therefore, nanoscale particles on silicon wafers can be detected and measured without the former problem of interference. Researchers expect that particles with diameters less than 0.1 μm may soon be routinely discernible. In addition, bidirectional ellipsometry is expected to become a powerful technique for identifying and characterizing defects in optical components, disk storage materials, and film coatings.

Copper Clusters Increase Adhesion at Film Interface

Researchers at the University of Illinois at Urbana-Champaign have developed a technique to make metal and polymer films, which are used in the fabrication of integrated circuits, stick together. The technique utilizes partially embedded copper clusters that act as "nanonails," anchoring a continuous metal coating to a polymer substrate. Copper is replacing aluminum as the metal of choice for making connections between components in large, multichip modules, graduate student Marlon Menezes said.

Menezes said, "First we form isolated nanosized copper clusters on the polymer surface using carefully controlled deposition rates and temperatures. Then, by controlling the time and temperature of the annealing process, we partially embed the clusters into the polymer before depositing the metal layer."

Bonds formed by the embedded cluster adhesion technique are stronger than those formed by other methods, such as surface roughening, which increase the available surface area for bonding but provide no mechanical interlocks.

"Because copper is a nonreactive metal, it does not chemically bond to the polymer films currently used to separate the wires between the chips," Menezes said. "Thermal stresses created during fabrication and operation can cause the films to delaminate, ruining the device."

Magnetic Coolant Made of Gadolinium-Silicon-Germanium Alloy Reaches 30–290 K

Scientists at Ames Laboratory have discovered a class of materials made of a gadolinium-silicon-germanium ($Gd_5Si_2Ge_2$) alloy that significantly advances the cooling power of materials currently used for magnetic refrigeration. Scientists discovered the class of materials when they lowered the magnetic ordering temperature of the compound, Gd_5Si_4, by substituting germanium for silicon. The compound $Gd_5Si_2Ge_2$ exhibits a magnetocaloric effect, the ability of certain materials to heat up when placed in a magnetic field and cool when taken back out, about twice as large as that exhibited by gadolinium, the best known magnetic refrigerant material for near room temperature applications.

The material, described in articles published in the June 9 issue of *Physical Review Letters* and the June 16 issue of *Applied Physics Letter*, has two advantages over existing magnetic coolants: It exhibits a giant magnetocaloric effect, and its operating temperature ranges from about 30 K to about 290 K depending on the ratio of silicon to germanium—the more the germanium, the lower the temperature.

Karl Gschneidner, senior scientist at the Laboratory, expects the discovery to launch applications for efficient refrigerators at very low refrigeration powers since the conventional gas-compression technology cannot be scaled down to such low cooling powers and since thermoelectric cooling is very inefficient (30 times less than magnetic refrigerants).

SBIR Update

Advanced Refractory Technologies, Inc. (ART) (Buffalo, New York) has been awarded a Phase I contract by the U.S. Air Force valued at $100,000 for thin-film coating materials for cryogenic coolers.

Essential Research, Inc. (Cleveland, Ohio) been awarded a Phase I grant of $70,000 from the National Aeronautical and Space Administration (NASA) to develop high-efficiency, monolithic tandem solar cells to provide on-board power for NASA spacecraft and communication satellites.

Increased Current Densities Enhance Risk of Electromigration Failure in Advanced Microelectronics

A team of materials scientists has measured the forces created during electromigration that may disable a chip or an entire computer. The phenomenon probably will not cause failure in existing computers, but will present a mounting problem to chip designers and manufacturers, said the researchers Slade Cargill of Columbia University, who is moving to Lehigh University for the position of Fairchild Professor of Materials and Engineering, and I.C. Noyan, a research staff member with the Materials and Processing Science Group at IBM's T.J. Watson Research Center. Cargill presented their work on March 17 at a meeting of the American Physical Society in Kansas City. "We have gone up in current density by an order of magnitude, and that's the problem," he said.

The researchers concentrated x-rays to a 10-μm beam by focusing them through a tapered glass capillary. That x-ray source provided the fine resolution needed to examine the microwire as electromigration took place.

For 70 hours, the researchers sent current through a flat aluminum wire half a micron thick, 10 μm wide and 200 μm long, covered with a layer of rigid silica insulation. As current passed through the tiny circuit, the team made x-ray measurements of changes in the wire's atomic structure. At the end of the wire where current was applied, about 30 μm of aluminum was stripped away, creating a gap.

At the wire's other end, researchers measured a continuous increase in stress as additional atoms were forced into the region. The maximum stress measured was 50,000 pounds per square inch, which is more than five times the usual load-bearing capacity of aluminum. After about 15 hours, they observed an abrupt decrease and then a more gradual increase in stress. The decrease in stress is thought to represent a deformation of the aluminum and a resulting break in the silica insulating material.

Electromigration is not a problem in households or most industries because moving a few thousand atoms will not affect wires millions of atoms in diameter. But in microelectronics, many wires are now less than one micron in diameter, and moving thousands of atoms around can have far more dramatic effects.

According to the researchers, computer failures because of electromigration first occurred in the 1960s, before hardware engineers were fully aware of the problem. They solved it by using new combinations of metals, by limiting current and the wires' length, and by encapsulating circuits in rigid insulating materials.

During the last 30 years, however, the size of microelectronic circuits has decreased by almost 40 times, Cargill said, while current in those circuits has decreased less rapidly, from the range of 10 to 50 milliamperes to about a tenth of that level now. With a two-time reduction in conductor line thickness and 40-time reduction in conductor line width, current density has increased by a factor of ten.

Once microwires shrink to a quarter of a micron in diameter and smaller, chip designers will have to discover ways to limit current sent through such wires, or find other ways to counter electromigration. Presently, other factors limit the current that can be carried in computer chips, Cargill said.

"These problems can be solved by changing the configuration and metallurgy of the chip," Noyan said. "However, new solutions will have to be found for each generation of chips, since electromigration is like an allergy. It can be mitigated but never fully cured."

Bower, Inventor of Self-Aligned Gate MOSFET, Inducted into the National Inventors Hall of Fame

Robert W. Bower, who invented the field-effect device with insulated gate, known as the self-aligned gate MOSFET (metal-oxide-semiconductor-field-effect transistor), has been announced as a 1997 inductee into the National Inventors Hall of Fame on June 16 at the National Press Club. Patented in 1969, Bower's invention made possible the fast electronic circuits that are now commonplace in computers and other consumer electronic products. His invention allowed the MOSFET to become the primary device used in virtually all modern integrated circuit designs. Bower developed the device while working at the Hughes Research Laboratories in Malibu, California.

Bower received an AB degree in physics from the University of California—Berkeley in 1962, earning his MS degree in Electrical Engineering the following year at Cal Tech (California Institute of Technology). He also received his PhD degree in applied physics from Cal Tech in 1973, after spending eight years with Hughes.

He holds 24 U.S. patents in the fields of semiconductor devices and technology, and is currently a professor at the University of California—Davis where he is focused on making three-dimensional microelectronics a reality.

Bower is to be inducted with seven other inventors into the National Inventors Hall of Fame, which is housed at Inventure Place in Akron, Ohio, during the annual Induction Ceremonies in September.

Changing Materials from Insulators to Conductors

Researchers from Brookhaven National Laboratory, Princeton University, and the University of Tokyo have discovered that a certain class of materials known as colossal magneto-resistive materials will change from an insulator to a conductor when exposed to x-rays. The materials exhibit dramatic changes in electrical resistance when exposed to a magnetic field. While using x-rays as probes to study a compound called praseodymium calcium manganese oxide at Brookhaven's National Synchrotron Light Source, the researchers found that the radiation changed the material's electrical characteristics effectively from an insulator to a conductor. According to the scientists, the x-rays made the sample magnetic. This unusual effect may lead to the ability to create and manipulate tiny magnetic structures for use in basic research on magnetism. Researchers expect that studying this effect will lead to insights on how magneto-resistive materials work. Since these materials are used in computer hard-disk drives and speed sensors of anti-lock brakes, this research may lead to improvements in these devices, as well as more sensitive x-ray detectors and other applications.

DMP Sponsors 1997 APS Fellows

The Division of Materials Physics (DMP), a division of the American Physical Society (APS), sponsored the following APS fellows: **Philip Edward Batson** (IBM T.J. Watson Research Center) for the development of both the experimental and interpretative aspects of high spatial resolution, high-energy resolution energy loss spectroscopy as a valuable addition to electron microscopy studies of matter; **Fenton Read McFeely** (IBM T.J. Watson Research Center) for his creative applications of photoemission techniques to the understanding of materials processes, interfaces, and electronic structure, including etching and deposition reactions underlying microelectronics technology; **Michael Raymond Melloch** (Purdue University) for innovative epitaxial growth of semiconductor epilayers, quantum wells, and superlattices which have led to new materials,

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novel devices, and important advances in the physics of nanostructures; **Karl L. Merkle** (Argonne National Laboratory) for his contributions to the basic understanding of radiation-induced defects in solids and internal solid interfaces; **Charles Steven Rosenblatt** (Case Western Reserve University); for his use of intense magnetic and electric fields in the study of liquid crystals and other soft materials; **Robert F. Sekerka** (Carnegie-Mellon University) for outstanding and significant contributions to the theory of crystal growth, especially for explaining the role of morphological instabilities; **Arthur Marshall Stoneham** (University College of London) for seminal and extensive contributions to the theory of defects and defect processes in solids through research articles and books, and for the promotion of physics research through effective management; **Gwo-Ching Wang** (Rensselaer Polytechnic Institute) for her contributions to the fundamental understanding of ordering and scaling in surfaces and overlayers, and for her pioneering work in ultrathin-film magnetic scaling; and **Hartmut Zabel** (Ruhr University, Bochum) for his seminal contributions to our understanding of the structure and dynamics of hydrogen-metal systems, graphite intercalation compounds, and magnetic metallic multilayers.

Frances Hellman (University of California—San Diego) was elected Vice Chair of DMP and Max Lagally (University of Wisconsin—Madison) and **Julia Phillips** (Sandia National Laboratories) were elected Members-at-Large of the Executive Committee of DMP for 1997–1998.

Woodall Receives Award for Compound Semiconductor Inventions

Jerry M. Woodall, the Charles William Harrison Distinguished Professor of Microelectronics at Purdue University, has received the 1997 Eta Kappa Nu Vladimir Karapetoff Eminent Members' award for his work on compound semiconductors. Woodall pioneered the use of liquid phase epitaxy to fabricate semiconductors using gallium arsenide, and heterostructures using gallium arsenide and gallium aluminum arsenide. The technique allows researchers and manufacturers to build such devices one thin layer at a time. At least half of the semiconductor market is based on fabrication methods and devices invented by Woodall.

These types of semiconductors play a central role in lasers, light-emitting diodes, and state-of-the-art solar cells. They also are the basis for cellular phones and consumer electronics such as compact disc and laser disc entertainment technology and optical storage technology. The semiconductors also are used in infrared remote control and signaling devices that not only change television channels, but also allow data transfer in notebook and laptop computers.

Wang Receives ASTM Award of Merit

Theodore P. Wang, president of Theodore P. Wang & Co., North Caldwell, New Jersey, has been named a 1997 recipient of the American Society for Testing and Materials' (ASTM's) Award of Merit for 23 years of exemplary service, including six years as secretary; and for continuing contributions to the technology of thermoelectric temperature measurement.

Wang's career concentration has been in directing research groups and developing new and improved products and processes from inception through customer satisfaction. Product areas have included thermocouples, resistance thermometers, electrical resistance, and corrosion resistance. He has received 15 U.S. and one non-U.S. patent and has published 55 papers in various technical journals. The title of Fellow accompanies the award.

Meyer Receives Germany's Humboldt Award

Christian Meyer, professor of civil engineering and engineering mechanics at Columbia University's School of Engineering and Applied Science, has received the Humboldt Research Award for Senior U.S. Scientists. Meyer will spend the academic year 1998–1999 at the University of Kassel in Germany to study reinforced concrete structures. He will investigate the mechanical behavior of fiber-reinforced cement composites and earthquake-resistant design of concrete structures.

The Alexander von Humboldt Foundation was established in 1860 in memory of the German scientist and explorer. Its primary aim is to support non-German researchers and doctoral candidates engaged in studies in Germany.

Twenty-Two Cottrell Scholars to Receive $50,000 Research and Teaching Awards

Twenty-two faculty scientists embarking on research and teaching careers in chemistry, physics, and astronomy have been named recipients of Research Corporation's Cottrell Scholar Awards, announced May 6. The $50,000 awards are unusually flexible in that they have no fixed budgets, letting recipients decide how best to apply funds to programs of research and teaching.

Elizabeth Nicol of the University of Guelph, Ontario, will investigate high-temperature superconductivity in alkali-doped fullerenes and other novel materials. Given better superconductors, it would be possible to improve the efficiency of electric machines and power transmission lines and, as one example, build magnetically levitated trains.

Melissa Hines of Cornell University is using advanced techniques to create an atomic-scale picture demonstrating what happens to silicon etched by aqueous fluorine solutions. Control of the surface smoothness of silicon is vital in making computer chips, yet state-of-the-art vacuum etching produces 2–3% defects, as compared to near-perfect surfaces possible with wet chemistry.

The research of **Clare P. Grey** of the State University of New York at Stony Brook bears on the zeolite molecular sieves used to help purify new refrigerants to replace Freon chlorofluorocarbons (CFCs). Several hydrochlorofluorocarbons (HCFCs) are promising substitutes for CFCs, but are costly to produce and must be purified. Grey's work aims at improved impurity separation and trapping.

Douglas L. Gin of the University of California—Berkeley is researching potentially economical, stable chemosensors. The ability to detect biologically active organic molecules easily—drugs, chemical wastes, or hormones—could improve health care and environmental monitoring. Gin would imprint fluorescent monomers with "target" molecules of substances to be detected, creating recognition sites. These could then be polymerized into rigid, portable, easily-used biosensors that emit light in the presence of the target substance.

Daniel Lathrop of Emory University's Department of Physics is developing an instrument to rotate liquid metal sodium at 25,000 rpm and demonstrate self-generation of a magnetic field. The rotation of the conducting liquid cores of planets and stars has been used to explain the magnetism of these bodies, yet no laboratory model has demonstrated such a dynamo.

Yi Lu of the University of Illinois is researching a new class of metalloenzymes: ribozymes (RNA with enzymatic activity) that incorporate metal ions are poorly understood, have not been investigated, and may be useful in designing drugs against AIDS and other retroviral diseases.

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Other 1997 Cottrell Scholars include **Cynthia A. Cattell** (University of Minnesota—Twin Cities) for a study of the effects of perturbations on energization and scattering of charged particles in a field-reversed magnetic field geometry; **John T. Fourkas** (Boston College) for exploring the role of attractive interactions in dynamics and structure of ultrafast spectroscopy of liquids at negative pressure; **James D. Martin** (North Carolina State University) for the study of metal-halide analogs of zeolites as the next generation of microporous materials; **Dominic Vincent McGrath** (University of Connecticut) for research on photoactive chiral dendrimers for light-controlled transport; **Daniel Raftery** (Purdue University) for the study of surface selective nuclear quadrupole resonant (NQR) spectroscopy; **Susannah L. Scott** (University of Ottawa) for research on a strategy for the preparation of surface-stabilized reactive organometallic fragments for C-H activation; and **Grzegorz Szamel** (Colorado State University) for developing a statistical mechanical theory of dynamics of supercooled liquids.

Teaching plans of the Scholars include "hands-on" laboratory science, audience participation in lectures and classes, peer mentoring and instruction, e-mail and student newsgroups for individual courses, and course websites. Curriculum revision, new courses and updates of old ones are heavily featured, especially in rapidly moving fields.

The awards are named after Frederick Gardner Cottrell, the scientist, inventor, and philanthropist who established Research Corporation, a science advancement foundation, in 1912. The goals of the foundation are to make inventions "more available and effective in the useful arts," and "to provide means for scientific research and experimentation."

Buried Channel in Thin-Film Transistor Expected to Enhance Laptop Computer Displays

Researchers at the University of Illinois developed a type of thin-film transistor that could improve the resolution of flat-panel, liquid-crystal displays used in laptop computers. The transistor contains a "buried channel" that allows electrons to move faster, permitting much higher switching speeds. To fabricate the buried channel thin-film transistors, John R. Abelson, a professor of materials science and engineering at the University of Illinois, and graduate student Cory Weber use a technique called reactive magnetron sputtering. This method, which uses a plasma to erode a silicon target and deposit a film, provides precise control over layer composition and electronic properties.

"To create a step in the conduction band, and thus a buried channel, we vary the amount of hydrogen gas injected into the plasma while we deposit the amorphous silicon layer," Abelson said.

The sputtering technique, as reported in the September issue of the *Journal of Vacuum Science and Technology*, also allows films to be deposited at much lower temperatures than currently possible with the plasma-enhanced chemical-vapor-deposition process used by industry.

"We have fabricated these transistors at a processing temperature of 125°C," Abelson said. "This opens up the possibility of using lightweight and impact-resistant plastic substrates in place of the glass substrates currently employed."

According to Abelson, in conventional thin-film transistors, electrons travel near the semiconductor-insulator interface, where the silicon is strained and is of poor quality. He said, "By creating a buried conducting channel, recessed about 50 Å away from the interface, we can increase the speed of the electrons and significantly enhance the performance of devices built with these transistors." □

Correction: In the article, "The Art of Simplification in Materials Science" by A. Cottrell (*MRS Bulletin*, May 1997, page 15), the units in Figure 4 should be Mbar, not MPa.

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