#### Superdielectric Properties Observed in SrTiO<sub>3</sub>/BaTiO<sub>3</sub> Superlattice

A group of researchers headed by Tomoji Kawai of the Institute of Scientific and Industrial Research at Osaka University, Japan, have produced a "dielectric superlattice" of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> using pulsed-laser deposition. Crystalline substances that are ferroelectric are commercially useful because of their capacity for spontaneous electric polarization that is reversible by applying an electric field. The dielectric properties of the superlattice show quite different behavior from those of SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, and (Sr,Ba)TiO<sub>3</sub> single-phase films. Dielectric and ferroelectric superlattices offer a promising approach to creating new superferroelectric materials and to clarifying the mechanism of ferroelectricity, according to the researchers. They also said that the new substance can be used in appliances in which an electrical impulse from an integrated circuit is changed into sound or vibrations and that it could help make everyday electronic devices smaller. The findings were presented at the annual meeting of the Japan Society of Applied Physics on March 28, 1994. They also were published in Applied Physics Letters, October 1994.

The new substance, which retains its ferroelectric properties at high temperatures, was made by depositing alternating layers of barium titanate (BaTiO3, hereafter called BTO) and SrTiO<sub>3</sub> (STO) using pulsed-laser deposition. This technique offers many advantages for film growth, including epitaxial growth at low substrate temperatures; congruent deposition of materials with magnetic stoichiometries, and facile deposition of materials with high melting points. In the experiment, stoichiometric sintered BTO and STO pellets were used as the targets. An ArF excimer laser (193 nm wavelength) was focused onto the target BTO and STO alternately, thus allowing BTO and STO layers to be deposited layer by layer onto Nb-doped single-crystal SrTiO<sub>3</sub>(100) substrates. A series of samples were made, each a total of 2,000 Å thick, but with individual layers ranging in thickness from 4 Å (1 unit cell) to 1,000 Å (250 unit cells) to induce different amounts of strain. The films were formed at 650°C under an oxygen/ozone (8%) pressure of 3 mtorr. The deposition rate was 10-15 Å/min.

Strain is produced by in-plane lattice parameter differences, with less strain relief in thinner layers. In the present superlattice, although the in-plane lattice parameters of the two materials differ only slightly, an extremely powerful lateral strain is generated at their interface. Under this strain, the BTO crystals are stretched vertically, which increases atom mobility in a vertical axis and increases the substance's ferroelectric properties. Kawai and his team thus describe these strained superlattices as having "superdielectric" properties. The dielectric constant of 2,000 Å of the BTO/STO superlattice is 950, in spite of such a thin-film thickness.

The temperature dependences of the dielectric constant measured at 10 kHz are particularly interesting; the dielectric constant of (Sr<sub>0.5</sub>Ba<sub>0.5</sub>)TiO<sub>3</sub> solid-solution thin films becomes zero at 35°C because of the phase transition from tetragonal to cubic structure. For the BTO/STO superlattices, however, a broad-peak dielectric constant, which is a typical feature of a ferroelectric film, is observed at around 50-60°C, and high values are maintained at the even higher temperature of 200°C in the 1/1 (layers of STO and BTO each one unit cell thick) and 3/3 superlattices, indicating that a ferroelectric transition occurs at high temperatures for the superlattice.

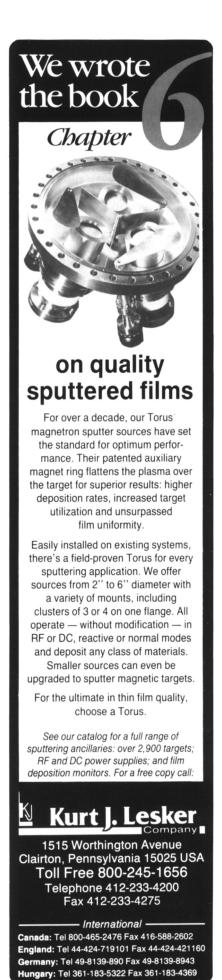
F.S. Myers

#### New Editorial Structure Slated for Acta and Scripta Metallurgica et Materialia

On January 1, 1995, Michael Ashby will retire as editor of Acta Metallurgica et Materialia and John Hirth will retire as editor of Scripta Metallurgica et Materialia. Gareth Thomas from the University of California-Berkeley will become editorin-chief for both journals, with overall responsibility for all aspects of their quality.

Responsibility for acceptance, rejection, or solicitation of manuscripts for the journals will rest with four newly appointed principal editors who will concentrate on papers in specified subfields of materials science. These editors will be responsible for papers to be published in either Acta or Scripta Metallurgica et Materialia.

The new principal editors and their areas of responsibility are: Hirotaro Mori from Osaka University will be responsible for the area of structural characterization of materials at all scales and utilizing all techniques; Timothy Sands from the University of California-Berkeley will be responsible for electrical, magnetic, optical, and thermal properties; Subra Suresh from the Massachusetts Institute of Technology will be responsible for mechanical behavior; and Richard



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Wagner from GKSS Research Center in Geesthacht, Germany will be responsible for synthesis, phase stability, phase transformations, and microstructural evolution.

#### Single Organic Material Used to Produce Various Colors of Light

Two AT&T Bell Laboratories research teams have reported significant progress in a new electronics field that uses organic semiconductors to emit light in different colors and to transmit data photonically.

Using a single electroluminescent material, the team produced miniature light-emitting diodes (LEDs) on glass that generate the three primary optical colors of red, green, and blue. Their achievement makes it unnecessary to integrate three distinct chemicals to achieve full-color displays. In addition, the team has fabricated LEDs that emit white light, leading to the possibility of low-voltage backlighting for portable displays.

The LEDs contain 8-hydroxyquinoline aluminum (ALq), a compound patented by Eastman Kodak that normally emits only green light. However, the process developed at Bell Labs does not limit the LEDs to a particular organic material.

The LEDs are formed by depositing a multilayered dielectric mirror on the rear surface of a glass screen. Transparent silicon nitride is then deposited and selectively etched to varying thicknesses. Films of ALq and other materials that facilitate electrical contact are deposited over the silicon nitride, followed by a top layer of magnesium or aluminum. The top layer acts as a second mirror that doubles as an electrode to stimulate light from the organic material. A microcavity is formed when the distance between the two mirrors equals the wavelength of the desired color, generally from 0.1-1 micron.

It's the easily patterned inert filler the silicon nitride—that determines an LED's color. Ananth Dodabalapur, a member of the Bell Labs staff, conceived the idea for the terraced structures he calls "patterned planar microcavities."

Helen Kim, another member of Bell's technical staff, has developed a technique to significantly boost the LED's light-emitting intensity. Kim realized that the typical light-emitting efficiency of the LEDs would be low if the plastics were deposited directly on the silicon base. When Kim applied a thin blanket of silicon dioxide to the base before adding the organic semiconductor, the diodes' internal quantum efficiency jumped 200 to 5,000 times to a maximum of 0.5%, depending on the material used.

The plastic LEDs can be applied to silicon wafers prepared with silicon dioxide simply by spincoating the light-emitting polymer onto its surface, then patterning the metal electrodes. LEDs can be deposited on the wafer's surface by evaporating the organic powder in a vacuum chamber. After it has condensed on the wafer, metal evaporation or sputtering

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can be used to produce one of the LEDs' electrodes. The other electrode is the heavily doped wafer itself.

#### Separating Polymer Chains Increases Efficiency of Light Emission

University of Rochester engineers report in the August 5, 1994 issue of *Science* that they have been able to boost the efficiency of light emission from polymers to four times the level previously achieved by improving the efficiency of the optoelectronic polymers—from 10 to 42%.

Polymers are notoriously inefficient light emitters because they waste a lot of energy by converting only a small fraction of one form of energy to another. Researchers have discovered that a polymer's efficiency depends on how close together the polymer's molecular chains are to each other. When a single polymer's chains are very close—within 3–5 angstroms—and when the polymer is excited by shining light on it or by applying a voltage, the chains form pairs of molecules known as excimers which exist for only a few billionths of a second. Excimers do not emit light efficiently.

The solution is to prevent excimers from forming by blending in another polymer or other molecules to keep the original polymer's chains separated. Properly spaced, the chains form a shortlived molecular sandwich known as an exciplex, which emits light very efficiently. According to Rochester engineers, conjugated polymer exciplexes are a new class of materials. Samson Jenekhe, associate professor of chemical engineering, said in the August 5 Science article that excimers are responsible for light emission from all conjugated polymers. He also wrote that by forming exciplexes and tweaking the type and spacing of the blending material, engineers will have better control over the color and efficiency of light a material emits. He and Osaheni have filed for a patent on the new class of materials and their optoelectronic applications.

#### **Fullerenes Encased in Glass**

In trying to overcome the inherent instability of fullerene molecules, researchers at Los Alamos National Laboratory encased fullerene powder in glass. The resulting rose-tinted glass may lead to the development of goggles, airplane canopies, or satellite lenses to shield eyes and equipment from highenergy laser light. Fullerene molecules have light-cutting characteristics—the

brighter the incoming light, the less light the molecules transmit.

Researchers Ben Mattes and Aaron Koskelo dissolved fullerene powder in a room-temperature, evaporative silica solution that shrinks and hardens to form glass. As the solution hardens, glass molecules condense around the fullerene molecules. Mattes and Koskelo theorize that the hollow, pyramid-shaped glass molecules surround the individual fullerene molecules, protecting them from oxidization.

"We thought we would see clusters of hundreds of carbon molecules as tiny little crystals," said Mattes. They found very few associated carbon molecules, instead discovering a more even dispersion. Mattes and Koskelo will continue their research, trying to produce glass with fullerenes that are less rose-colored.

#### Centrifugal Slip Casting Orients Grains of Superconducting Tubes

Greg Steinlage, a doctoral student in Purdue's School of Materials Engineering, is the first to use a technique called centrifugal slip casting to make superconducting tubes out of BSCCO, a high-temperature superconductor containing bismuth, strontium, calcium, copper, and oxygen. The process involves spinning the material at very high speeds to orient grains as they form. Steinlage used tubes because tubular superconducting devices are now used to protect sensitive electronic equipment against stray electromagnetic fields. Superconducting tubes are also being adapted by utilities to transmit electrical power more efficiently. The tube shape allows liquid nitrogen to flow through the center to keep the material cool enough to super-

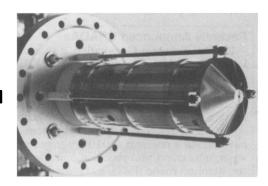


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Visit MRS Exhibit Booth No. W29 conduct. Although BSCCO is relatively expensive, about \$1 to \$3 per gram, Steinlage says devices made from BSCCO may actually be cheaper to use than traditional superconductors because it is much less expensive to cool.

Superconductors also make excellent shields because as current flows through the material it forms a very stable magnetic field around the outside of the tube. The field bends incoming external fields away from it or cancels them out entirely. Inside the tube, the magnetic field is zero, so electronics placed inside are safe and operate more efficiently. Steinlage feels that the prototype of his superconducting tube can easily be scaled up to dimensions that will accommodate electronic equipment.

To make his device, Steinlage starts with a small amount of BSCCO material that has been crushed into a fine powder. The powder particles are shaped like very rough-edged dominos. The greatest amount of current flows through BSCCO material when all the grains are lined up and stacked in layers like a brick wall. Using centrifugal slip casting, Steinlage then mixes the grains with hexane and a special dispersant containing polymers, to make a slurry. The mixture is then injected into a three-inch-long tubeshaped plaster mold lined with silver powder, that is spinning in a lathe. As

the hexane is squeezed out through the pores in the plaster due to the centrifugal force, the grains align themselves. The polymer chains help the grains line up by attaching themselves to grain edges and interconnecting with chains on adjacent grains. The tube is then placed in a furnace to sinter. One advantage of using this technique is that as a tube gets larger, it is easier to produce. The larger the radius of the tube, the more centrifugal force that is generated as the materials spin around. If the radius is doubled, the force on the particles is doubled, so they are apt to push each other farther outward, making the tube more dense and better aligned.

#### Domain Epitaxy Aids Single-Crystal Growth

Researchers at North Carolina State University have developed a novel method for producing single-crystal thin films on substrates having a large lattice mismatch. A U.S. Patent has been granted and a series of papers have been published in *Applied Physics Letters* and in the *Journal of Applied Physics*. Jagdish Narayan and his graduate students describe their method of thin-film growth, called domain epitaxy, where a set of lattice constants or lattice planes of the film match with another set of the substrate.

This method provides a significant improvement over conventional methods for growing single-crystal films on substrates with a large lattice mismatch. Matching domains instead of individual lattice constants has resulted in novel materials and three-dimensional epitaxial device structures. Materials such as single-crystal titanium nitride thin films on silicon substrates, grown by domain epitaxy, have low resistivity and can be used directly for contact metallurgy and as diffusion barriers for shallow junctions needed for next-generation integrated circuits.

### Radioactive Waste Minimization Reduces Risk

The Idaho National Engineering Laboratory has developed waste minimization techniques resulting in the unrestricted use of 25 previously contaminated facilities. Waste minimization practices developed at INEL include metal melting, decontamination and reuse, institutional control, sorting and separation, and mixed waste treatment. Another technique utilized at INEL is decontamination followed by continuous institutional monitoring, since radioactive decay can reduce the contamination to unrestricted levels within a certain amount of time.

EDITOR'S NOTE: The December issue of MRS Bulletin will focus on nuclear waste disposal.

#### Barmak, Rickman Receive National Young Investigator Awards

Katayun Barmak and Jeffrey M. Rickman, both assistant professors of materials science and engineering at Lehigh University, have been named National Young Investigators by the National Science Foundation. The award provides scientists with \$25,000 a year in research support for five years and up to \$37,500 a year more in matching funds.

Rickman, who earned a PhD degree in physics from Carnegie Mellon University, studies computer modeling and simulation, especially of crystalline defects. Rickman is also developing methods to predict, using a computer workstation, the new properties that a material will acquire when combined with other materials.

Barmak, who earned a PhD degree in materials science from MIT and worked at IBM before joining Lehigh in 1992, studies nanostructured metal films. She also researches functionally graded materials (FGMs) with Harmer, Chen, and Arnold R. Marder, professor of materials

#### **Recently Announced CRADAs**

**Hoechst Celanese Corporation**, a subsidiary of Hoechst AG of Germany, and the U.S. Department of Energy's Oak Ridge Y-12 Plant are collaborating on a six-part project to create a new method of predicting chemical, physical, and mechanical properties of high-performance materials based on their chemical nature. They plan to use neural networks, genetic algorithms, graph theory, quantum mechanics, and molecular dynamics to produce a molecular-based computational system.

TRS Ceramics, Inc., State College, Pennsylvania and Argonne National Laboratory have signed a one-year \$100,000 agreement to improve electronic actuators used in sonar, ultrasound, and precision optics systems. Research will center on lead-zirconium-titanium oxide (PZT), a standard commercial actuator ceramic; specialty PZT materials made by TRS's proprietary processes; and lead-magnesium-niobium oxide.

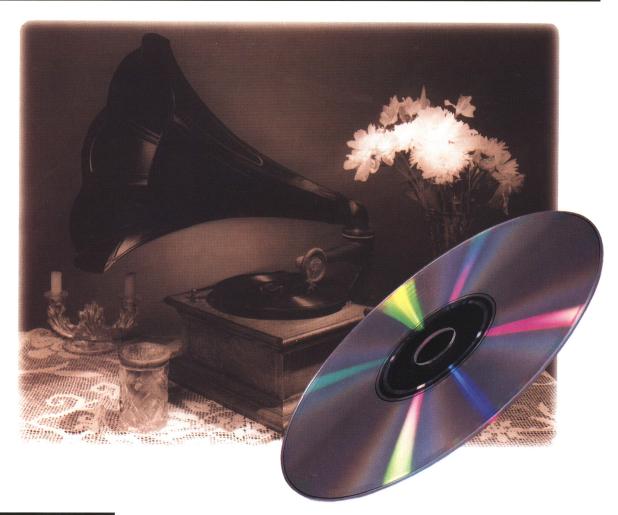
**Lawrence Berkeley Laboratory**, (Berkeley, California) and the Advanced Lithography Group (Columbia, Maryland) will develop an advanced ion source for use in the ALG's preproduction lithographic tool.

#### **SBIR Update**

Advanced Refractory Technologies, Inc. (Buffalo, New York): Phase II award from the Department of Energy to fabricate sintered porous aluminum nitride materials that are suitable for separators in lithium-metal sulfide batteries. ART will pursue performance optimization in conjunction with cost reductions for the separator. Phase I award from the Department of Defense to study the use of diamondlike nanocomposites as tailorable, hard, low-friction coatings.

**Quest Integrated, Inc.** (Kent, Washington): Small Business Technology Transfer award from the Air Force to develop aluminum nitrite (AIN) ceramic packaging for use in integrated circuits.

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science and engineering. FGMs are a composite of ceramic and metal that change gradually from a 100% ceramic composition to 100% metal composition. Barmak is seeking to development new electrochemically based processes to fabricate the FGM coatings. She also wants to learn more about the thermal and mechanical properties of materials so that these coatings can be used in extremely high temperatures.

# Chiral Polymers to be Developed for Their Optical Properties Using Enzymatic Process

The Materials Directorate of Wright Laboratory, U.S. Air Force, has awarded a contract to Molecular OptoElectronics Corp. (MOEC) of Watervliet, NY to develop and produce chiral polymers via an enzymatic process.

Certain monomers have a specific right-or left-handedness to their chemical structure, called "chirality," which can lead to unique optical properties for the polymers fabricated from them. Thus far, the lack of a commercial supplier has hampered the research into and application of such materials. Because of the natural specificity of enzymes, an enzymatic process is a logical way to produce pure monomers in quantities suitable for specialty optical applications.

Romas J. Kazlauskas, professor of chemistry at McGill University in Montreal, an expert in biocatalytic techniques to resolve chiral monomers, will act as consultant with MOEC on this program.

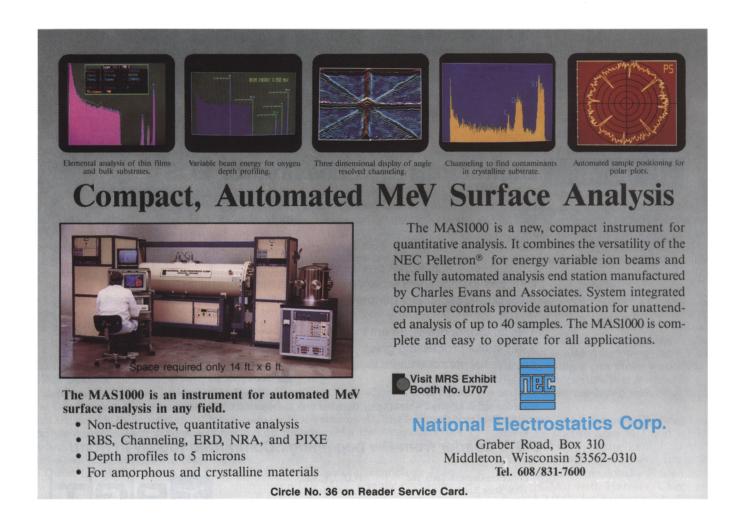
## Toroid Cavity Imager Provides Detailed Map of Materials

The U.S. Department of Energy's Argonne National Laboratory has invented the Toroid Cavity Imager, based on MRI methods similar to those used in hospitals. It can be used to provide an image of sample materials with up to 100 times better detail than conventional MRI methods. The imager can potentially

detect objects as small as 5 micrometers in fluids; in solids and polymers, it can see objects as small as 1 micrometer.

The imager is a hollow metallic cylinder, about 4 cm long and 1 cm wide, with an electrode running down its center. The current version can be used at 500 times normal atmospheric pressure and at temperatures as high as 250°C.

Like conventional MRI devices, the Argonne cavity maps the internal chemical and physical properties of materials by surrounding them with a strong magnetic field that lines up the material's atoms like tiny compass needles. Next, a strong pulse of radio-frequency signals disturbs the alignment. After the pulse, the atoms relax and realign, giving off radio-frequency signals in the process. These signals give information about the locations and identities of the atoms that make up the material. The cavity's alternating magnetic field is strong at the central electrode but weaker as the distance from the electrode increases. This varia-



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tion gives detailed information unavailable with a static magnetic field.

The invention won a 1994 R&D Award for Argonne scientist Jerome Rathke and his colleagues, Robert Klingler and Klaus Woelk.

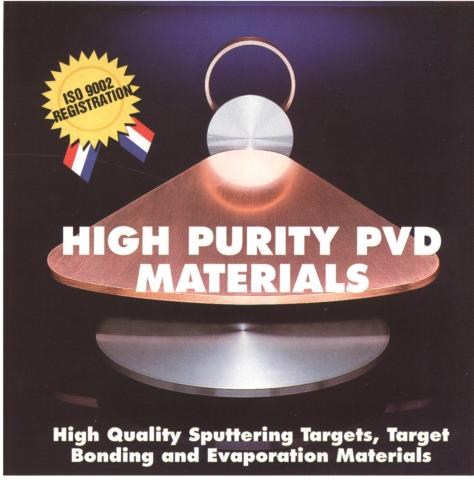
### Organic Structures Similar to Zeolites Developed

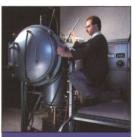
Organic structures analagous to zeolites have been fabricated by chemist Jeffrey Moore at the University of Illinois. Like zeolites, the organic structures are honeycombed by relatively large and long internal corridors, but these are more predictably aligned and sized than their natural counterparts. Researchers have achieved a regularly repeated relation of large channels formerly found only in inorganic crystals. The advantage is that the building blocks and, therefore, the final material can be made to order.

Scientists are interested in controlling the size and shape of zeolite channels because that could improve the catalytic operations and molecular separations necessary in many industries. The difficulty in building a zeolite-like structure in a laboratory is that building-block molecules try to clump together rather than leave spaces between themselves, due to attractive forces on the atomic level. Also, collections of organic molecules tend to change shape to achieve the lowest collective internal energy state. The molecular collapse decreases the number of corridors in the structure. One of the researchers' goals is to make the molecules as stiff as possible to prevent collapsing.

Moore's building blocks are joined employing techniques that are used to efficiently construct large organic molecules. Moore chemically masks one set of potentially active atoms to prevent them from interacting at will, and then unmasks them when the desired molecular partner is present.

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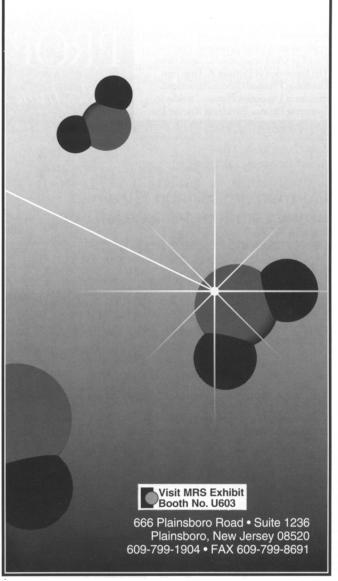
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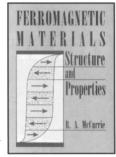
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