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Oak Ridge National Laboratory REVIEW

Vol. 32, No. 3, 1999

Brave New Nanoworld...

REVIEW
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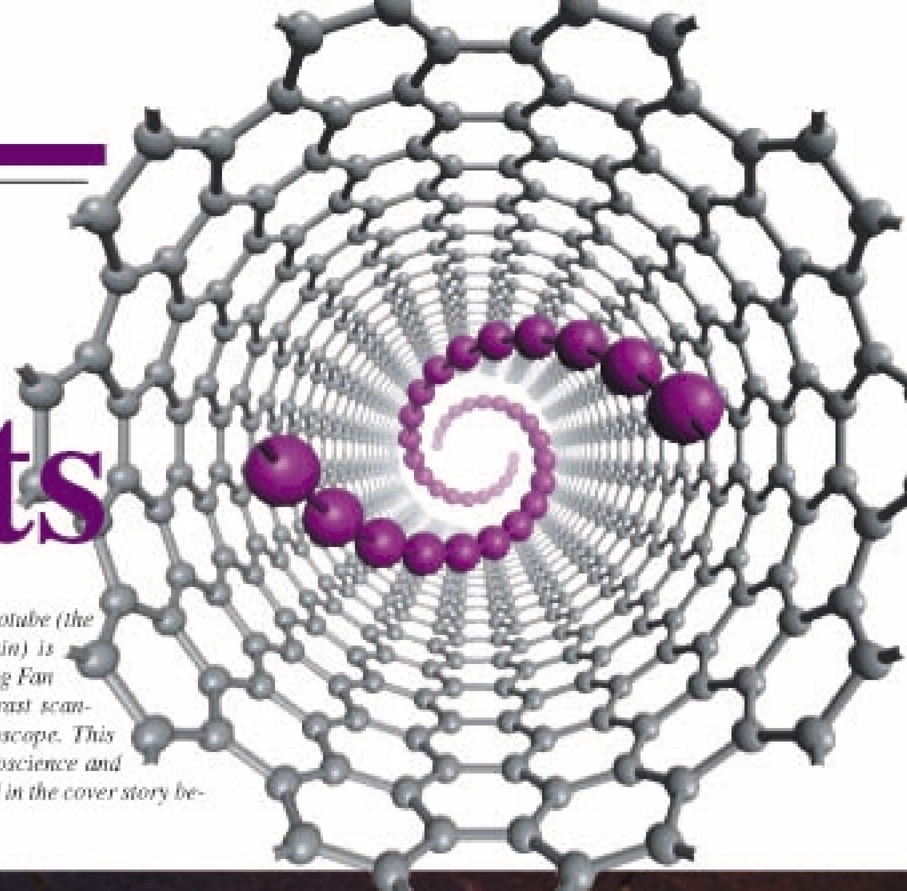
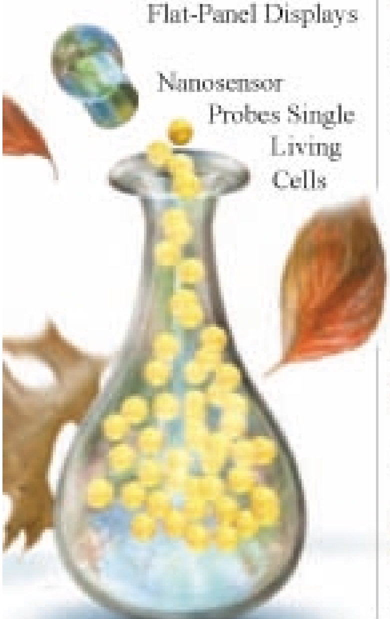
Contents



This visualization of a carbon nanotube (the purple balls form an iodine chain) is based on an image taken by Xudong Fan (see back cover) using the Z-contrast scanning transmission electron microscope. This work is one of ORNL's many nanoscience and nanotechnology projects described in the cover story beginning on p. 2.



ORNL is studying ways to capture more carbon from the atmosphere using terrestrial ecosystems. See p. 21.

Embedded precipitates of vanadium oxide, like the rod-shaped particles shown here, can be produced in the near-surface region of sapphire single crystals by using an accelerator to implant vanadium and oxygen ions and then heating the implanted crystal in an appropriate atmosphere. The small vanadium oxide precipitates are effectively "lined up" by the sapphire crystal structure leading to the triangular-shaped pattern formed by the particles shown in the interference contrast optical micrograph. (The pink and blue structure near the center of the image is an unusual defect on the sapphire crystal surface.) Vanadium oxide particles undergo a phase transition to a metallic state at a temperature of about $77^{\circ}C$. This mechanism provides the basis for the creation of a "smart" material that can automatically transform the surface from a window to a mirror. For more information on ORNL's research in advancing nanotechnology, see the article beginning on p. 2. **Micrograph provided by Janie Gardner and Lynn Boatner and enhanced by Greg Lumb.**

Editorial: Science of Tiny Features Faces Big Future

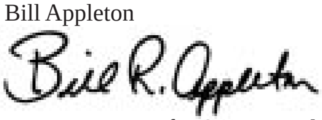
The cover story in this issue of the *Review* highlights some of the research and development (R&D) work being done by ORNL staff on the fascinating science that emerges when materials and structures are fabricated with defining dimensions in the "nanoscale" (1–100 x 10^{-9} meters) range. This R&D is called nanoscale science, engineering, and technology (NSET), which refers broadly to the rich new science that arises when materials and structures are made in the transition region between truly atomic systems and bulk materials.

In this nanoscale range, new properties and phenomena arise because sample sizes become comparable to many physical parameters that determine materials properties such as quantum wavelengths, mean free paths, coherence lengths, and domain dimensions. These dimensions also bridge the region where our classical and quantum models are used to describe behavior. Some of our R&D deals with materials actually fabricated with nanoscale dimensions, such as carbon nanotubes, quantum dots, and molecular electronic devices. But NSET can also refer to macroscopic systems formed from nanoscale components, such as ceramic materials made of nanoscale powders. Or it may encompass an electronic or mechanical system engineered from nanoscale-dimension devices. As you will see from the work presented in the *Review* cover story, NSET science can result in new electronic devices, new materials and materials properties, medical probes, and other applications limited only by the imagination.

ORNL is an ideal place for the seeds of NSET to grow because all the ingredients for success are here. What is needed for a successful NSET program are: (1) a strong core materials science and engineering program, (2) a variety of capabilities and expertise to synthesize new materials and process them into nanoscale configurations molecule by molecule, (3) world-class characterization facilities that can "see" new materials configurations at the atomic level and determine their properties, and (4) high-performance computer modeling and simulation capabilities to understand materials properties and predict new configurations. This list of needs perfectly matches ORNL's core competencies. That is why ORNL selected NSET as a major focus area to receive targeted internal funding from our Laboratory Directed Research and Development Program over the next three years.

Finally, the most compelling reason for emphasizing NSET at ORNL is that it promises to position us for new science and technology in the years to come. Recent reports by the National Research Council [1] and the DOE Office of Science [2][3] predict that most of the new science and technological breakthroughs in the 21st century will come from complex materials and structures "engineered" at the atomic level. A close examination of these reports shows that what is required to fabricate and understand complex materials and structures is NSET. Thus, by emphasizing this important area now and building on our already strong programs, ORNL will not only be ready, but will be a leader of this new science in the future.

Bill Appleton



Deputy Director for Science and Technology, ORNL

1. *Condensed Matter and Materials Physics: Basic Research for Tomorrow's Technologies*, National Research Council, National Academy Press, 1999.
2. *Complex Systems: Science for the 21st Century*, U.S. Department of Energy Office of Science Workshop at Lawrence Berkeley National Laboratory, March 5–6, 1999.
3. *Nanoscale Science, Engineering and Technology Research Directions*, Oak Ridge National Laboratory, August 1999.

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Oak Ridge National Laboratory is a multiprogram, multipurpose laboratory that conducts research in energy production and end-use technologies; biological and environmental science and technology; advanced materials synthesis, processing, and characterization; and the physical sciences, including neutron-based science and technology.

Brave New Nanoworld

Aircraft wings made of lightweight, high-strength carbon nanotubes only a few billionths of a meter in diameter. Magnetic storage disks that could hold 100,000 times more data than current disks. These are some possible applications of new nanoscience research now being conducted at ORNL.

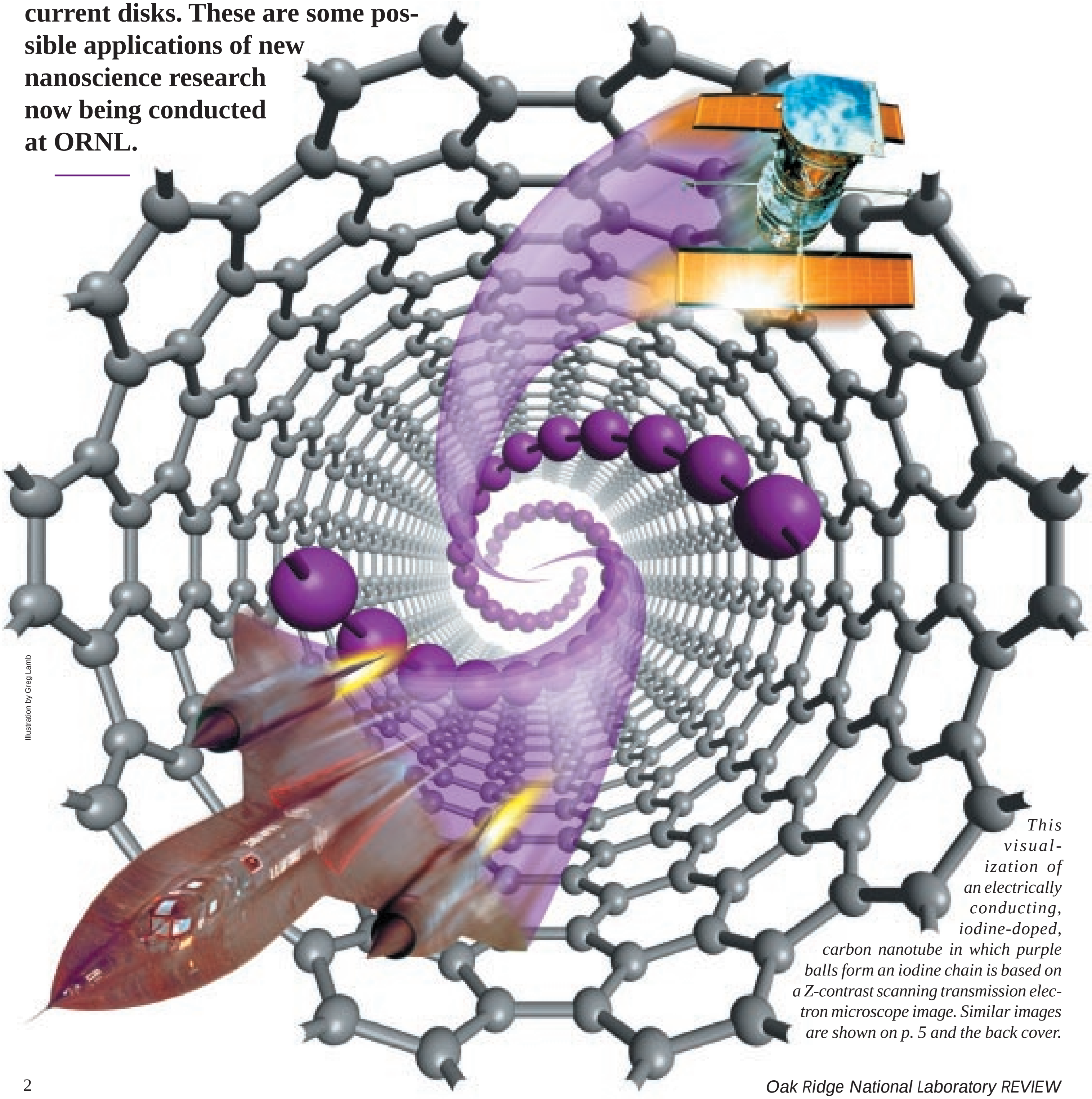


Illustration by Greg Lamb

This visualization of an electrically conducting, iodine-doped, carbon nanotube in which purple balls form an iodine chain is based on a Z-contrast scanning transmission electron microscope image. Similar images are shown on p. 5 and the back cover.

Like toddlers learning to build complex castles from toy blocks, a growing number of researchers are studying ways to assemble materials and devices from atoms. If their products stand up, the applications could be truly astonishing. Already, the growth of tiny crystals from a relatively small number of atoms in the 1980s has brought us more protective sunscreens and better cosmetics. Improved electronic devices ranging from cheaper flat-screen televisions to palm-size computers that recognize speech could be next. Thanks to the use of new techniques that allow scientists to "see" and manipulate atomic and molecular building blocks, such new technologies may be possible.

"It's amazing what one can do just by putting atoms where you want them," says Richard Smalley, co-discoverer of the buckyball in 1985 and winner of a 1996 Nobel Prize in Chemistry. Smalley, a Rice University chemist, is talking about nanotechnology, a new field focused on the very small that could become very big. It's a field that has been explored by just a few ORNL researchers for several years; however, more are expected to become involved because supporting nanotechnology and nanoscience research projects using ORNL's internal funds in the Laboratory Directed Research and Development (LDRD) program is a new initiative at the Laboratory. The more successful projects may qualify for federal funding that will likely come later. In FY 2001 budget guidance given to heads of federal departments and agencies, the White House Office of Science and Technology Policy identified nanotechnology as one of 11 R&D areas that are "important national efforts requiring coordinated investments across several agencies."

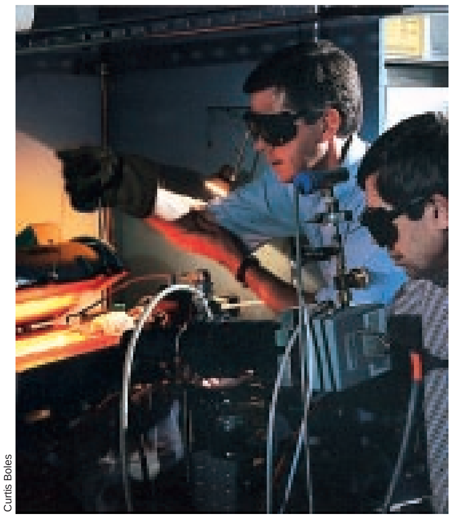
Nanotechnology is the study and use of materials, devices, and systems on the scale of a nanometer (a billionth of a meter, or 10^{-9} m). If researchers can learn to manipulate individual atoms at this scale, some experts believe the results could lead to a revolution in computing, electronics, energy, materials design, manufacturing, medicine, and numerous other fields.

Interior view of target chamber.

In testimony given on June 22, 1999, before the House Science Subcommittee on Basic Research, Eugene Wong, a National Science Foundation assistant director, called the nanometer "truly a magical unit of length. It is the point where the smallest man-made things meet nature." He suggested that, using atom-by-atom manipulation, scientists could change the properties of a material without altering its chemical composition. Instead of discovering a new phenomenon by accident, he said, scientists can now look for one systematically and soon may be able to design it to order.

Why Go Nano?

For most of this century, scientists have practiced "top-down science," a reductionist approach in which the goal is to simplify our understanding of matter by breaking it into its basic building blocks, ranging from quarks to neutrinos. But, in recent years, interest has arisen in complexity. Scientists want to know how simple atoms and molecules come together and arrange themselves to form complex systems, such as living cells that make life possible on earth. This "bottoms-up" science, which deals with how complex systems are built from simple atomic-level constituents, spawned nanoscience. It is the study of the properties of tens of or hundreds of atoms or molecules in a space with a diameter of less than 50 nanometers (a nanometer is about the size of two large atoms or four small ones).



Curtis Boles

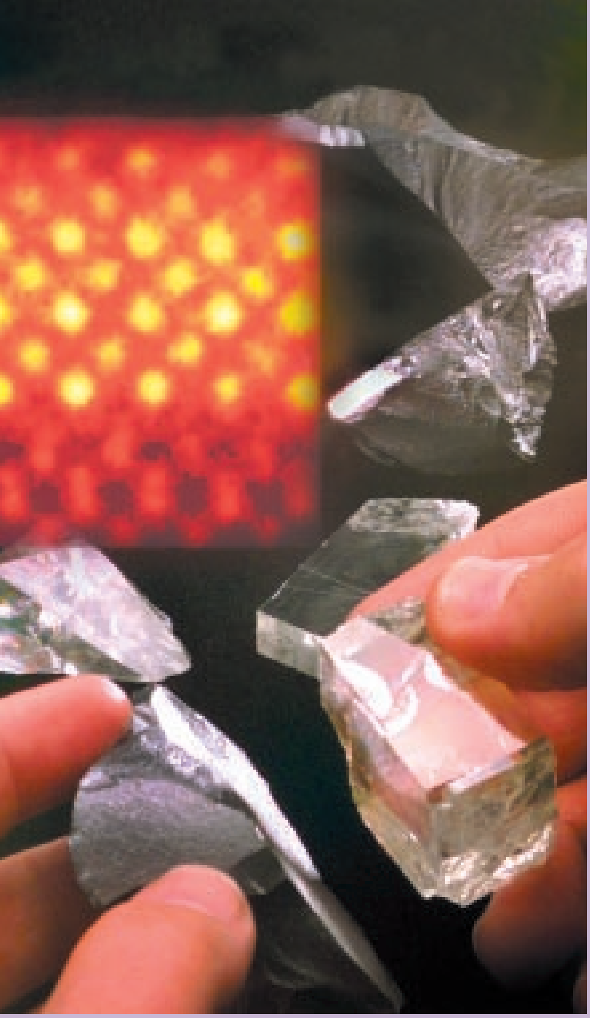
Dave Geohegan and Alex Puretzky use laser ablation to form carbon nanotubes for potential use in improving electronic devices.

"This field really took off in 1986 after the discovery of the buckyball, which is a stable cluster of 60 carbon atoms," says John C. Miller, a section head and physicist in ORNL's Life Sciences Division (LSD), who has been doing research in nanoscience for 10 years. In 1993 Bob Compton, then in LSD, started a project to produce and study buckyballs using laser ablation, the method used to produce the first buckyballs. ORNL is a world leader in laser ablation, which is the most versatile and powerful technique available for synthesizing many nanomaterials.

As part of this project, in 1994, Dave Geohegan of ORNL's Solid State Division (SSD) and Alex Puretzky, a visiting scientist working with Compton, obtained the world's first digital photographs of how buckyballs form in a bubble of carbon atoms confined in argon gas. In 1995 ORNL researchers Don Noid, Bobby Sumpter, and others working in nanoscience developed a computer visualization of helium flow pushing a "buckyball piston" in a carbon nanotube. This image was published on the cover of the Nos. 1 & 2, 1996 issue of the *ORNL Review*.

Besides the need to build complex materials and devices from atoms and molecules, a major driving force behind the interest in nanotechnology is the desire to build faster computers that will more quickly handle complex calculations. Fortunately, nanofabrication techniques are enabling the construction of smaller and faster logic devices, which will be needed for such difficult tasks as speech recognition and voice synthesis.

Computers have been getting faster and cheaper in large part because of the silicon revolution. According to an observation in the 1960s by Gordon Moore, co-founder of Intel, the number of transistors being packed into integrated circuits (semiconductor chips) doubled every year. He predicted this trend would continue, and the observation became known as Moore's Law. Actually, since 1975, the number of transistors on a semiconductor chip has doubled roughly every 18 months, enabling microprocessors to work faster and memories to grow larger while computer prices plummet. The key to this trend is the incredible shrinking of transistors with each chip generation. By



This micrograph shows a mock field-effect transistor with a layer of crystalline strontium titanate instead of silicon dioxide as the gate electrode. The layer was grown in registry with the silicon template making up the transistor's base. ORNL tests show that the transistor works.

Materials Advance May Help the Semiconductor Industry

A barrier to future increases in computing power is a restriction set by a compound of silicon itself. As transistors are downsized, the use of silicon dioxide to control electron flow will limit transistor performance.

After 10 years of research, Rodney McKee of ORNL's Metals and Ceramics (M&C) Division, Fred Walker of the University of Tennessee, and Matt Chisholm of the Solid State Division, have found a solution. They demonstrated that amorphous silicon dioxide conventionally used on silicon chips can be replaced with a crystalline oxide whose superior electrical properties will allow reduction in transistor size without loss of performance. In March 1999 the team built a field-effect transistor (FET) using crystalline strontium titanate and demonstrated that it performs as well as conventional transistors.

A FET is a common switching device used in modern electronic equipment. This tiny semiconducting device consists of three metal electrodes and a silicon base. When a conventional FET is turned on, electrons injected by a source electrode flow as a current through the silicon base for collection at a drain electrode. To turn the transistor off, a gate electrode between the other electrodes applies an electrical voltage to a dielectric film, causing it to "pinch off" the current by raising the silicon base's resistance. In this way, a transistor can function as an on-and-off switch. It can also store bits of information (a "1" if switched on, a "0" if switched off).

As transistor size is reduced, the silicon dioxide layer needed for the dielectric film will eventually become so thin (<3 nm) that it will be useless. The reason: it will leak electrons through quantum mechanical tunneling.

For decades, crystalline oxides have been considered a promising solution to this problem for the semiconductor industry. These materials have the physical thickness to support an electric field yet are able to store electrical charges more effectively. But no one had been able to produce the high-quality layer needed to support shrinking semiconductors. Using molecular beam epitaxy, a precisely controlled process for growing thin films under ultrahigh vacuum, and a $400 video camera to tape the deposition of oxide films on silicon, McKee and Walker learned which conditions allow film crystals to grow in registry with the silicon crystal template beneath, producing a perfect film.

Because strontium titanate exerts a stronger influence on the transistor's conductivity than silicon dioxide, the gate electrode can take up less space, compressing the area between the source and drain electrodes and shortening the distance the electrons would travel. The benefits? Transistors with strontium titanate are likely to be smaller and faster.

squeezing more transistors and other features into integrated circuits, the travel distances of electrons are shortened so calculations can be made faster using less power.

To keep up this current rate of improvement in computing power, the Semiconductor Industry Association declares that the minimum size of transistors, which is now around 250 nanometers (nm), must reach 130 nm by 2003 and 50 nm by 2012. Mike Simpson, an electrical engineer in ORNL's Instrumentation and Controls (I&C) Division, sees the problem this way:

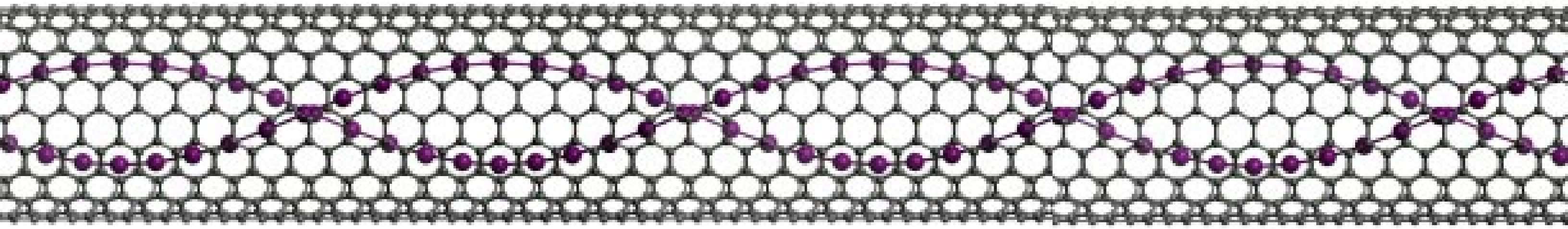
"If you make devices too small using silicon, they will run up against physical limits such as unwanted quantum effects. For example, electrons could leak, or 'tunnel,' through insulating layers, causing circuits to short. In addition, to make smaller silicon devices, a fabrication facility costing as much as $30 billion may be required. Semiconductor chip fabrication could become prohibitively expensive."

So what are the answers? "One solution," Simpson says, "is to switch to materials other than silicon that take advantage of quantum effects to increase the speed and density of features on chips. Examples of alternative materials being explored at ORNL are spinach proteins for diodes and carbon nanotubes for pins and molecular wires. Then we must find ways to get nano-objects made of these materials to assemble themselves to bring down the costs of device fabrication."

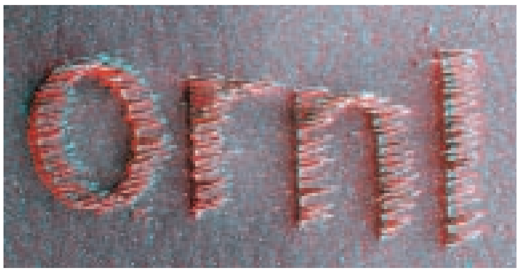
Carbon Nanotubes: The Strongest Material

Since 1991, many organizations, including ORNL, have developed and tested various ways to make carbon nanotubes and put them to use. Carbon nanotubes are tiny strips of graphite sheet rolled into tubes a few nanometers in diameter and up to hundreds of micrometers (microns) long. The graphite has a network of hexagonal rings, leaving it with many unpaired electrons. Carbon nanotubes conduct electricity and heat amazingly well, so they are being considered for use as wires for nanosized electronic devices in future computers, charge-storage devices in batteries, and electron guns for semiconductor chip etching and flat-screen televisions and computer monitors. They also could store hydrogen gas to power fuel cells. Furthermore, carbon nanotubes are the world's strongest material in terms of tensile strength and they are lightweight and flexible. Consequently, they could be useful as ultralight structural materials for wings of advanced aircraft and space probes to make them stronger and more energy efficient. Thus, there is intense interest in finding a way to produce nanotubes in large quantities.

Geohegan and fellow SSD researchers Puretzky, Xudong Fan, and Steve Pennycook have synthesized these long, thin tubes through laser ablation and then studied the results. They use a pulsed ultraviolet or visible laser to vaporize a graphite target containing a small amount of metal catalyst in a quartz tube that is heated in an oven to over 1000°C. Streaming from the target is a "bubble" of 10^{16} carbon and metal atoms



that is confined by a low-pressure background gas of argon. If the argon gas is cool, it forces the carbon and metal atoms to collide frequently with each other so that they form nanoclusters (up to 2 nm in diameter) and nanoparticles (up to 100 nm in diameter). But when the argon gas is hot, the metal transforms the carbon with astonishing efficiency into single-walled nanotubes, which consist of one layer of carbon atoms.



The Laboratory's initials have been constructed from carbon nanotubes using plasma-induced CVD on predeposited catalyst patterns. The letters are started by forming a pattern using electron beam lithography followed by electron-gun evaporation of the iron catalyst.

Until this past year, no one had witnessed this synthesis process. But in 1999 the SSD researchers used special imaging and diagnostic techniques (digital imaging, laser-induced fluorescence, spectroscopy) to determine what forms when during nanotube synthesis. Transmission electron microscope (TEM) images reveal the product of laser ablation: bundled ropes of single-walled nanotubes that resemble a pile of spaghetti.

"One of our goals," Geohegan says, "is to learn how to use laser ablation to control the length, structure, and electrical properties of carbon nanotubes we make for nanoelectronic devices being constructed at ORNL. Another goal is to understand how carbon nanotubes form and grow. This information could lead to methods for scaling up production to meet the need for ultralight structural materials that are one hundred times stronger than steel but have only one-sixth the weight."

The secret to making carbon nanotubes lies in the target—a pellet made of graphite powder and cement mixed with particles of a metal, such as cobalt, nickel, or iron. During laser ablation, the metal forms tiny nanoparticles that serve as seeds to catalyze the formation of the carbon nanotubes.

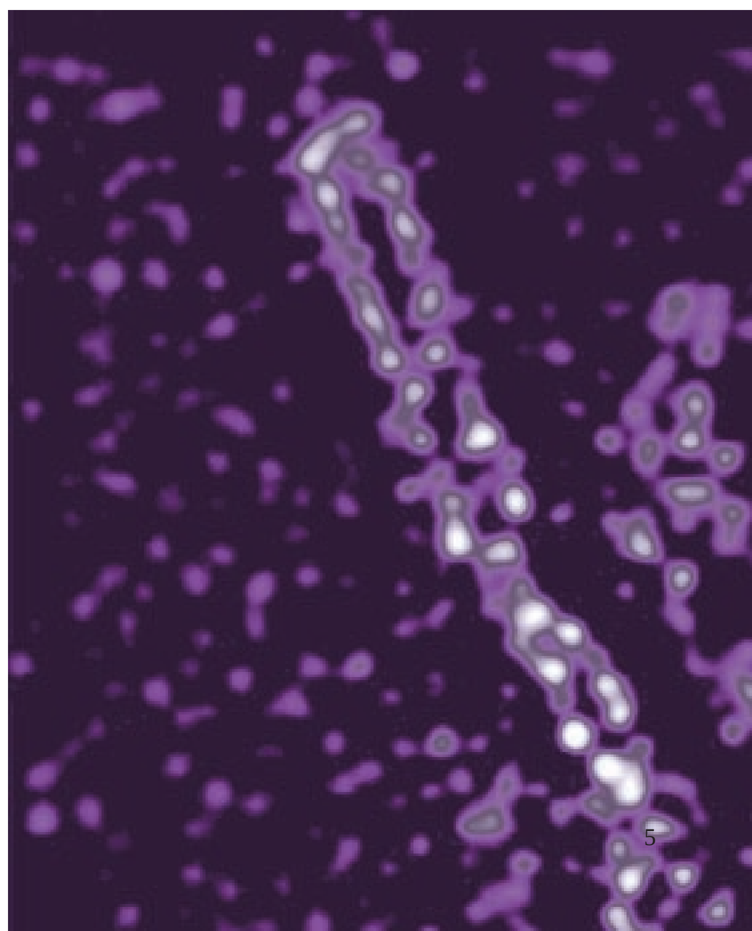
By obtaining a sequence of stop-action images of the laser ablation process and the carbon-catalyst plume, the ORNL researchers are addressing these questions: When do the metal catalyst atoms and carbon atoms disappear and form nanoparticles? Do nanotubes grow from atoms or nanoparticles? When does growth begin, and how fast do the nanotubes grow? What role does catalyst particle size play in the growth?

Using digitized snapshots and spectroscopy of the vaporized plume during nanotube formation, Geohegan and Puretzky are removing some of the mystery of nanotube synthesis, controlling the time available for growth, and producing short nanotubes for electronic applications. Together with Fan's TEM analysis of nanotubes produced under various controlled conditions, the researchers have measured the first growth rates of nanotubes made by laser ablation and gleaned clues as to how to scale up the process. This research led to a seed money project with Roland Seals of the Oak Ridge Y-12 Plant's Development Division to come up with a manufacturing process that would produce large quantities of carbon nanotubes for direct use in structural materials.

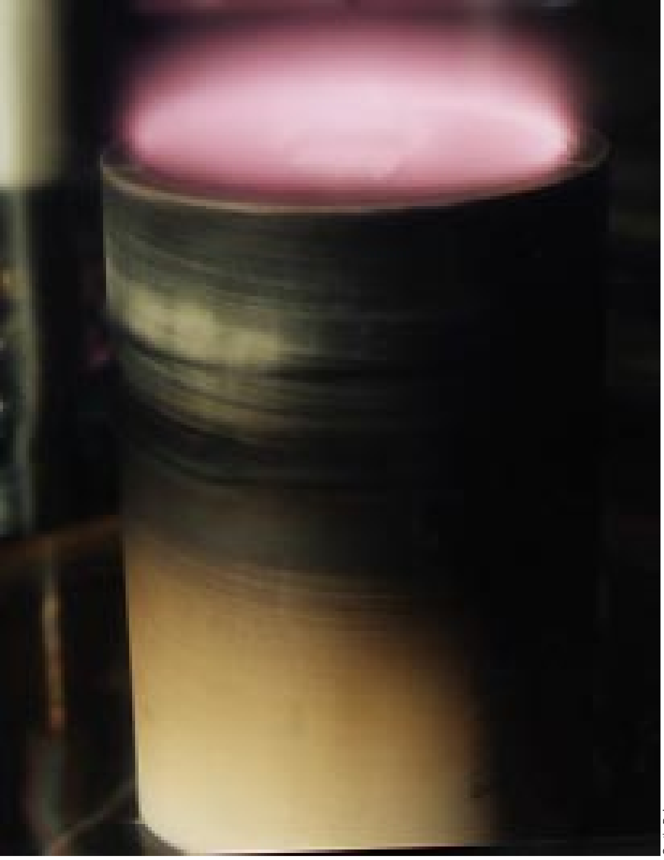
Doug Lowndes, Gyula Eres, and postdoctoral researchers Vladimir Merkulov and Yayi Wei, all of SSD, are using chemical vapor deposition (CVD) and plasma-enhanced CVD to make arrays of carbon nanotubes for use as field emitters of electrons for an ORNL-developed electron lithography method of making faster silicon chips (see "Carbon Nanotubes for Chip Writing?" on p. 8). The first tubes grown in the summer of 1999 using CVD produced multiwalled tubes (tubes within tubes) that are microns in length and 20 to 40 nm in diameter. Lowndes and Merkulov also evaporated metal catalyst particles, such as nickel or iron, onto a silicon substrate and then exposed it to a carbon-bearing gas mixture to produce arrays of vertically oriented carbon nanotubes on silicon. The process is being fine tuned to produce multiwalled nanotubes as small as 10 nm in diameter.

In 1999, the researchers developed a nanotube transistor using a carbon nanotube to bridge electrically conducting catalyst electrodes fabricated by electron beam lithography. The multiwalled tube was grown between the electrodes using selective area thermal CVD.

"In addition to its great mechanical strength," Lowndes says, "the nanotube is capable of ballistic conduction, similar to photons flying through optical fibers. Electrons flow through a nanotube without scattering off any atoms, so they encounter hardly any resistance and lose virtually no energy. In fact, a superconducting



Z-contrast scanning transmission electron microscope image of iodine atoms in a carbon nanotube (visualized above).



Curtis Boles

The pink glow enveloping the square sample results from plasma-induced chemical vapor deposition, which is used to grow carbon nanotubes. The sample has a layer of a metal catalyst, such as iron or nickel, to promote nanotube growth.

Using a model of a carbon nanotube, Phil Britt shows how he and Shane Bromley chemically alter a nanotube with modified thiol molecules to get it to bind to the surface of a gold electrode. Below: Carbon nanotubes are chemically modified by heating them in a solution of alkanethiol, which enables them to assemble themselves in the proper orientation on a gold pad. Chemically treated nanotubes may someday be used as molecular wires in newly developed electronic devices.

current was recently induced in a carbon nanotube at low temperatures." Carbon nanotubes can carry an electric current as high as 10^9 amps/cm^2.

Geohegan, Lowndes, Simpson, Phillip Britt of the Chemical and Analytical Sciences Division (CASD), and David Joy of ORNL's Metals and Ceramics (M&C) Division and the University of Tennessee have received LDRD funding to study carbon nanotubes. They seek to determine the effect of a nanotube's atomic-scale structure on its electronic properties. They hope to understand better how carbon nanotubes grow and how they operate as electronic wires and semiconductors. Such knowledge is needed to move nanotubes toward commercial application in electronic devices.

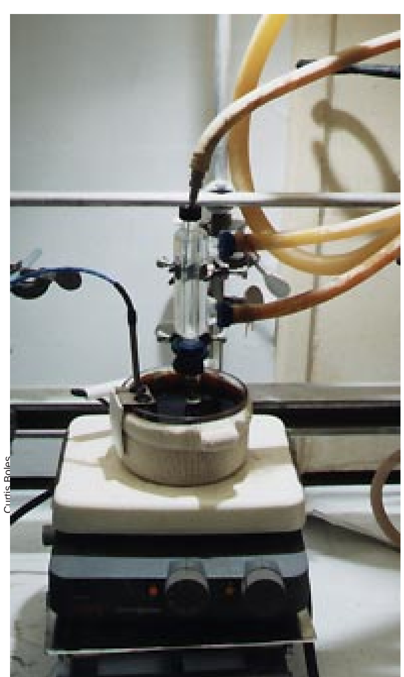
Nanoelectronic Devices: Made of Spinach Proteins And Carbon Nanotubes?

In the 1990s, three researchers in ORNL's Chemical Technology Division—Eli Greenbaum, James Lee, and Ida Lee—gathered evidence that spinach is a plant with potential. They became particularly interested in a chlorophyll-containing protein in spinach called Photosystem I (PSI, pronounced PS One). They knew it performed photosynthesis using the energy of the sun to make plant tissue. But another amazing feature of this photosynthetic reaction center was that when it receives a photon of light, electrical current flows through it in one direction in 10 to 30 picoseconds—100 times faster than in a silicon photodiode. Thus, spinach proteins could be used as a photo battery or solar electric cell.

The ORNL researchers' challenge was to show that PSIs could be lined up perpendicular to a metal surface such as that of an electrode. Then these 10-nm spinach proteins could be used as nanodiodes to transmit current in one direction and block it in the other in the absence of light, making possible the fabrication of biomolecular electronic devices. The researchers met the challenge, suggesting that the next generation of opto-electronic devices may be based on spinach, not silicon.

After isolating PSIs from spinach leaves, they learned how to make current flow along spinach proteins by depositing a platinum electrical contact on the end of each PSI. Next they showed that platinum anchors PSIs to a gold surface.

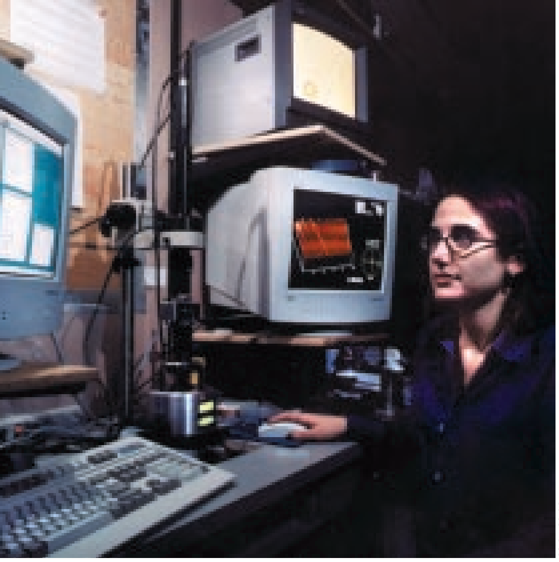
A major challenge was to orient the PSIs so that all the same ends point in the same direction either perpendicular or parallel to a metal surface. In 1997 the researchers found an effective way to achieve preferred orientation of PSIs: chemical treatment of the atomically flat gold surface on a mica substrate. They coated gold surfaces chemically with 2-mercaptoethanol and found that most of the PSIs point up, like lawn grass. The sulfur atom in this molecule attaches strongly to gold, and the molecule's other end selectively binds to the positively charged free end of a PSI, causing it to be perpendicular to the surface.



Curtis Boles

The next step was to build a biomolecular device. Greenbaum met with Simpson to plan the design of a hybrid nanodevice using spinach reaction centers as the diodes. Other ORNL participants in the project are Lowndes, Geohegan, and Britt. Their expertise is needed because the nanodiodes made of oriented spinach proteins are to be connected by nanowires made of carbon nanotubes.

Simpson and two University of Tennessee graduate students have been building



Curtis Boles

Shane Bromley, a University of Tennessee graduate student, displays images of single-walled carbon nanotubes (yellow features) attached by sulfur-bearing (thiol) molecules bonded to a gold surface (reddish area) on a silicon-titanium substrate, as seen through the atomic force microscope shown in the photograph.

molecular electronic devices that do signal processing and logic functions using spinach protein nanodiodes. Eventually, these devices will have wiring made from carbon nanotubes. These tubes are produced by laser ablation in SSD and delivered to the I&C Division as black soot in a jar.

ORNL's first biomolecular electronic device using spinach proteins as diodes was built in the spring of 1999. PSIs, each measuring 10 nm by 6 nm, stood like soldiers in a tunnel with their feet on the floor and their heads against the ceiling. The gold electrode was treated with a chemical that binds strongly to both gold and the positively charged free ends of the PSIs, making them point up to the platinum electrode to which they adhere. The PSIs were illuminated by pulses of light from the device, causing them to conduct a current in one direction and block it in the other. This current was measured on the device, showing that the spinach biochip worked.

"We made the first device with two electrodes only 15 nanometers apart and with PSIs oriented between the electrodes," Simpson says. "We have atomic force microscope images that show the PSIs are perpendicular to the electrodes."

At the Cornell University Nanofabrication Facility, Michael Guillorn, a UT graduate student who works with Simpson, recently constructed a molecular logic gate in which a PSI is placed in a 15-nm gap among three electrodes—two gold and one platinum.

While PSIs are building blocks for logic gates, it is hoped that carbon nanotubes can be used on the ORNL hybrid biochips as molecular wiring to connect the logic gates. "Carbon nanotubes," Simpson says, "also could be used

Imitating Nature: Nanopowders for Ceramics

A fleck of dust that attracts a crowd of water vapor molecules may give rise to a drop of rain or a snowflake. Similar processes creating nanoclusters that form fog and clouds are described as nucleation, growth, and transport (NGT) phenomena. Michael Z.-C. Hu, a researcher in ORNL's Chemical Technology Division, studies NGT phenomena at the microscopic level with a practical application in mind. He is trying to imitate nature (the biomimetic approach) in his search for low-cost, environmentally friendly processes for synthesizing nanostructured materials from nanopowders and nanocrystals. His team has demonstrated that nanocluster-based material growth processes can be used to build nanoelectronic devices.

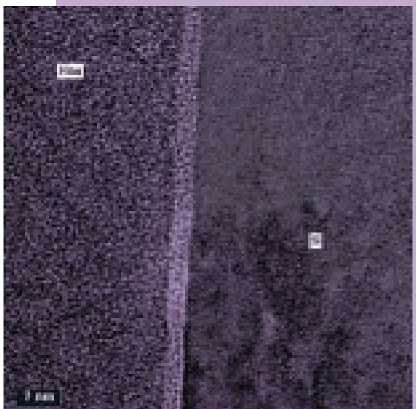
Novel materials with special properties have been created from nanopowders—building blocks smaller than 100 nm in diameter. When a ceramic is fabricated from nanopowders, the resulting advanced nanophase material has dramatically improved properties. For example, it may be stronger and less breakable than conventional ceramics. It may conduct electrons, ions, heat, or light more readily than conventional materials. It may have improved magnetic or catalytic properties.

"Because the nanoparticles we make are so small," Hu says, "each particle has a greater grain boundary area than in ordinary ceramics. The continuous connections between larger numbers of grains make the material more stretchable and ductile so it doesn't easily crack. Ceramics made of nanopowders are, therefore, tougher and stronger. You may cut a piece of nanophase ceramic just like a piece of plastic."

Electrical, magnetic, optical, and catalytic properties are improved in nanostructured materials because they are made of tight clusters of very small particles. The overlapping electron clouds of closely packed nanoparticles induce quantum effects because of the multiplied influence of short-range, molecular forces. One result may be more efficient conduction of electricity or light.

To produce materials with desirable properties, Hu applies his understanding of NGT phenomena to the development of chemical processes to control the size, shape, and surface properties of nanoparticles.

"To measure particle size, we use dynamic light scattering and small-angle X-ray scattering," Hu says. "We found that we can make molecular clusters smaller than half a nanometer. For example, we prepared and observed a zirconium tetramer—which is four zirconium atoms coupled together—as the starting species for further nanoparticle synthesis."

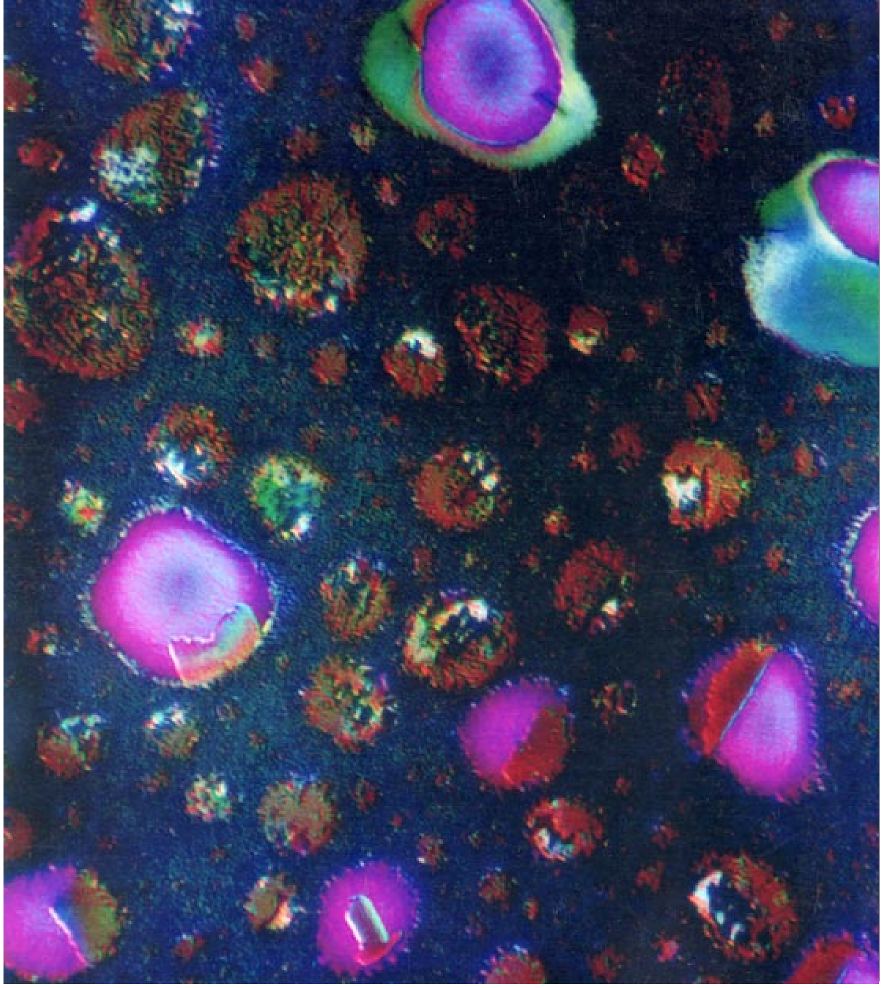


*High-resolution transmission electron micrograph (cross section) of a high-quality optical titania thin film on a single-crystal silicon wafer prepared by a newly discovered molecularly directed solution deposition approach. It shows that the film (left side of the SiO_2 interface) contains uniformly distributed short-order nanostructures (1–3 nm) in a somewhat amorphous background. (*Image by Larry Allard.*)*

Using a simple process at speeds of interest to industry, Hu has produced ceramic oxide nanoparticles. He has synthesized microspheres of various materials, including zirconium oxide, titanium oxide, barium titanate, and titanium zirconate. He has shown his process can also produce films and coatings.

To make nanopowders, Hu came up with a new twist on an old process using a novel dielectric-tuning solution (DTS) synthesis route. His technique involves speeding up forced hydrolysis—a process using heat and an aqueous solution of an inorganic salt (e.g., zirconium chloride)—by introducing an organic solvent. The solvent is usually a simple alcohol, such as isopropanol, which fine-tunes the nucleation and growth of nanoparticles (e.g., zirconium oxide).

The DTS method can cause a ceramic material to form perfect spheres rather than the cubes that result from conventional forced hydrolysis. Ultrafine, monodispersed microspheres made of nanocrystals such as barium titanate and zirconium titanate can be produced this way. Such microspheres could be useful for the fabrication of miniaturized multilayer electrical capacitors as well as resonators and filters in microwave electroceramic devices.



This interference color optical micrograph shows voids and defects on the surface of an oriented single crystal of sapphire implanted with vanadium and oxygen ions and then subjected to rapid heating.

for molecular components such as diodes, transistors, logic gates, or field emitters of electrons for supercomputer chips that will perform molecular computing."

Simpson sees carbon nanotubes as the solution for the input-output problem involved in setting up communications between nanodevices and the larger world outside. "Right now each chip is nestled on a larger block of pins that communicate through attached wires with the outside world," Simpson says. "If you have 18 million transistors or 10^{12} gates on a chip, the device would have to be much bigger just to make space for that many more pins. So, we're proposing to replace the pins and wires with electron beams emitted by arrays of carbon nanotubes placed in an electric field both on and off the chip. Carbon nanotubes in arrays outside the chip would serve as field emitters of electron beams that 'talk' with an array of beam-emitting carbon nanotubes on the chip."

Simpson envisions a supercomputer the size of a grain of rice that is wired with carbon nanotubes. He sees it surrounded by arrays of carbon nanotubes that would beam data into the nanocomputer and retrieve from it any needed information.

To build a device with nanowires, ORNL staff members purify carbon nanotubes, cut them to the appropriate size range, and separate them by size. Britt and Shane Bromley, a UT graduate student who works with Simpson, treat them chemically by attaching molecules at their ends and on electrode surfaces, causing the nanotubes to assemble themselves in place in proper orientation.

"Carbon nanotubes," says Simpson, "could be the silicon of the future."

Carbon Nanotubes for Chip Writing?

Today's circuit patterns are etched on chips on silicon wafers by use of light—optical lithography. A mask containing a circuit pattern is imaged on each layer of every silicon chip, and a beam of light carves a circuit in the chip part not shielded by the mask. The size of the circuits made by optical lithography is limited by the wavelength of light.

Because the wavelength of electrons is so much shorter than that of light photons, an electron beam could etch a much narrower winding path in the chip, creating a finer, more closely packed circuit. Today's state-of-the-art circuits are about 200 nm wide, but ORNL researchers led by C. E. (Tommy) Thomas of the I&C Division think their chip-writing technique using precise electron beams from carbon nanotube-tipped field emitters could make a circuit only 100 nm across or even as small as 10 nm. They believe that by 2004, they will meet the semiconductor industry's goal of making production chips whose circuits are 8 times denser and up to 16 times faster than chips of the same size currently being etched by optical lithography.

ORNL's proposed addressable-field-emitter array (AFEA) is a two-dimensional array of miniature electron beam sources. The sources will use carbon nanotubes made by Lowndes and Merkulov using plasma-enhanced CVD. Early tests by Larry Baylor of the Fusion Energy Division (FED) show that when the Oak Ridge carbon nanotubes are placed under a certain voltage, they are 10 times more efficient than amorphous diamonds as field emitters of electrons.

When a computer-controlled bias grid places an array of nanotubes under a voltage, it will emit electrons. When the voltage is dropped to zero, the nanotube array will stop emitting electrons. Each nanotube array is addressable by a computer, enabling the programming into the AFEA of the desired circuit patterns to be written onto the chip.

The chip-writing program will be allocated to a network of 100 parallel computers that will send turn-on and turn-off signals to the AFEA logic and memory circuits connecting the cathodes. This digital "mask" can be reprogrammed to create

Caged Atoms for Flat-Panel Displays

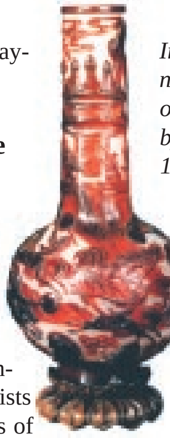
Flat-screen, high-definition televisions and flat-panel displays to replace bulky computer monitors consume lots of power. Thinner screens with reduced power appetites may someday become available as a result of an emerging ORNL technology involving nanoparticles doped with light-emitting atoms. This technology could make possible flat-panel displays that are sharper than laptop computer screens. It should also lead to higher-resolution detectors of gamma rays, X-rays, and other ionizing radiation, as well as of fluorescent tags on DNA fragments. Highly efficient laser diodes for optical circuits may also be made using this technology.

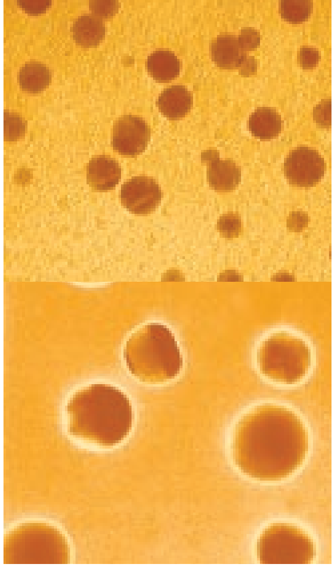
Thomas Thundat of LSD, SSD's Doug Lowndes, Gilbert M. Brown of CASD, postdoctoral scientist Adosh Mehta, Arun Majumdar of the University of California at Berkeley, and Ramesh Bhargava of Nanocrystals Technology, Inc., are developing a new class of nanosensors and nanodevices using caged atoms in doped nanoparticles. Each particle is doped with a few atoms of a rare-earth element that emits light of a specific color when excited by an electric field, ultraviolet light, or mechanical action. The dopants are europium (emitter of red light), thulium (blue light), and terbium (green light).

different circuit patterns on new layers within milliseconds.

Making New Smart-Surface Materials for Miniature Devices Using Ion Beams

A team led by Lynn Boatner of SSD has demonstrated the concept of creating "smart nanocomposite surfaces" on inactive materials to make them both "sensors" and "actuators." The scientists used accelerators to implant ions of vanadium and oxygen in a single crystal of aluminum oxide (Al_2O_3), or sapphire. Then the sapphire host was appropriately heated in the correct atmosphere to remove ion-implantation damage and induce the growth of dispersed rod-like crystallites of vanadium dioxide (VO_2). Because the sapphire has a smart nanocomposite surface that can both detect and react to light or heat, this patented material could be a candidate for a number of optical-device applications, including "smart windows."





In this art-glass vase (left) crafted during the reign of the Chinese Emperor Chi'en Lung (1736-96), very small single crystals of either gold or copper produce the beautiful red-colored glass by scattering light through a process first explained in G. Mie's 1908 theoretical work. Four-nanometer-diameter gold particles like those shown in the transmission electron microscope image (top right) would produce a light pink color, while larger ~30-nm-diameter gold particles would produce a deeper red color (bottom right). Though unaware of it, artisans were applying nanotechnology for hundreds of years before the electron microscope revealed the presence of the gold or copper nanoparticles responsible for the red coloration of art glass. The Corning Museum of Glass, Corning, New York, gift of Benjamin D. Bernstein.

In a smart window application, intense light like that from a powerful laser strikes the nanocomposite surface and rapidly heats up the embedded VO_2 particles, transforming them into a metallic "mirror-like" state. Instead of letting the incoming light through, the window now reflects it back in the direction of its source. Such smart windows might be used, for example, to shield a satellite's sensitive internal optical components from either accidental damage or intentional sabotage.

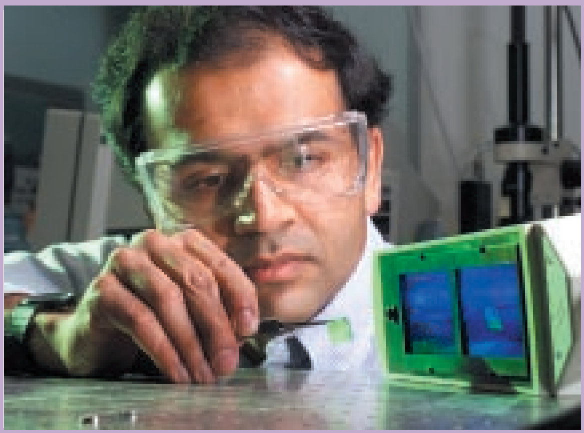
"Our patented sapphire surface nanocomposite contains nanometer-thick crystallites of vanadium oxide that can be up to microns in length," Boatner says. "The vanadium oxide crystallites are embedded nanophase precipitates that effectively 'activate' the near-surface region of an inactive material like Al_2O_3. The VO_2 crystallites can both sense a signal and respond to it, making the surface nanocomposite a classic smart material."

Boatner and Tony Haynes of SSD lead a team of SSD and Engineering Technology Division (ETD) researchers who recently received LDRD funding to apply this smart surface-layer concept to the development of new miniature devices. Because the surface nanocomposites are formed by ion implantation and thermal processing, the research will require the development of appropriate ion implantation conditions as well as heating and cooling rates for the thermal processing of a wide variety of host materials.

The SSD and ETD researchers will look at ways of applying vanadium oxide nanocom-

"The dopant atoms caged inside the nanoparticles show interesting properties as a result of quantum confinement," Thundat says. "Because of the overlap of the electron shells of the dopant and host atoms, the nanoparticles are more efficient photon sources."

The researchers are building a flat-panel display that uses low voltage for operation. "In a clean room in the Solid State Division, we are making silicon devices with microchannels and demonstrating electroluminescence," Thundat says. "When the device is under an electrical potential, the electrons excite the doped nanoparticles sandwiched between the silicon base and a conducting glass electrode on the top. The light from these doped particles should be sufficiently intense for a flat-panel display because they have a much higher quantum efficiency than undoped nanoparticles."



Curtis Boles

Adosh Mehta holds a glass plate that glows green in ultraviolet light. The plate's tiny channels are packed with gadolinium oxide nanoparticles doped with terbium.

Some scientists are trying to find ways to control the sizes of nanoparticles because size determines the color of the light they emit. Doping the nanoparticles with rare-earth atoms to get the desired color removes the need for stringent control of the size of conventional nanoparticles.

In a TV set, each tiny square, or pixel, on the screen contains emitters of the different colors—red, blue, and green—behind which are sources of electrons that stimulate the emission. If the pixel for the image being shown must be red, then only the voltage source for the red emitter will be turned on for that pixel. In the ORNL device, each microchannel represents one pixel. The nanoparticles are arranged so that only one type of doped particle is electrically activated if light of only one color is desired.

Because of the smaller sizes of the nanoparticle light emitters, very little power will be used and less space required for the power sources. Thus, the doped nanoparticle approach could enable the development of thinner flat panel displays and could extend the lifetime of laptop computer batteries.

In a radiation detector made from the ORNL nanodevice, the gamma rays excite the caged atoms in the nanoparticles. The radiation detector consists of hundreds of vertical channels 10 microns in diameter and 300 microns deep. Packed inside each channel are thousands of 2–3-nm particles of gadolinium oxide. The emitted light from the doped nanoparticles travels through the channels and reaches a photodetector at the base.

"Today, it takes more than five incoming photons to produce an outgoing photon that can be detected in a photodetector," Mehta says. "Our device will have a much higher quantum efficiency because it will produce a photon for every photon coming in, providing a much sharper image or giving a more precise reading."

ORNL researchers showed that cyclopentadienyl (C_5H_5) rings could be imaged and manipulated with a scanning tunneling microscope (STM) at room temperature. They discovered that the STM probe could be used as a "molecular broom" that "sweeps" C_5H_5 rings to the side, perpendicular to the probe's scan direction. As the probe moves, the rings make quantum jumps across the silver surface, leaving a zigzag track (as shown above).

posites to integrated optical devices, including switches and attenuators. ETD's Steve Allison has envisioned several configurations of fiber optics and thin-film integrated optics in which these nanocomposites may be used to modify and control light signals in new and useful ways. Such materials can also store data recorded on them by a laser beam, because at each point heated above the VO_2 transition temperature by the beam, the surface reflectivity not only changes but also does not return to its original value. Optical-transmission effects resulting from the phase transition in a VO_2 nanocomposite surface can also be controlled by overlying the surface with a transparent thin film of tin oxide as a resistive heater. When an applied current heats up the tin oxide film, the VO_2-host nanocomposite surface changes from the transparent to the reflective state, creating an optical switch.

Haynes and Boatner and their SSD associates, including Al Meldrum and John Budai, have been studying iron nanocrystals implanted in yttrium-stabilized zirconia (YSZ) for their magnetic and ferromagnetic properties. "The beauty of having iron particles embedded just below the surface," Haynes says, "is that they don't oxidize—that is, rust—because they are protected from the atmosphere by the surrounding host material. In addition, crystalline YSZ is an ideal substrate for iron particles because it lines them up crystallographically. The result is a smart ferromagnetic material that senses an applied magnetic field and responds by changing its state and retaining a magnetic field proportional to the field that was originally applied."

SSD's Frank Modine and Shinichi Honda showed that the intensity of specially polarized light passing through iron nanocrystals in YSZ changes when a magnetic field is applied (an effect known as magnetic circular dichroism). They plan to study nanocrystals of three other magnetic materials—nickel, cobalt, and magnetite (Fe_3O_4)—embedded in zirconia. "If we could make a material with evenly spaced 10-nanometer magnetic particles," Haynes says, "we might be able to develop the highest-density and most stable data storage disk on which data could be read and written by using magnetic fields." Most recently, Jim Thompson, a visiting scientist from the University of Tennessee and one of his doctoral students, K. J. Song, have been using the ORNL superconducting quantum interference device magnetometer to characterize new ferromagnetic nanocomposite surfaces.

ORNL researchers also plan to use the ion-implantation-thermal processing technique to make "shape memory" nanocomposites in which the precipitated particles can change and restore their shape in response to temperature variations. Such shape-memory surface nanocomposites might find applications as actuators in microelectromechanical systems (MEMS) devices. Magnetostrictive particles that change their size when a magnetic field is applied could also be formed in appropriate hosts for similar micromechanical applications.

SSD researchers led by Woody White, a co-principal investigator in this LDRD project, have also created other types of surface nanocomposites by using ion implantation and thermal processing to form semiconducting and metal precipitates embedded in a variety of host materials. "We are learning how to control both the size and location of metallic and semiconducting nanocrystals in a material to obtain desired optical and electrical properties," White says. "Size is important because it determines a semiconducting nanocrystal's ability to absorb and emit light. Because size determines the color of emitted light, full-color flat panel displays for computers may someday be made of appropriately sized semiconductor nanocrystals formed by ion implantation."

To have even better control over nanocrystal precipitate size and location in a matrix and to develop new devices based on fiber-optic, thin-film, and integrated chip configurations, ORNL scientists will use Vanderbilt University's new finely focused ion beam facility in collaboration with Len Feldman, an ORNL Distinguished Visiting Scientist from Vanderbilt. This finely focused ion beam can implant atoms into dots as small as 5 nm at precisely controlled locations. "Ion implantation," White says, "could be useful for making modulators and optical switches and as a good prototyping tool to verify that nanocrystals of the desired size and spacing can be made to produce materials with desired properties."

Molecular Broom and Quantum Dots

John Wendelken and Zhenyu Zhang's first foray into nanoscience resulted in a story in the February 16, 1998, issue of *Chemical & Engineering News*. The work involved using a scanning tunneling microscope (STM) probe to induce molecules to move in a specific direction. In an STM, a probe scans across a surface, holding a gap of less than 1 nm between the STM tip's last atom and the surface atoms. By maintaining a constant current with a sensitive feedback mechanism, the undulations of the STM tip as it is scanned across the surface are interpreted as an atomic-level image of the surface.

In one set of experiments performed by Wendelken and his former postdoctoral researcher Larry Pai in late 1997, the STM was used to image a silver substrate exposed to low-pressure ferrocene gas $[Fe(C_5H_5)_2]$. The STM tunneling current decomposed the gas, separating iron from the hydrocarbon molecules. In this same way, the STM could be used to fabricate iron-containing nanoscale structures having arbitrary shapes. At the same time, it was found that when ferrocene gas was decomposed on another surface, ring-shaped cyclopentadienyl (C_5H_5) radicals were deposited on the silver substrate. The ORNL researchers were the first to show that these C_5H_5 rings could be imaged and manipulated with the STM at room temperature.

Pai discovered that the STM probe could be used as a "molecular broom" that "sweeps" C_5H_5 rings to the side, perpendicular to the probe's scan direction at room temperature. The discovery came shortly after SSD theorist Zhang predicted that the C_5H_5 rings would make quantum jumps perpendicular to the scan direction on the silver surface. Indeed, Pai's STM images show the rings jumping across the silver surface, leaving a zigzag track.

We don't know exactly why the rings move in steps the way they do," Zhang says, "but we believe the repulsive force between the tip and the negatively charged radicals perturbs the rings, giving them enough energy to jump over the natural barrier to their forward motion as they try to diffuse."

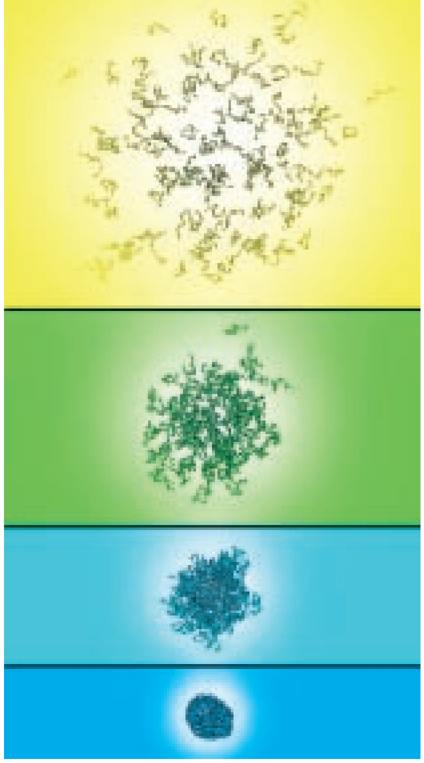
This process of using an STM to make iron-containing nanoclusters and depositing C_5H_5 rings represents an inefficient, serial approach to nanofabrication, or self-assembly of nanoscale structures. The SSD group has received LDRD funding to develop a parallel approach to nanofabrication to speed up the production of useful devices. Zhang, Wendelken, and Jian Shen hope to make a large number of quantum dots—each a nanocluster of a few hundred atoms—that have the same size and are spaced equally. The idea is to take advantage of natural Coulomb repulsion in which two particles with electrical charges of the same sign repel each other.

The researchers are developing a "buffer layer assisted growth" process to enable self-assembly of nanoclusters with a uniform size and spacing. They have been depositing iron atoms on a solid buffer layer of frozen xenon gas on copper and silicon substrates at low temperature. Xenon was chosen as a buffer layer because it does not absorb electrons, provides a high-mobility surface for atom diffusion, and isolates the growing quantum dots from the substrate. Zhang predicted that the iron atoms would slide around on the xenon layer and form three-dimensional islands, or nanoclusters. The researchers use a low-energy electron source to deposit electrical charges on the nanoclusters. According to Zhang's theory, the charges will limit the growth of the nanoclusters, keeping them at about the same size because additional charged atoms moving their way would be repelled. In addition, because the charged nanoclusters are about the same size, they will repel each other the same amount, resulting in an array of equally spaced, immobilized atom clusters.

In a preliminary test of Zhang's prediction, Wendelken and Pai used the UT-ORNL variable temperature STM, which they operated at 30°K. After they warmed the sample to remove the buffer gas, they found that the iron clusters on the copper substrate were substantially smaller and more uniform in size when the clusters were charged than when they were not. However, these clusters were not equally spaced. Zhang says, nevertheless, that even this improved size distribution is enough to enhance the optical properties of the material, suggesting it might have potential for quantum dot lasers as nanoscale sources of light for optical circuits.

Why was the ordering not as good as Zhang predicted? "We had to remove the electrically insulating buffer gas so the clusters could be imaged by the STM," Wendelken says. "It may be that the desorption of the gas disturbed the nanocluster pattern. When the variable-temperature STM atomic-force microscope we have ordered arrives, we will be able to image an insulating surface and see if a highly ordered pattern exists before the xenon is desorbed."

One likely use for perfectly ordered patterns of magnetic quantum dots (such as iron or cobalt) may be in magnetic high-density storage disks that could hold 100,000 times more data than current disks.



In this molecular dynamics simulation, a nanosized polymer droplet is formed in a solvent and forced through a micron-sized orifice. Submicron polymer particles exhibit unique properties that could make them extremely useful for optical displays and industrial coatings.

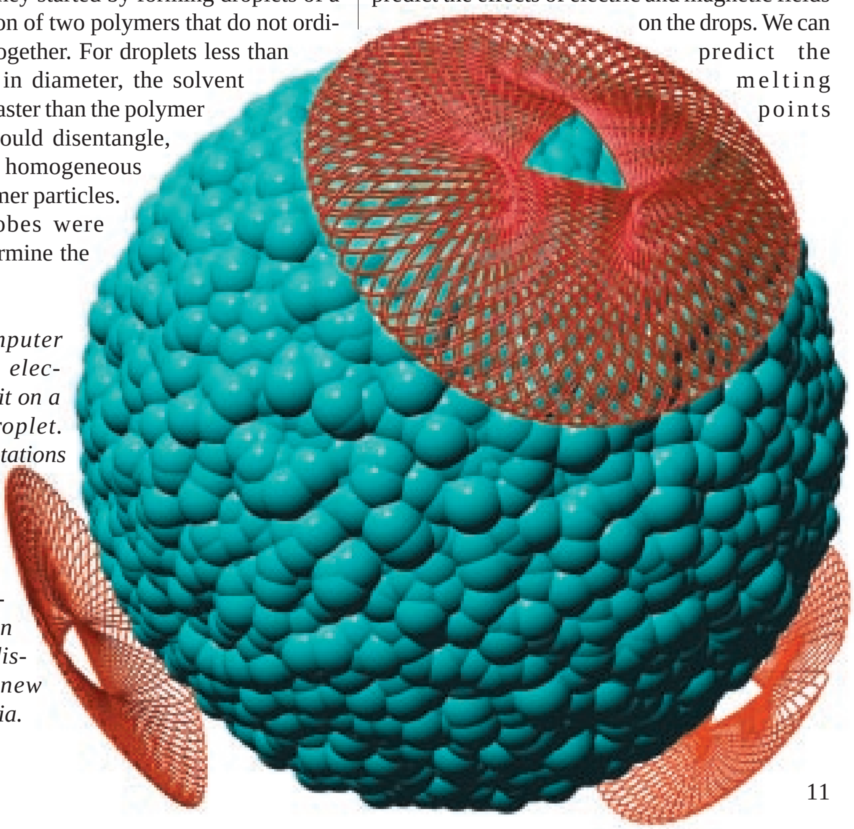
Quantum Drops

Materials that normally don't mix can now be blended within single microparticles and nanoparticles, thanks to a droplet technique discovered at ORNL for producing arbitrarily sized particles. The technique may lead to new materials with tunable properties with applications to drug delivery systems, improved coatings, and faster components for electronic devices.

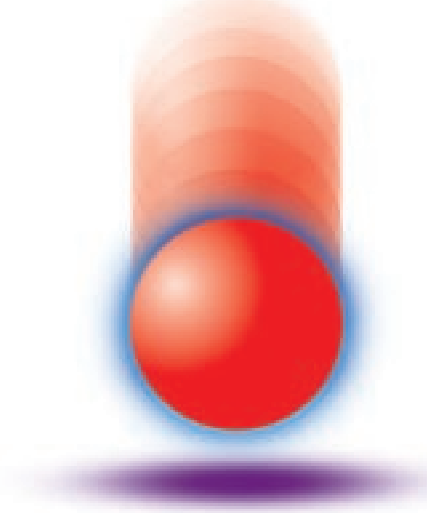
In 1998 Don W. Noid, Bobby Sumpter, and Michael D. Barnes, all CASD researchers, developed a novel way to prepare electrically charged, submicron-diameter, spherical composite particles of organic polymers of nearly uniform size. They started by forming droplets of a dilute solution of two polymers that do not ordinarily mix together. For droplets less than 10 microns in diameter, the solvent evaporates faster than the polymer molecules could disentangle, resulting in homogeneous mixed-polymer particles. Optical probes were used to determine the material homogeneity, size, and dielectric constant of the particles. The work showed that material properties of the particles could be tuned simply by adjusting the mixture of polymers in solution.

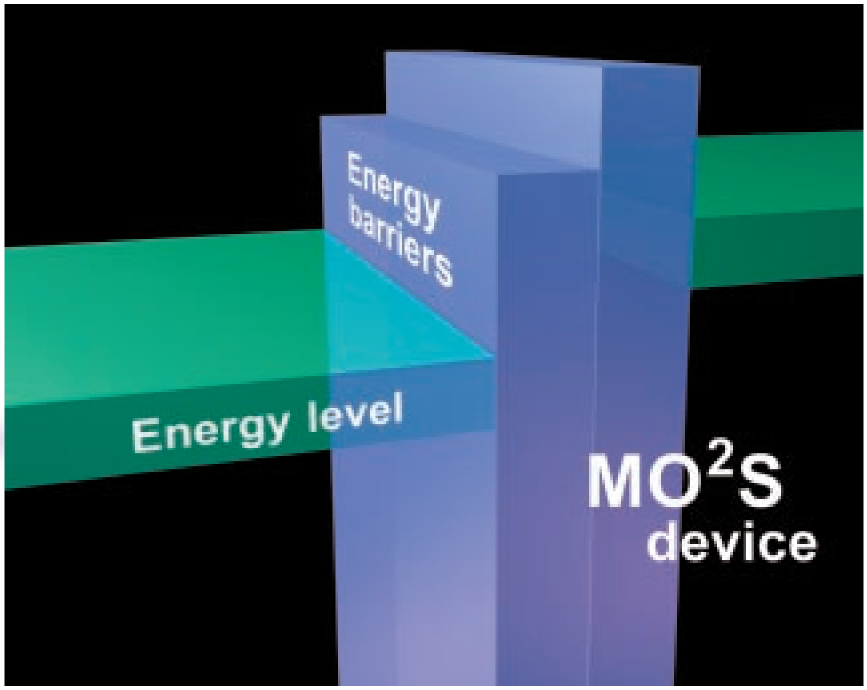
Barnes, Noid, Sumpter, Thomas Thundat of the Life Sciences Division (LSD), and M. Alfred Akerman of ETD have received LDRD funding to refine this technique to make "quantum drops," clusters of one or more different types of charged polymer molecules predicted to act like "artificial atoms" with tunable electronic properties. Electrons, like photons, possess both "wave" and "particle" properties; the characteristic (DeBroglie) wavelength of a particle (usually very nearly zero for macroscopic objects) is inversely proportional to its momentum. When electrons are confined to a "box" whose dimensions are comparable to their wavelength, discrete, or "quantized," energy levels are observed whose spacing increases with decreasing "box" size. Thus, such systems are termed artificial atoms because the colors of light they absorb or emit depend on the size of the particle. The researchers will investigate whether these spherical 2- to 10-nm drops (which may contain more than 10,000 atoms) exhibit size quantization behavior similar to that of more familiar semiconductor quantum dots, as predicted by computational simulations.

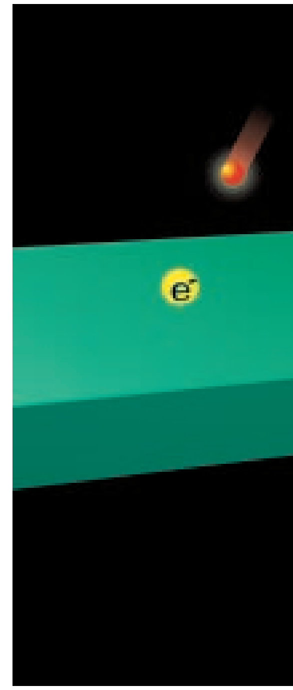
"When we model quantum drops," Noid says, "we can predict their electron energy levels and their chemical potential, or electron affinity—that is, whether they have the correct symmetry to make it easy to attach electrons. We can predict the effects of electric and magnetic fields on the drops. We can predict the melting points



In this computer simulation, electron orbits sit on a polymer droplet. Such computations could guide the development of new materials for possible use in flat panel displays and new storage media.







This series shows a metal-oxide-oxide-semiconductor photovoltaic device in which an electron, energized by a photon of sunlight (above), hops over a multiple quantum barrier after one barrier is lowered by an electric field.

of the particles in the drops, which become lower as particle size gets smaller."

"We think our drop technology will enable us to tune, or select, the size of the drop particles and the number of electrons on each particle," Barnes says. "The particle size is determined by the droplet size and the concentration of polymers in the droplet solution. The material properties of the quantum drops are determined by the polymer composition.

"The electronic properties of quantum drops, such as their ability to emit light of a particular color, can be tuned by adjusting or selecting the particle size or the number of excess electrons. The resulting quantum drops could be a new class of luminescent particle."

Sumpter notes that his simulations predict that the hardness of a polymer can be tuned by mixing the hard material with a squishy polymer using the droplet technique. Mixing polymers to make particles can also alter the index of refraction or strength and compressibility of each material.

Quantum drops could be used for applications ranging from catalysis to quantum computing. In the gas phase these particles could speed up reactions because their high surface area increases the opportunity for contact and electron exchange between the particles and the reactant species diffusing throughout the reaction chamber.

Quantum dots theoretically could be tuned to make each electron represent a bit of information: Each electron with an up spin could be a "1" and each electron with a down spin could be a "0." "We propose to use the droplet technique to encode several memory elements on each nanoparticle," Barnes says. "If we are successful, this technique could be useful for the proposed development of a quantum computer."

"We have to learn how to make a variety of mixed-polymer particles and sort them by size," Noid says. "Then we must use spectroscopic tools to measure their electron energy levels experimentally and verify that the mixed-polymer particles behave like artificial atoms, as predicted by our simulations."

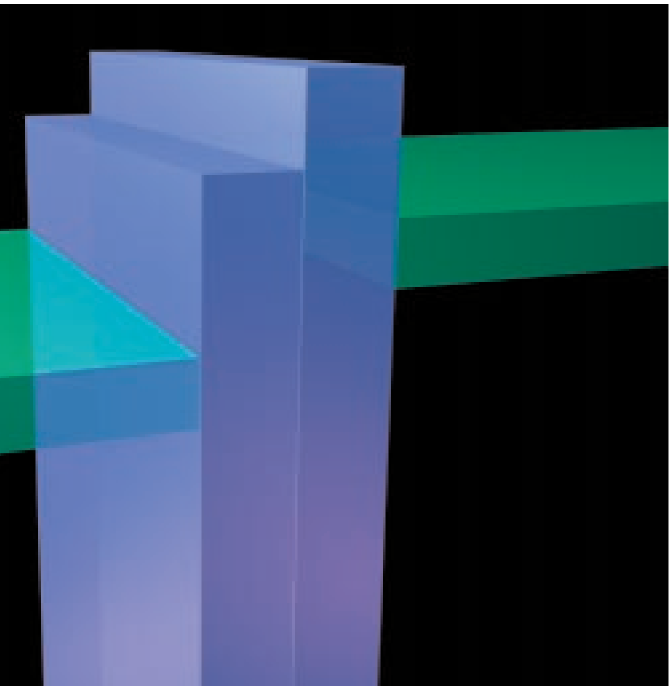
New Semiconductor Devices Using Micromechanical Quantum Wells

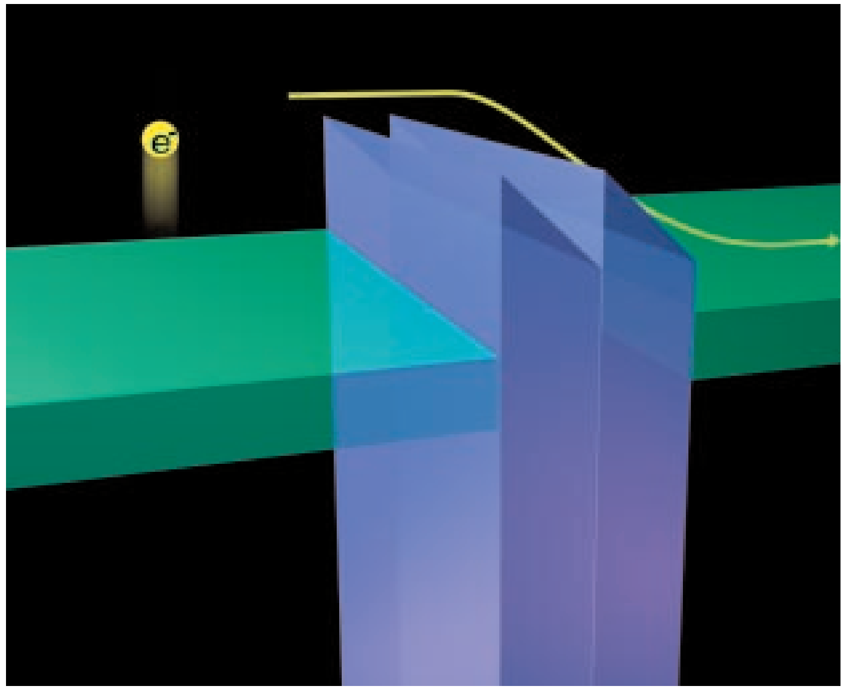
Imagine going outdoors one dark night and seeing the vivid colors of the scene as if the sun were shining. A hand-held night-vision device to make this possible may emerge someday from the LDRD project of a team led by Panos G. Datskos of ETD. Datskos, Slo Rajic (ETD), H. M. Meyer (ETD),Thomas Thundat (LSD), Ray Zuhr (SSD), John Wendelken (SSD), David Zehner (SSD), Bill Butler (M&C), and Don Nicholson (Computational Physics and Engineering Division) will be developing and studying a new class of tunable semiconductor devices that rely on nanoelectromechanical systems (NEMS). These devices may be used to generate power and detect electromagnetic fields and toxic chemicals.

At the microscopic level, a slice of silicon or some other semiconducting material will bend when zapped with high-energy photons of light. This ORNL-discovered photo-induced effect that quickly results in a microscopic mechanical stress in the material also causes changes in it at the nanoscale level.

For the NEMS project, ORNL researchers will apply their experience in making MEMS devices using focused ion beam milling and diamond turning, their theoretical and modeling tools, their materials analysis techniques, and their ability to form nanostructures and thin films. Relying on semiconducting materials, such as silicon, germanium, silicon nitride, gallium arsenide, and indium antimonide, they will fabricate thin-film nanostructures that confine electrons in microscopic springboards (microcantilevers).The team hopes to show that by using photons to bend microcantilevers and applying an electric field, the electrons trapped in or blocked by these nanostructures—quantum wells, quantum barriers, and quantum contacts—will be permitted to flow.

One of the team's goals is to begin developing a revolutionary class of uncooled photon detection devices by building an infrared detector that will operate at room temperature. This device can be tuned to specific far infrared wavelengths. It will be smaller and use less energy than today's detectors, which are cooled by liquid nitrogen. It will use photo-induced electronic stresses in quantum wells. When incoming photons stress the device's microcantilevers, its quantum wells will shrink in width, causing the energy levels of electrons inside the wells to rise enough for the trapped electrons to hop out and flow. The size of the resulting electrical current will be proportional to the intensity of the photons.





The team believes that tunable pulsed-power devices can be fabricated using quantum barriers made of layers of insulating material. An electric field can be used to raise and lower quantum barriers, which block electron flow. When the field lowers a quantum barrier, electrons energized by photons start to flow. Such devices could produce power using sunlight.

Another of the team's goals is to create a new kind of semiconductor device—a nanomechanical single-electron transistor (SET). A SET might replace today's field-effect transistor, which relies on a gate electrode to pass or block current flowing from a source electrode toward a drain electrode. In a SET, incoming photons will bend two microcantilevers meeting each other at a quantum point contact, where electron flow is blocked. The mechanical stress will raise the energy level of the electrons enough to push them across the quantum contact. SETs will be useful in smart nanosensors needing on-off switches and in data storage.

Tom Cerniglio

Joe Cunningham uses a diamond-turning machine for one of the steps of making a device based on a microelectronic mechanical system.

Quantum Computing by Connecting the Dots

The world's first practical computation on a fabricated nanoscale device may be achieved by a team led by Jacob Barhen of ORNL's Center for Engineering Science Advanced Research (CESAR) and the Computer Science and Mathematics Division (CSMD). The team has received LDRD funding to develop a quantum dot array to perform this task. For this project, quantum dots are clusters of atoms, a few nanometers in diameter, surrounded by an insulating layer. The relatively small size of the metallic dots planned for the ORNL array will enable operation at room temperature (because no cooling will be needed).

Leon Maya, a team member from CESAR and CASD, has already fabricated platinum particles about 2 nm in diameter. For this project, gold particles approximately 1.5 nm in diameter will be produced by trapping them in tiny cavities of polymer molecules.

Because of his knowledge of the structure of DNA, which he has studied using an atomic force microscope, Thomas Thundat will use a DNA molecule as an architectural template for positioning quantum dots on a surface between two electrodes to program the device. "By attaching complementary four-base-DNA sequences to the quantum dots," Thundat says, "we should be able to place them at predetermined spatial locations on the DNA backbone with sub-nanometer precision."

Gold electrodes that provide access to the quantum dots from the macroscopic environment will be fabricated. The two electrodes, which will anchor each end of the pre-designed DNA sequence, will be laid on a flat substrate and separated by a narrow gap a few nanometers in length. A novel technique will be used to decompose the DNA template without altering the geometrical position of the electrodes and quantum dots.

The practical goal of the ORNL team is to build a device that emulates a neural network. Instead of the neurons and connecting synapses found in the brain, the nanoscale computer will depend on electrically charged quantum dots connected by electrons that tunnel between them at different rates.

Using colloid chemistry, Maya will fabricate and coat the gold quantum dots. Thundat will assemble them using the DNA templates and an atomic force microscope. Jack Wells of CESAR/CSMD and David Dean and Michael Strayer, both of the Physics Division, will develop a first-principles simulation of the device on ORNL's IBM-SP3 parallel supercomputer. "The simulation," Barhen says, "should provide immediate and invaluable feedback to the experimental de-

Nanosensor Probes Single Living Cells

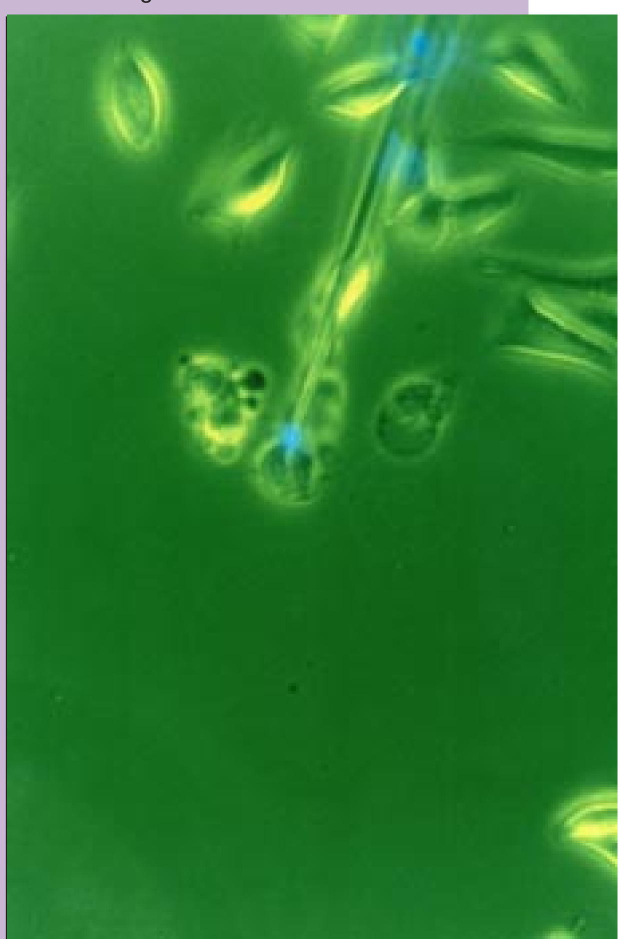
A "nano-needle" with a tip about one-thousandth the size of a human hair pokes a living cell, causing it to quiver briefly. Once it is withdrawn from the cell, this ORNL nanosensor detects signs of early DNA damage that can lead to cancer.

To simulate exposure to a carcinogen, the cell has been incubated with a metabolite of a chemical called ben-zo[*a*]pyrene (B*a*P), a known cancer-causing environmental agent often found in polluted urban atmospheres. Under normal exposure conditions, the cell takes up B*a*P and metabolizes it. The B*a*P metabolite reacts with the cell's DNA, forming a DNA adduct, which can be hydrolyzed into a product called benzo(*a*)pyrene tetrol (BPT).

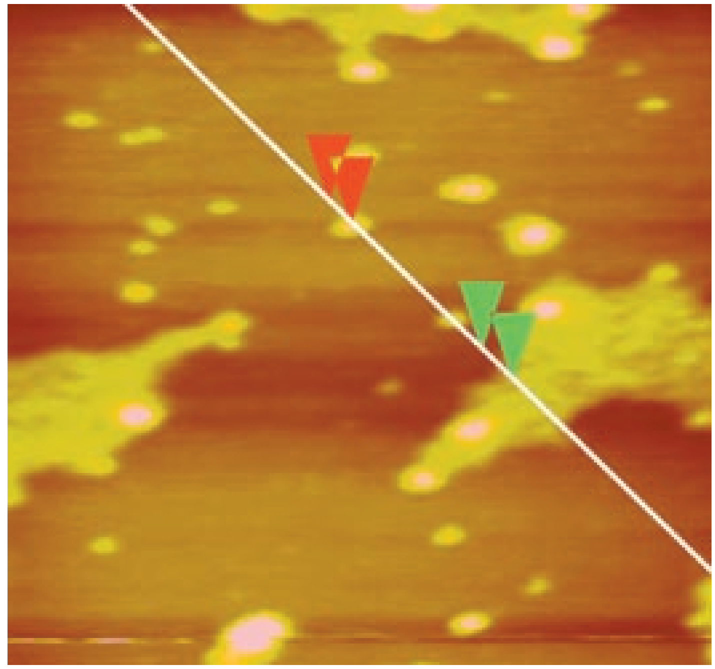
The nano-needle is really a 50-nm-diameter silver-coated optical fiber that carries a helium-cadmium laser beam. Attached to the optical fiber tip are monoclonal antibodies that recognize and bind to BPT. The laser light, which has a wavelength of 325 nm, excites the antibody-BPT complex at the fiber tip, causing the complex to fluoresce. The newly generated light travels up the fiber into an optical detector. The layer of silver is deposited on the fiber wall to prevent the laser excitation light and the fluorescence emitted by the antibody-BPT complex from escaping through the fiber.

This nanosensor of high selectivity and sensitivity was developed by a research group led by Tuan Vo-Dinh and his coworkers Guy Griffin and Brian Cullum. The group believes that, by using antibodies targeted to a wide variety of cell chemicals, the nanosensor can monitor in a living cell the presence of proteins and other species of biomedical interest.

"Parallel arrays of these nanosensors could be used to detect gene expression and protein production in target cells," Vo-Dinh says. "They also can be used to screen tiny amounts of drugs to determine which ones are most effective in blocking the action of disease-causing proteins in single cells. With advances in nanotechnology, we are now approaching the ultimate limit of assessing the health of individual human cells."



A nanosensor probe carrying a laser beam (blue) penetrates a living cell to detect the presence of a product indicating that the cell has been exposed to a cancer-causing substance.



Using colloid chemistry, Leon Maya fabricated these 2-nm platinum quantum dots, which appear as round yellow spots in this atomic force microscope image.

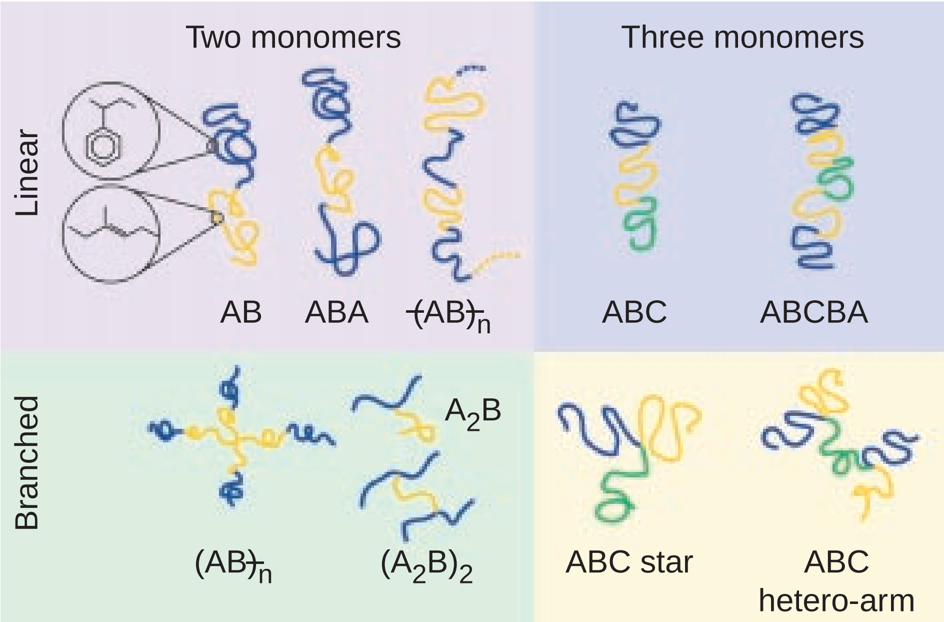
sign and help us accurately specify the parameters needed to use the device as a computer."

Barhen, Yehuda Braiman, Vladimir Protopopescu, and Nageswara Rao, all from CESAR/CSMD, will develop the methodology and algorithms needed to implement neuromorphic computations on the quantum-dot array. This implementation involves innovative techniques that modify the electron tunneling rate between dots. For demonstration purposes, the researchers intend to solve a pattern recognition problem. An example of such a problem would be the analysis of sensor data to identify seismic patterns indicating the presence of a porous sandstone layer that might contain oil.

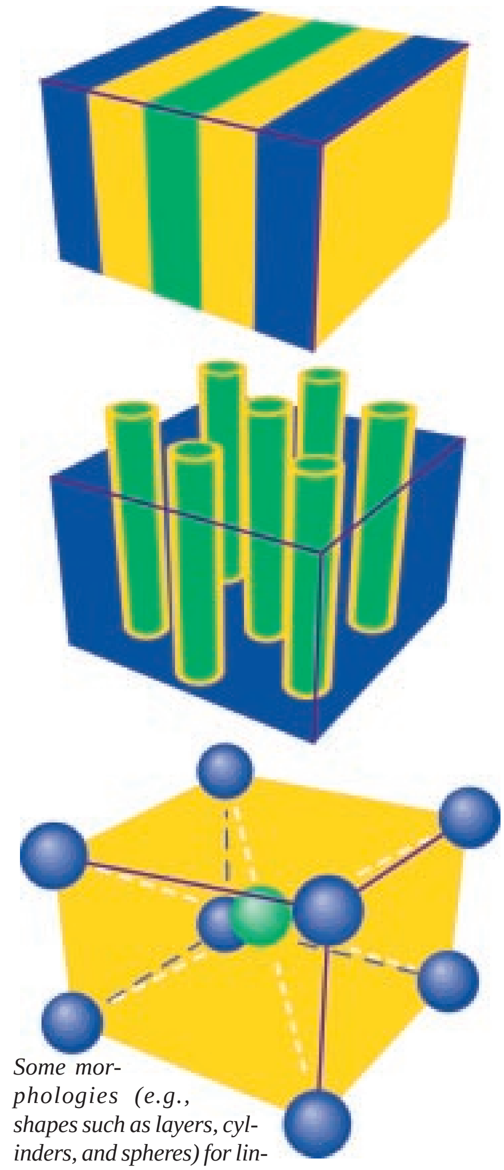
"This project," Barhen says, "is motivated by the information processing needs of future generations of intelligent systems. On one hand, there is a need to meet the tremendous constraints on power consumption, size, and temperature. On the other hand, novel sensors, such as hyperspectral cameras used for imaging landscapes, require ever more powerful, dedicated processors. Thus, we are targeting applications that can exploit the emergent collective computational properties of an ensemble of nanostructures."

Self-Assembling Triblock Copolymers

Triblock copolymers are made by joining three chemically distinct polymer blocks (large molecules), each a linear series of identical monomers (small molecules). Because the blocks may be thermodynamically incompatible, they will separate on the nanometer scale (5–100 nm), producing complex, ordered nanostructures by self-assembly. Examples of these structures are the lamellar morphology in which the three blocks form alternating sequential layers; a regular arrangement of spheres of one or more blocks in a matrix of another; and similarly ordered rods in a



Block copolymers can be configured into a nearly limitless number of molecular architectures based on two, three, or more monomer types.



Some morphologies (e.g., shapes such as layers, cylinders, and spheres) for linear ABC triblock copolymers. The ability to select block sequence (ABC, ACB, BAC), composition, and molecular weights provides a significant opportunity to create new morphologies.

matrix or layered structure. A particularly interesting morphology is the continuous core-shell gyroid structure. An electrically conducting polymer core could be formed in an insulating shell, embedded in a matrix of a third block, providing other mechanical or electrical properties. The properties of these self-assembled nanostructures can be manipulated by independent selection of the three triblock components, the block sequence, and block length.

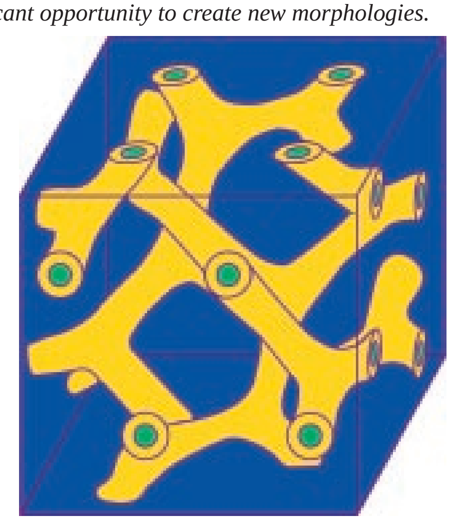
Recent advances in synthetic chemistry have made possible the controlled production of compositionally uniform triblock copolymers. Frank Bates and his associates at the University of Minnesota will be synthesizing a variety of triblock copolymers using block sequences based on various existing polymers. As part of this LDRD project, George Wignall of SSD and Tony Habenschuss of CASD will use powerful scattering tools, especially small-angle neutron scattering, to probe the structure of the triblock copolymers, while Bates' group will measure their mechanical, optical, electrical, ionic, barrier, and other physical properties.

"Our first goal is to understand the effects of A, B, and C homopolymer additives in controlling the morphology in ABC triblock copolymers," Habenschuss says. "Our second goal is to apply multi-continuous three-monomer block copolymer membranes to fuel-cell technology."

In some fuel cells, electrolytic membranes must allow passage of protons between anode and cathode while restricting the flow of fuel, such as methanol. Today's proton-exchange membranes are very expensive and are prone to leaking fuel while allowing protons to pass. An alternative proton-exchange membrane must combine suitable ionic transport with solvent resistance, mechanical strength, and processability at a competitive cost. Because the constituent blocks can be selected independently and several multi-continuous morphologies are known, ABC triblocks and blends represent an attractive opportunity for improving this technology.

Research on these triblock copolymers could lead to other applications. "Nanoscale reinforced, ordered polymer composites" could be made in which one component could be a high-strength reinforcing material such as nylon. Triblocks could be used as "templates" by modifying the copolymers after synthesis so that they retain their morphology but possess properties different from those in the original materials. "Nano-porous materials" could be made by leaching out channels to create filters having controlled channel size (block length), or, conversely, by leaching out the matrix component to get an open aerogel-like structure. The research at ORNL and the University of Minnesota should help generate the scientific knowledge base needed to make practical use of these marvelous materials.

ORNL researchers will continue to explore our brave new nanoworld to find out how best to exploit its out-of-this-world features.



Core-shell gyroid structure showing a conducting polymer (green) encased in an insulating polymer (yellow) inside a matrix (blue) made of another polymer.

ORNL Wins Eight R&D 100 Awards

ORNL's eight R&D 100 awards in 1999 boost its total to 104, placing it first among DOE laboratories.

In 1999, ORNL researchers won eight R&D 100 Awards, pushing their total to 104 since the awards began in 1963. The awards are presented annually by *R&D Magazine* in recognition of the year's most significant technological innovations. ORNL's 104 R&D 100 awards place it first among Department of Energy laboratories. The honored inventions and processes are described here.

Tuan Vo-Dinh (holding instrument), Alan Wintenberg (left), Nance Ericson, Gordon Miller, Narayan Isola, and J.P. Alarie developed the multifunctional biochip to provide rapid medical diagnoses in the doctor's office.

Photographs by Curtis Boles

Disease Detector Microchip for the Doctor's Office

An electronic biochip that can rapidly screen for and detect various diseases has been devised at ORNL for possible use in physicians' offices. A biochip is a device that combines electronic microchip technology and biological probes. The ORNL device is called a multifunctional biochip because it can detect various types of biological systems—such as nucleic acids, proteins, and cellular components—simultaneously in a single device. This novel biochip, which also received the R&D 100 Editors' Award for Most Promising New Technology, is an important improvement over ORNL's previously developed DNA chip technology. The silicon-based chip can hold not only specific DNA sequences but also antibodies, proteins, and cellular probes for detecting disease-causing agents and other biomedical targets. The palm-size device contains a sampling platform for the probes, a set of lenses, light sources, a detector array microchip, electronic circuitry, and an on-board data collection capability.

Disease-causing agents or genes that bring about illnesses, which may be present in a processed drop of blood, will be detected if target DNA samples pair with complementary probes or if target proteins bind to antibody probes affixed to the chip's platform. The biochip will process up to 100 samples in 30 minutes.

Expected applications of the biochip are DNA sequencing; identifying and mapping genes; screening blood, vaccines, food, and water supplies for infectious agents; and diagnosing diseases, including AIDS, hepatitis, genetic-based cancers (such as breast, colon, and prostate cancer), and Alzheimer's disease. Other uses may be high-throughput drug screening, environmental sensing of biochemical species, occupational health monitoring, and rapid detection of biological pathogens.

The multifunctional biochip was developed and evaluated by ORNL's Tuan Vo-Dinh, Alan Wintenberg, Nance Ericson, J. P. Alarie, Gordon Miller, Minoo Askari, and Narayan Isola from the Life Sciences and Instrumentation and Controls divisions. (For more information, see the *Review*, Vol. 32, No. 1, 1999, p. 13.)

The biochip could be produced on a large scale using low-cost, integrated-circuit technology. Widespread use of this technology in doctors' offices should reduce the cost of medical diagnoses, thus cutting health care costs.

Controlling the Process of Making Rust-resistant Steel

Most automobiles manufactured today do not rust as quickly as older vehicles because galvanneal sheet steel is used in their construction. To save energy, reduce waste, and ensure a quality product, ORNL has developed a measurement system for the steel industry that allows control of the temperature when galvanneal steel forms.

Steve Allison (left), Wayne Manges, Tim McIntyre, Mike Cates and David Beshears are part of the team that developed the galvanneal temperature measurement system, which provides crucial on-line thermal process control information during the manufacture of rust-resistant, galvanneal steel used in automobiles.

The galvanneal process creates a protective layer on a steel sheet by dipping it in molten zinc and heating the coated sheet in a furnace to make the iron and zinc atoms form an alloy on the surface. The problem is that the metal surface temperature may vary in the furnace, making the product quality nonuniform.

ORNL's galvanneal temperature measurement system makes it possible to strictly control steel surface temperature, enabling the production of uniform, high-quality galvanneal steel. The system uses a computer; laser; light detector; optical fibers; and white phosphor powder, which is dusted on each steel sheet by a computerized phosphor-deposition device. The laser light excites the phosphors, which emit light for a short time, based on how hot they and the steel sheet are. Measurements of the time it takes for the light emissions to disappear are used by the computer to calculate the surface temperature of the galvanneal steel. The real-time monitoring information is used by steel producers to determine whether furnace operation must be adjusted to maintain the correct temperature.

The system was developed by ORNL's Steve Allison, David Beshears, Mike Cates, Mitchell Childs, Wayne Manges, Tim McIntyre, and Marc Simpson (from the Engineering Technology and the Instrumentation and Controls divisions) in conjunction with the American Iron and Steel Institute (AISI), Bailey Engineers, and the National Steel Technical Center. This effort was supported by DOE's Office of Industrial Technology and AISI, a steel industry consortium that managed the project. (For more information, see the *Review*, Vol. 32, No. 1, 1999, pp. 17–18.)

In 1998 the ORNL system was installed and successfully tested at Bethlehem Steel's facility in Burns Harbor, Indiana. The technology has been licensed to Bailey Engineers. Just recently a system was made part of a West Virginia steel manufacturer's production line.

Frostless Heat Pump

Although relatively popular in U.S. regions with a temperate climate and low electricity rates, the air-source heat pump presents two problems to homeowners in winter. Its supply air temperature for the house is relatively low, a condition called "cold blow," and frost accumulates on the outdoor coil. As a result, the comfort of occupants and the reliability of this energy-efficient heating and cooling system are reduced.

Richard Murphy (left), Fang Chen, Ron Domitrovic, and Vince Mei (the leader) developed a frostless heat pump that greatly reduces frost formation on the outdoor coil and boosts indoor comfort during the winter.

During the heating season, when the ambient temperature is below about 4°C (40°F) and the air is humid, water vapor condenses and a deposit of tiny ice crystals builds up on the heat pump's outdoor heat exchanger. The temperature of the indoor heat exchanger coil and the air it supplies to heat the indoor space starts to drop. To defrost the coil, a control system causes a four-way valve to temporarily reverse the heat-pump cycle. Heat is taken from the house interior to raise the outdoor coil temperature enough to melt the accumulated frost. Resistance-heating elements are turned on to compensate for the heat loss in the house.

Even so, the occupants often experience cold blow, which is especially noticeable when the outdoor temperature is below -0.1°C (30°F). The periodic cycle-reversing stresses heat pump components, reducing system reliability and contributing to periodic power surges in the electric utility grid.

To reduce the frequency of defrost cycling, Vince Mei, Fang Chen, Richard Murphy, and Ron Domitrovic, all of ORNL's Energy Division, have developed a frostless heat pump. It should increase occupant comfort and heat pump reliability and reduce utility power surges.

The ORNL researchers' innovation is to add heat to the accumulator (by installing two cartridge electric heaters) to increase outdoor coil temperature a few degrees. This change not only dramatically retards frost formation at outdoor temperatures at which frost is most likely to form but also boosts heat pump supply air temperature and heating capacity. The heat pump will likely cycle off before the defrosting cycle is initiated. Cold air drafts are almost completely eliminated because of higher heat pump supply air temperature. There will be no cold blow even during the cycle-reversing defrosting period when outdoor temperatures are very low, because the indoor blower motor will be off.

"Resistance-heating elements will still be used to heat the house when the outdoor temperature is very low," Mei says. "But the frequency of use of the heating elements will be reduced because the heat pump heating capacity is improved. "

Test data show that frostless technology could eliminate 80% of potential heat pump cycle reversing in the East Tennessee area. Two engineering frostless heat pumps have been built for field tests by the Tennessee Valley Authority. Two heat pump manufacturers have expressed interest in the device, which could be the first heat pump to provide a consistently warm supply of air to houses in winter.

ORNL's Two Joint Winners with UT

Jack Dongarra, an ORNL–University of Tennessee (UT) Distinguished Scientist, received two R&D 100 Awards for his computer science developments. One winning entry was NetSolve 1.2, which he developed jointly with Dorian Arnold of UT and former UT student Henri Casanova, who is now at the University of California at San Diego. The other was ATLAS, which he developed with Clint Whaley and Antoine Petitet of UT.

NetSolve 1.2 transforms an organization's hardware and software resources into a unified, easy-to-access computational service that makes available enormous amounts of computational power to users. It allows users to tap into geographically distributed hardware and software resources to achieve supercomputing levels of power without changing the way they work.

Jack Dongarra, an ORNL-UT Distinguished Scientist, was a co-winner of two R&D 100 Awards in 1999 for two computer science developments: NetSolve 1.2, a client-server system that enables users to solve complex scientific problems, and ATLAS, an automatic software production program.

"Most scientists do not have easy access to the supercomputer power needed to analyze the mass of images and data that stream in from our satellites and reactors, or to perform the complex simulations required for aircraft design or biomedicine," Dongarra says. "Now, an engineer using common programming languages can formulate a large model or simulation and turn it over to the NetSolve system. NetSolve will orchestrate the use of distributed resources on the company's intranet to perform the computations in the most efficient way possible."

ATLAS (Automatically Tuned Linear Algebra Software) generates highly optimized Basic Linear Algebra Subroutines (BLAS) that exploit all the speed the underlying hardware can deliver. It replaces time-consuming, tedious hand tuning with intelligent, self-adapting software that automatically rewrites itself within a few hours to maximize its performance on a particular computer processor.

"ATLAS will be critical to computer science," Dongarra says, "because new processors and computer systems are developed more quickly than human programmers can hand-tune the BLAS routines. The faster BLAS can run, the faster science gets done."

Self-cleaning Carbon Air Filter

Sometimes the air in a room can smell worse than the air outside. It may make us sneeze, get a headache, or feel burning in our eyes, nose, and throat. It may contain pollutants that irritate the human respiratory system or damage materials and equipment.

To get rid of airborne toxic gases such as formaldehyde, a carbon filter is usually installed downstream of the particulate filter in the room air conditioner. The problem with today's carbon filters in industrial, commercial, school, and home air conditioners is that they can be used only once. The dirty filter containing loose, granular, activated carbon must be replaced with a clean filter.

ORNL researchers Kirk Wilson of the Administrative Services Division and Tim Burchell and Rod Judkins, both of the Metals and Ceramics Division, have developed a self-cleaning carbon air filter that has a much longer life than conventional carbon filters. "One in five U.S. schools has problems with indoor air quality, which may partly account for the increased incidence of asthma among American children," Wilson says. "A January 1999 report for ORNL that summarized scientific research on the causes of indoor air-quality problems in schools identified the need for simple, effective, and energy-efficient ways of improving indoor air quality in schools. So, we developed a low-cost indoor air filter that uses less energy and requires less maintenance than filters used today."

The self-cleaning filter, which has been successfully demonstrated in the laboratory, is made from an electrically conductive, activated-carbon-fiber composite that removes gaseous indoor air pollutants. It can be installed in existing or new filter banks of industrial, institutional, commercial and residential air conditioners.

Tim Burchell (left), Kirk Wilson, and Rod Judkins invented a self-cleaning carbon air filter made from an activated-carbon-fiber composite that removes gaseous indoor air pollutants.

When the filter becomes dirty, an automatic reverse-air-cleaning cycle passes an electric current through the filter, releasing pollutants into a purge air stream that exhausts harmful pollutants outdoors. After the cleaning cycle finishes, the unit returns to normal operation. The filter lasts through numerous cycles.

ORNL has been trying to market the concept to carbon manufacturers that could provide the filter media to end users. Several industrial firms have expressed interest in developing the technology for improving indoor air quality in buildings, automobiles, aircraft, and submarines.

Micromechanical Quantum Detector

It could let firefighters see through smoke, give drivers and pilots better night vision, and measure the temperature of hot objects. It could help energy experts spot air leaks and missing insulation in buildings and enable physicians to detect skin cancer.

A camera that could do these things would be compact, fast, sensitive, and versatile, beating the competition. It could cut the cost of infrared cameras by one-third. It would be based on ORNL's new micromechanical quantum detector (MQD), developed by Panos Datskos, Boyd Evans, Slo Rajic, all of ORNL's Engineering Technology Division, the late Charles Egert of the Oak Ridge Y-12 Plant, and Irene Datskou, formerly of ORNL. Datskou (now president and chief executive officer of Environmental Engineering Group, Inc.), Datskos, and Rajic are co-inventors of the MQD.

The MQD is a highly sensitive miniature imaging device that can be tuned to respond to photons in a wide range of the electromagnetic spectrum, from the far infrared through visible light to the vacuum ultraviolet. The detector consists of an array of numerous springboards, each very small (~10^{-5} cm^2), that are made of the appropriate semiconductor material.

It is known that, when low-energy photons are absorbed in a semiconductor, its temperature changes. "When we looked at how semiconductor microstructures behave in interaction with high-energy photons, we stumbled onto the photo-induced effect," Datskos says. "We discovered that high-energy photons stress the crystal electronically. Electrons and positive holes are generated, causing a mechanical stress in the material. We saw a way to use this effect to make an infrared detector that operates at room temperature."

By taking advantage of emerging micromachining techniques for making microelectromechanical systems, or MEMS, the ORNL group created an array of springboards, or microcantilevers, and demonstrated that photo-induced stresses can cause them to bend in a measurable way. The more intense the incoming photons, the more the microcantilevers bend.

The researchers have shown in the laboratory that an MQD made of silicon or indium antimonide provides infrared imaging at room temperature. Today's infrared photon devices must be chilled to cryogenic temperatures by liquid nitrogen. Because the MQD will not require cooling equipment, it will cost less, weigh less, and use less electricity than today's infrared photon detectors, but it will be just as sensitive and fast.

The development was funded by DOE (through ORNL seed money) and by the Defense Applied Research Projects Agency. Lockheed Martin, Northrop Grumman Corporation, Honeywell, and a number of smaller companies have expressed interest in the device. The technology is expected to be licensed soon to a commercial vendor.

Irene Datskou (left), Boyd Evans, and Panos Datskos were among the developers of the micromechanical quantum detector, which may lead to a better and cheaper infrared camera.

Superconducting Wire Technology

In the past five years, ORNL researchers have developed the rolling assisted, biaxially textured substrates (RABiTS™) technology, which has been licensed to five companies. It is believed that this simple, scalable technology will make possible the manufacture of long lengths of ultra-high-performance superconducting wires. Such high-temperature superconducting wires could be used to make highly efficient transmission cables, as well as motors, transformers, fault current limiters, and magnetic separation devices that take up less space, cost less to operate, and use less energy than today's electric power devices. (For a history of the RABiTS™ development, see the *Review*, Vol. 29, Nos. 3&4, 1996, pp. 2-19.)

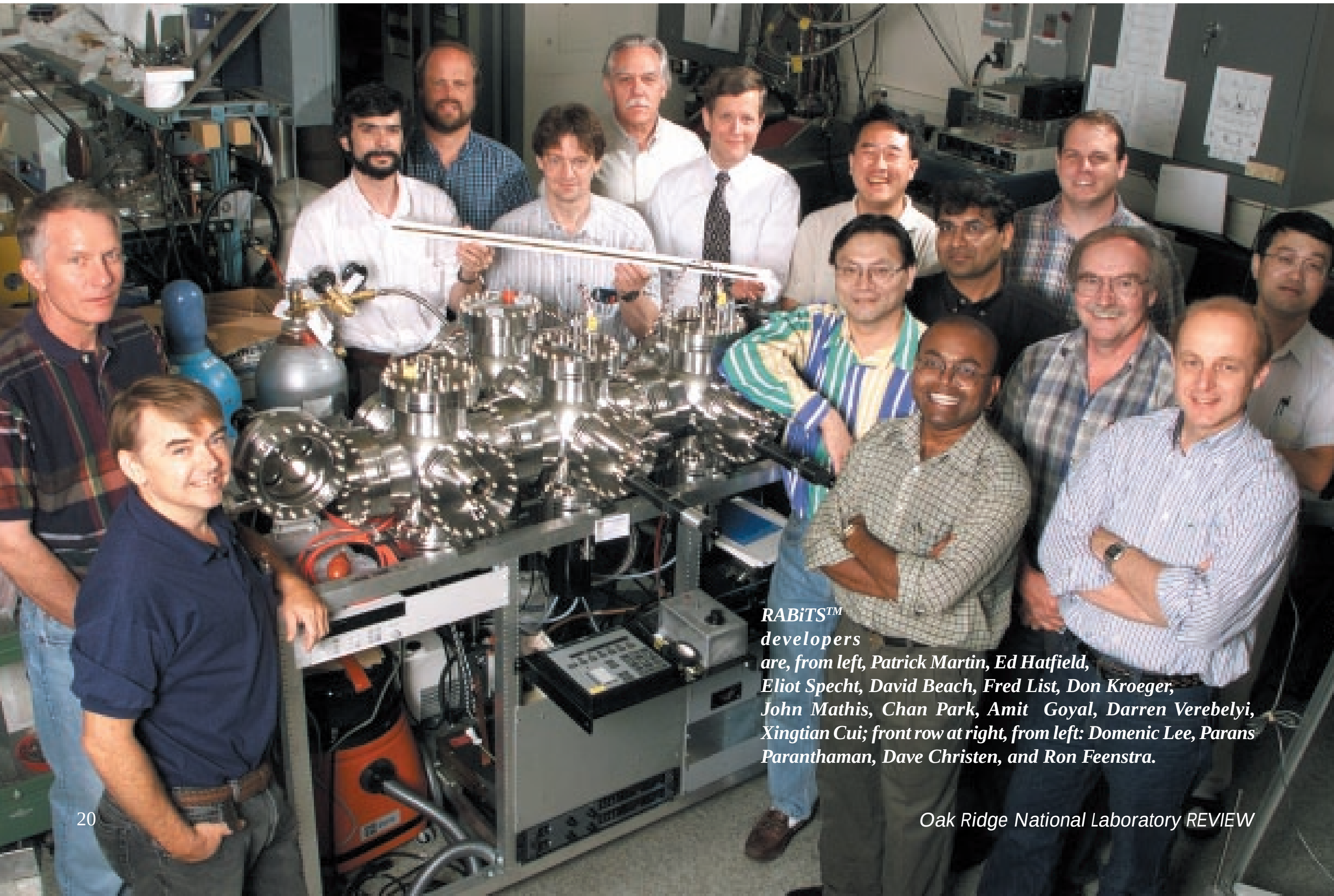
The developers of this award-winning technology are Amit Goyal, John Budai, David Norton, Eliot Specht, Dave Christen, Donald Kroeger, Parans Paranthaman, Frederick List, Ron Feenstra, Dominic Lee, Bob Williams, David Beach, Patrick Martin, Richard Kerchner, Ed Hatfield, John Mathis, Chan Park, Xingtian Cui, Thomas Chirayil, Claudia Cantoni, and Darren Verebelyi.

The researchers showed that texture introduced to metal (e.g., nickel) by rolling it into sheets can be transferred to a superconductive oxide coating—for example, yttrium-barium-copper oxide—through buffer layers deposited on the metal substrate. The resulting orientation of crystals in the superconductive oxide allows it to conduct large electric currents without resistance at liquid nitrogen temperature (77K). The ORNL group has developed a rolling, annealing, and coating process for mass producing kilometer lengths and centimeter widths of flexible, single-crystal-like substrates of a wide range of materials—including oxides, nitrides, and semiconductors—at only a fraction of the cost of conventionally growing single crystals (which are not flexible).

In the past two years, the ORNL researchers improved the RABiTS™ technology in three ways to make it more attractive to industry for fabricating coated conductors. First, they alloyed nickel with appropriate additions of chromium or vanadium and modified the rolling and annealing steps to make a textured metal template that is mechanically stronger and less magnetic at 77K than pure nickel. (For some applications, pure nickel may be too weak and too magnetic to enable superconductor operation in high magnetic fields.)

Second, they reduced the complexity and thickness of the buffer layers that separate the nickel-alloy substrate from the superconductive oxide coating, improving the coated conductor's ability to carry large amounts of current. Third, they demonstrated that a high-quality superconductive oxide coating can be made using a greatly simplified, lower-temperature vacuum, thin-film deposition process that eliminates the need for introducing heat and oxygen into the deposition chamber. As a result, more rapid scale-up of the fabrication process is likely.

The ORNL technology, developed using DOE funds from the Office of Energy Efficiency and Renewable Energy and from the Office of Science, has been licensed to 3M Company; Midwest Superconductivity; Oxford Superconducting Technology; MicroCoating Technologies, Inc.; and EURUS Technologies, Inc. The RABITs™ technology could prove valuable for the fabrication of high-temperature ceramic superconductors. According to industry figures, sales of large-scale devices using superconducting wires and tapes are expected to exceed $50 billion in 2010.



RABiTS™ developers are, from left, Patrick Martin, Ed Hatfield, Eliot Specht, David Beach, Fred List, Don Kroeger, John Mathis, Chan Park, Amit Goyal, Darren Verebelyi, Xingtian Cui; front row at right, from left: Domenic Lee, Parans Paranthaman, Dave Christen, and Ron Feenstra.

Capturing a Role in Carbon Storage Studies

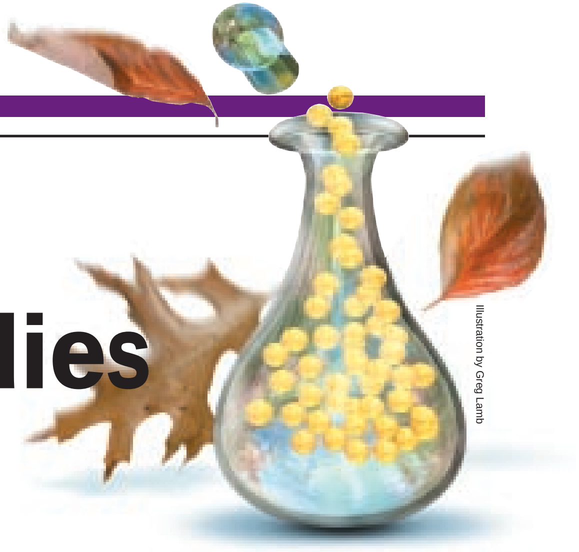


Illustration by Greg Lamb

ORNL is a leader in DOE studies of carbon sequestration.

The quantity of carbon in the earth's atmosphere—currently 780 billion tons—has been rising by roughly 3.3 billion tons per year over the past 10 years. Three approaches are being considered in an attempt to reduce the buildup of carbon dioxide in the atmosphere because of concerns that it may be contributing to global warming and potentially devastating climate change.

One approach is to trim emissions of carbon dioxide by using energy more efficiently. A second is to burn fuels (e.g., hydrogen) or produce energy in systems (e.g., hydropower, solar power, or nuclear power plants) that emit little or no net carbon dioxide. This approach would include burning woody biomass and producing liquid fuels from renewable resources, such as ethanol from corn. A third approach is both new and not yet well understood. This approach entails capturing carbon dioxide from the atmosphere and from stack emissions of fossil-fuel combustion facilities, converting some of it into useful products, and transferring most of it to above-ground and below-ground terrestrial ecosystems—such as forests and underground coal seams—and to the ocean. The process of long-term storage of captured carbon is called carbon sequestration.

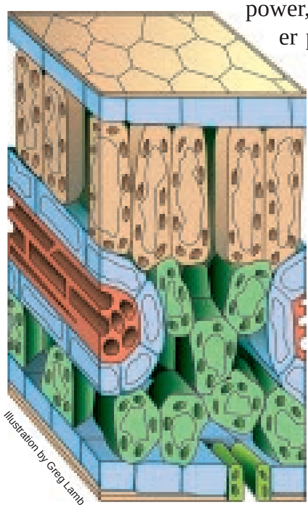


Illustration by Greg Lamb

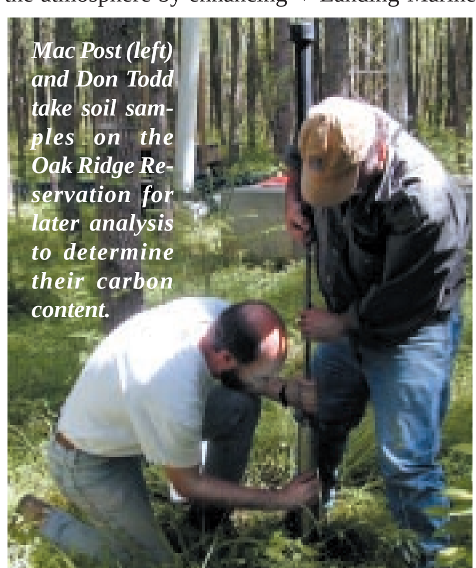
Structure of a leaf that is less efficient than some grasses at fixing carbon.

As part of its climate change technology initiative, the U.S. Department of Energy's Office of Science in 1999 formed two centers to study carbon sequestration: one focusing on terrestrial ecosystems and the other on oceans. The centers will conduct research and help focus and coordinate research across a wide range of disciplines. The goal is to find environmentally acceptable ways of keeping atmospheric carbon dioxide from reaching concentrations that could cause unacceptable climatic changes.

The DOE Center for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSITE) is led by a consortium comprising DOE's Oak Ridge, Pacific Northwest, and Argonne national laboratories. The center's co-leaders are Gary Jacobs of ORNL and Blaine Metting of Pacific Northwest National Laboratory (PNNL).

This center will receive $6 million over three years. Collaborating in center studies will be researchers from Colorado State University, North Carolina State University, Ohio State University, the Rodale Institute in Pennsylvania, Texas A&M University, the University of Washington, the Joanneum Research Institute in Austria, and the U.S. Department of Agriculture.

From the viewpoint of terrestrial ecosystems, carbon sequestration is the removal of carbon dioxide from the atmosphere by enhancing natural absorption processes and storing the carbon for a long time in vegetation and soils. Carbon sequestration may be accomplished by fixing more carbon in plants by photosynthesis, increasing plant biomass per unit land area, reducing decomposition of soil organic matter, and increasing the area of land covered by ecosystems that store carbon.



Mac Post (left) and Don Todd take soil samples on the Oak Ridge Reservation for later analysis to determine their carbon content.

Research to date has shown that one way to increase carbon sequestration is through better land management. If modest changes in farming and forestry practices are made, plants and soils may more efficiently remove carbon dioxide from the atmosphere and store it in long-lived "pools" such as forest reserves, wood products, or soil organic matter. The longer that carbon is sequestered, the slower the rate of increases in atmospheric carbon dioxide.

Field research will be conducted at several sites, including DOE's national environmental research parks at ORNL and the Fermi National Accelerator Laboratory, as well as U.S. Department of Agriculture sites in Alabama and South Carolina, the Rodale Institute Research Center in Pennsylvania, and forestry industry research sites in the Pacific Northwest and the Southeast.

The second center, which is focusing on ocean carbon sequestration, is led by a consortium of DOE's Lawrence Berkeley and Lawrence Livermore national laboratories. The DOE Center for Research on Ocean Carbon Sequestration (DOCS) will receive a total of $3 million over three years. DOCS will have collaborators from the Massachusetts Institute of Technology, Moss Landing Marine Labs, the Pacific International Center for High Technology Research, Rutgers University, and the Scripps Institution of Oceanography. Center co-leaders are Jim Bishop (Lawrence Berkeley) and Ken Caldeira (Lawrence Livermore). DOCS will study the feasibility, effectiveness, and environmental acceptability of injecting carbon dioxide into the ocean and fertilizing marine organisms on the ocean's surface.

Earth's Vegetation and Soil: Natural Scrubber for Carbon Emissions?
An Interview with ORNL's Gary Jacobs

As co-leader of the new DOE Center for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSITE), Gary Jacobs of ORNL's Environmental Sciences Division (ESD) explains some of the concepts that the center's 28 scientists are studying and some of the questions they seek to answer.

How can forests, pastures, croplands, and soils reduce carbon dioxide levels in the atmosphere in an era of increasing industrialization, and how can CSITE facilitate this process?

Mac Post of ESD, one of our experts on the carbon cycle, says that several lines of evidence indicate that the terrestrial biosphere, most likely the Northern Hemisphere, could be taking up a net amount of nearly 2 billion tons of carbon per year. Some of this uptake is perhaps due to regrowth of forests harvested previously this century in North America and Europe. Another factor may be the enhanced growth of natural vegetation resulting from rising atmospheric carbon dioxide concentrations stimulating photosynthesis. This Northern Hemisphere sink is larger than the estimated 0.5 to 1.5 billion tons of carbon emitted to the atmosphere through conversion of natural ecosystems to agriculture, primarily in tropical regions. Thus, the earth's vegetation and soil could act as a huge natural scrubber for carbon dioxide emissions from industrial sources and land-use changes.

Terrestrial ecosystems remove atmospheric carbon dioxide by plant photosynthesis during the day, which results in plant growth (roots and shoots) and increases in microbial biomass in the soil. Plants release some of the stored carbon back into the atmosphere through respiration. When a plant sheds leaves and roots die, this organic material decays, but some of it can be protected physically and chemically as dead organic matter in soils, which can be stable for up to thousands of years. The decomposition of soil carbon by soil microbes releases carbon dioxide to the atmosphere. This decomposition also mineralizes organic matter, which makes nutrients available for plant growth. The total amount of carbon stored in an ecosystem reflects the long-term balance between plant production and respiration and soil decomposition.

*CSITE co-leaders Blaine Metting (left) and Gary Jacobs inspect a field of Queen Anne's lace (*Daucus carota*) at the Fermi National Accelerator Laboratory's National Environmental Research Park.*

CSITE seeks to demonstrate through research that forests, pastures, cropland, other vegetation, and their associated soils can be managed and manipulated to sequester even more carbon from the atmosphere. People can help reduce carbon dioxide releases to the atmosphere and enhance carbon sequestration by protecting and adding to ecosystems that store carbon. For example, we can preserve forests instead of burning them to clear land for farms. We can grow more trees. We can reduce soil erosion. Some agricultural and forestry management techniques are already helping to sequester additional carbon. The focus of our center, however, is to do research to determine the most effective, most acceptable ways to manipulate and manage ecosystems to increase carbon storage in above-ground biomass and below-ground roots and soil. For example, we will look at different approaches to fertilizing and cultivating forest plantations and crops. R&D is needed to understand, measure, implement, and assess these strategies.

What is the scope of research for CSITE?

We will try to discover how changes in land use and land management affect the ability of vegetation and soil to sequester carbon. To measure and predict these changes, we will rely on various tools, ranging from remote sensing to simulation modeling. We seek to understand how microbial activity, soil aggregation, and other processes at the molecular level control carbon sequestration in vegetation and the soil. We will also do several assessments: We will determine scientifically the national potential for sequestering carbon in terrestrial ecosystems. We will evaluate the actual net effect on greenhouse warming potential of practices that enhance carbon sequestration in terrestrial ecosystems. This assessment will take into account the greenhouse gas costs of improving plant productivity, such as the increased carbon dioxide and nitrogen oxide emissions associated with fertilizer production and machinery operation. We will develop a quantitative understanding of the environmental impacts of increasing carbon sequestration in terrestrial ecosystems and create improved tools for predicting impacts. Finally, we will analyze soil carbon sequestration to determine its economic and social impacts, especially possible pressures on land use and production in the agricultural and forest sectors.

Why is ORNL particularly well qualified to study carbon sequestration in terrestrial ecosystems?

CSITE's proposal was successful partially because we formed a national partnership with some of the best researchers and institutions in the field. The future success of CSITE depends on whether our collaborative team can address the most pressing scientific challenges. As for ORNL's specific qualifications, several ESD researchers—Mac Post, Jeff Amthor, Gregg Marland, Stan Wullschleger, and Bob Luxmoore, for example—have considerable experience modeling, monitoring, and conducting large experiments on forests and other ecosystems, with an emphasis on understanding the carbon cycle and impacts of global change on ecosystems. Rich Norby, Paul Hanson, and others have studied the effects on forest growth of increasing carbon dioxide concentrations and changing inputs of water. Janet Cushman and Lynn Wright have managed a national program for developing better ways to raise faster-growing biomass crops for energy production. ESD staff also played a key role in writing a chapter on soils and vegetation for DOE's report, *Carbon Sequestration: State of the Science*, which was compiled, edited, and published by ORNL staff. (This chapter is the source of much of the material in this interview.) ESD also is home to several key global climate change data centers, such as the Center for Carbon Dioxide Information and Analysis, a NASA Distributed Active Archive Center, and the Atmospheric Radiation Measurements Program data center. Studying the ecological effects of global change has historically been one of the Lab's strengths.

Why is soil management important for carbon sequestration?

Soils are estimated to contain about 75% of all terrestrial carbon. Because 25 billion tons of soils are lost through wind and water erosion each year, there is an incentive to prevent erosion not only to benefit agriculture but also to increase carbon sequestration. One solution is to produce and protect soils high in carbon-containing organic matter because they have better texture and are better able to absorb nutrients, retain water, and resist erosion. Soil organic matter processes are a particular emphasis of ESD's Chuck Garten and our Argonne National Laboratory collaborators, Julie Jastrow and Mike Miller.

Jeff Amthor and others estimate that some 40 to 60 billion tons of carbon have been lost from soils since the great agricultural expansions of the 1800s. Removal of natural perennial vegetation and cultivation of the land have caused declines of soil organic matter by 50 to 60% in the top 20 centimeters of soil and 20 to 30% in the top meter of soil. This decline is due largely to a decrease in the formation of new organic matter below the ground and the loss of natural mechanisms that protect soil organic carbon from decomposition and oxidation. Cultivated soil is exposed to the air, so during decomposition by soil microbes, the soil organic matter is oxidized, and the carbon is released to the atmosphere as carbon dioxide.

Which changes in farming practices enable soils to store more carbon?

Cesar Izaurralde and Norm Rosenberg, two of our PNNL partners, are experts in agricultural systems. They point out that soil carbon can be increased by reduced-till agriculture, in which the soil is barely disturbed before crops are planted, and by the practice of returning crop residues to soil to reduce wind erosion. The U.S. Conservation Reserve Program (CRP) of the U.S. Department of Agriculture, which since 1985 has been paying farmers to retire land from cultivation for up to 15 years and plant it in grass to stabilize it, is also increasing soil carbon storage. Some evidence suggests that levels of soil organic carbon have doubled over the past 20 years in the upper 18 centimeters of soil placed in the CRP. In addition, erosion of the land enrolled in the CRP has decreased 21%. All of these practices reflect mainly the "recovery" of soil carbon previously lost because of earlier cultivation.

Which changes in forestry practices would make plants and soils more efficiently remove carbon dioxide from the atmosphere?

Forests in the United States are being managed to produce harvestable fiber and maintain cover, increase water storage, and retain litter. One major challenge is to slow the rate of deforestation. If this trend could be reversed and if reforestation occurs, some modeling studies suggest that, globally, forests could sequester from 200 to 500 billion tons of carbon by 2090. These values are large and controversial, and estimating the potential for carbon sequestration is one of the research challenges. A big challenge is to determine how to manage forest nutrients to achieve both profitable productivity and net carbon storage. Strategies are needed to address both fertilization and incorporation of forest residue into soils.

How can more carbon be stored in soils and plants?

More carbon can be stored below ground by increasing the depth of soil carbon, boosting the density of carbon in the soil, and decreasing the rate at which soil carbon decomposes. CSITE will be focusing initially on the latter two. Harvey Bolton of PNNL, Jizhong Zhou of ESD, and Mike Miller of ANL will be looking at microbiological processes that could be manipulated to reduce decomposition rates of soil organic matter. ESD's John McCarthy will be investigating molecular-scale interactions among clay particles and soil organic matter in search of a better way to protect the organic matter. We hope that other research programs will provide complementary results. For example, advances in biochemical research may produce a "smart fertilizer" that increases a soil's organic content and ability to retain water, protects its organic matter, and improves its texture so it can hold more carbon. Another important R&D area would be the development of new ways to produce fertilizer that use less energy and reduce carbon emissions.

More carbon can be sequestered in vegetation, possibly even by genetically engineering plants to increase their carbon retention. Plants could be engineered to produce cellular structures more resistant to decomposition, increasing the lifetime of soil organic matter and thus sequestering more carbon in soils. We need to find ways to make carbon accumulate faster, increase the vegetation's carbon density, and use biomass carbon in long-lived structural materials and industrial products.

What are the other benefits of storing more carbon in vegetation and soils?

Creating conditions for higher plant productivity and accumulation of soil organic matter will not only sequester more carbon but also restore degraded ecosystems worldwide. Carbon sequestration strategies would improve soil and water quality, decrease nutrient loss, reduce soil erosion, improve wildlife habitats, increase water conservation, and produce additional biomass for energy and other products. Understanding how to increase soil carbon stocks in agricultural lands may be critical to the future sustainability of food production.

How will you know if carbon sequestration is increasing in a terrestrial ecosystem?

A critical question is whether new sensors will be required or if process knowledge—rules of thumb—will be sufficient to estimate changes in carbon sequestration based on the implementation of observable land management practices. Developing measurement and sensing techniques to verify increased carbon sequestration in terrestrial ecosystems and to monitor its effects will be challenging. Detecting changes in terrestrial carbon concentrations at large scales will not be easy. An important R&D goal identified by DOE in its roadmap report is to develop *in situ*, nondestructive, below-ground sensors to quantify rates and limits of carbon accumulation over various times and land areas. To determine whether increases have occurred in above-ground biomass, new advances in satellite-based-remote sensing will be required. ORNL could certainly play a role in developing some of the needed sensor technology.

Amazing Microbes

Microorganisms that grow under extreme conditions are being studied at ORNL because of their potential to make useful materials, trap uranium contaminants, and produce hydrogen for energy.

Bacteria have been found two miles deep within the earth. Will they be found 100 meters beneath the surface of Mars by a NASA space probe planned for 2013 to 2020?

Illustration by Greg Lamb

Tommy Phelps is a microbe hunter who will go to extremes to find exotic bacteria. In the late 1980s the microbiologist, then at the University of Tennessee at Knoxville (UTK), picked through buffalo dung in Yellowstone National Park to find a microorganism that produced an enzyme that had special characteristics sought by the client, Eastman Kodak. Three years later, the enzyme was being used in laundry detergent manufactured in Europe.

In 1993, as a research staff member in ORNL's Environmental Sciences Division (ESD), he set up a lab by a Texaco oil-and-gas exploration rig near Fredericksburg, Virginia. Studying samples extracted by Texaco workers from the Taylorsville Triassic Rift Basin, he discovered novel bacteria in a mixed culture. Incredibly, these subsurface microbes had been geologically isolated for some 100 million to 140 million years. They had lived at a depth of 2800 meters (9100 feet) at a temperature of 75°C (167°F). Later Phelps showed that a strain of these bacteria produced fine-grained particles of magnetic material that might have industrial uses.

Tommy Phelps (left) and his wife, microbiologist Susan Pfiffner, are suited up for their two-mile descent into a South African gold mine to hunt for bacteria with useful talents.

These bacteria are called extremophiles because they love extreme environments. Extremophiles, microorganisms that grow under extreme conditions, thrive in environments we would avoid, such as boiling or ice-cold water, concentrated brine, household ammonia, or vinegar. The bacteria from Virginia are thermophiles because they love heat, just like their cousins who flourish in hot springs.

Other extremophiles prefer environments that are very cold (psychrophiles), high in salt (halophiles), very acidic (acidophiles), or high in alkalinity or pH (alkalinophiles). Their habitats may be Alpine glaciers, cold polar seas, deep-sea sediments, highly saline lakes, carbonate springs, or soda lakes. Extremophiles are of great interest to ORNL researchers trying to find better ways to make useful materials, prevent uranium pollutants from leaving Department of Energy sites, or produce hydrogen for energy.

Phelps (right) and geologist T. C. Onstott of Princeton University take samples of bacteria from the South African gold mine.

A Gold Mine for Extremophiles

In his search for other extremophiles that might prove useful, Phelps went to extremes again in 1998 as part of an expedition by a number of scientists to South Africa's East Driefontein gold mine. (This expedition is described in the cover story of the July 1999 issue of *Discover* magazine). He joined his wife Susan Pfiffner, a UTK microbiologist, and a team of American scientists in braving temperatures between 32°C (90°F) and 49°C (120°F) for 4 hours a day in a gold mine shaft 2.3 kilometers (2 miles) deep. The participating organizations in this daring venture, which was funded by the National Science Foundation, included ORNL, UTK, Princeton University, Cornell University, and two other DOE labs—Pacific Northwest National Laboratory and Idaho Engineering and Environmental Laboratory. The microbe hunters took samples of bacteria from brown stains on the seam of the gold mine. Thermophiles were found in "carbon leaders,"

One type of bacteria (PB1) studied at ORNL produces both magnetic iron oxide and calcium carbonate (first test tube at left) when exposed to carbon dioxide. Under controlled conditions (second test tube) the bacteria produce a nonmagnetic ferritic oxide. In the third test tube, the bacteria produce magnetic iron oxide only when not exposed to carbon dioxide. Stirring-bar magnets are placed between the test tubes.

fractures in quartzite that allowed the flow of seawater from which gold and organic matter precipitated.

"My wife and I brought back 70 cultures of extremophiles called acetogens," Phelps says. "We found evidence of fermenting microbes that feed on hydrogen and carbon dioxide, reduce sulfates, and produce acetic acid."

Bacteria That Make Magnetite

The samples collected in Virginia in 1993 contained micron-sized bacteria and nanometer (nm)-sized particles of magnetic iron in what Phelps calls "their bug poop." Phelps brought the samples back to ORNL. He and his ESD colleagues Chuanlun Zhang and Jizhong Zhou later purified the samples, isolated a strain of bacteria they named TOR-39, and showed that these anaerobic (non-oxygen-breathing), rod-shaped extremophiles can convert iron hydroxide to magnetic iron, or magnetite.

"These bacteria respire iron," Phelps says, while sliding a horseshoe magnet along a test tube to coax the microbes' black residue inside to rise up the wall, showing it is magnetic. "Just as humans get rid of electrons by forming carbon dioxide and water from their food, these bacteria dump electrons on nearby electron-accepting metals, such as iron."

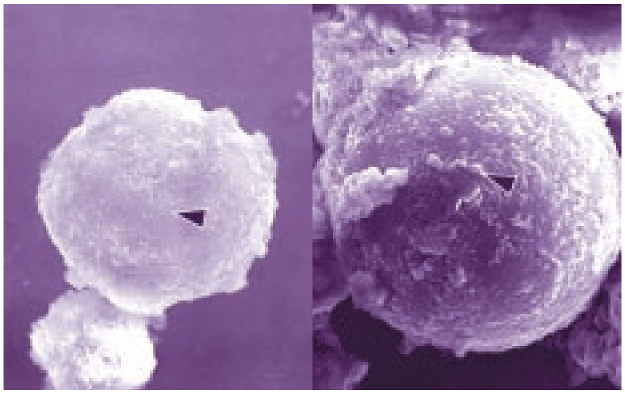
In the process, they reduce iron hydroxide [$Fe(OH)_3$] to magnetic iron oxide (Fe_3O_4). Zhang learned in 1996 that TOR-39 bacteria can also ferment glucose and other carbohydrates when grown at temperatures from 50°C (122°F) to 70°C (158°F). Phelps says that these bacteria, when properly fed, form carbonates from carbon dioxide.

Phelps is working with Bob Lauf of ORNL's Metals and Ceramics Division to stir up industrial interest in the magnetic particles produced by the TOR-39 bacteria (for which a patent application has been filed). Lauf has found that if the biologically formed magnetite is doped with cobalt, nickel, or palladium, it becomes more magnetic. Phelps and his colleagues have shown that the TOR-39 bacteria efficiently produce 10-nm to 300-nm of magnetic particles in a temperature range of 45 to 70°C. They also found that magnetite particles of a desired size can be obtained by harvesting the bacteria at the proper time.

"We believe that these particles could be used to make superfine magnetic coatings that may be needed by the computer industry for faster magnetic disks and by companies that need faster motors for drills and other uses," Phelps says.

The discovery that microscopic creatures of the deep may produce magnetite by respiration is of great interest to scientists. It suggests that bacteria may have played a role in the evolution of the atmosphere and of creatures that breathe (like us). It suggests further that bacteria may be partly responsible for the banded iron formations that provide Earth's magnetic field. Because biologically formed magnetite is similar to extraterrestrial magnetite in the Martian meteorite ALH84001, some scientists see this as evidence supporting the existence of past biological activity on Mars. But future space probes may have to dig deep to find positive proof.

In fact, an unmanned NASA space probe planned for 2013–2020 will drill 100 meters beneath the surface of Mars to obtain samples that may contain bacteria. Tommy Phelps has been named to this project's science team, so once again he is going to extremes as he joins the scientific search for extraterrestrial life.



The micrograph at left shows carbonate-coated fly ash as a result of bacterial action. Coal fly ash is shown at right.

Can Microbes Sequester Carbon?

One of DOE's interests is to find better ways to capture carbon from power plant emissions and the atmosphere and store it securely. The goal is to prevent atmospheric carbon dioxide levels from climbing enough to cause potentially devastating climate change. To achieve such carbon sequestration, Phelps believes that extremophiles such as TOR-39 bacteria could play a role.

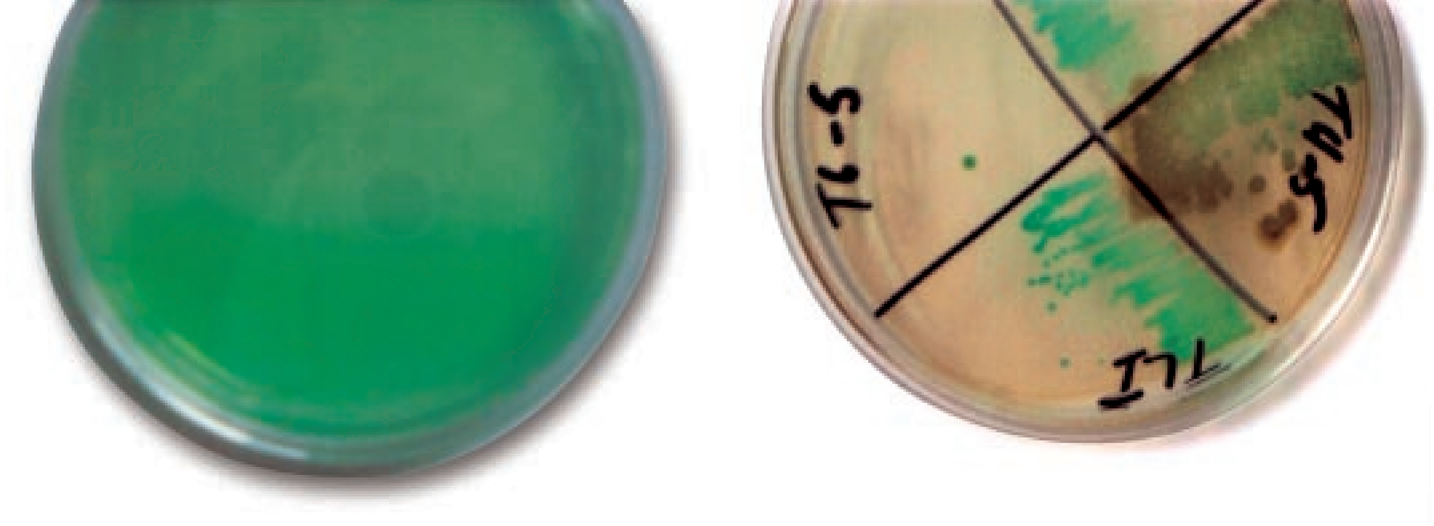
"We have shown that, when exposed to carbon dioxide dissolved in water in a test tube medium, our TOR-39 strain precipitates carbonates faster than other microbes," Phelps says. "We propose using our bacteria to coat fly ash and waste coal dust from coal power plants with carbonates as a way of sequestering carbon. Then instead of hauling this material to the landfill, it could be sold as road fill."

A possible microbial route to removing carbon from power plant emissions might be to lace a pond next to a coal-fired power plant with the TOR-39 bacteria. Carbon dioxide could be captured from the stack emissions and injected into the pond. The bacteria could use the dissolved waste gas to produce iron carbonate or calcium carbonate, which would settle into the pond's bottom sediments as a mineral.

Phelps and his colleagues have done experiments that show that PB-1 bacteria from a marine environment can produce iron carbonate a week after being exposed to carbon dioxide. But further studies showed that TOR-39 bacteria, when fed sugar and exposed to carbon dioxide, can produce iron carbonate in less than a week. Phelps thinks it is possible to make the TOR-39

Jim Richmond

This carbonate-containing "bioherm" conglomerate was found in halophilic algae in the Great Salt Lake in Utah.



Indicator media are used to detect the activity of the enzyme phosphatase, which breaks down organic compounds containing phosphorus. The control plate (left) contains organic phosphorus and a dye, which appears bright green. The plate at right contains several strains of Pseudomonas *bacteria that have been growing on the organic phosphorus. The strains are genetically engineered to produce large amounts of the enzyme. As a result, the bright green areas are disappearing and, in some cases, the dye is concentrated in the organic phosphorus-metabolizing bacteria (the green streaks).*

bacteria generate the material within one to three days.

“Many people think that biologically sequestered carbon in rocks such as calcium carbonate conglomerates is formed only in the presence of light and photosynthesis,” Phelps says, showing a carbonate-containing “bioherm” conglomerate that he found in halophilic algae in the Great Salt Lake in Utah.

“However, there is evidence from methane gas hydrates deep in the ocean that carbonate-containing conglomerates can be formed without photosynthesis. It is possible that extremophiles may serve as nucleation catalysts for the formation of minerals. If this is so, we might be able to identify or design bacteria that could form conglomerates much faster and better for carbon sequestration.”

Bacteria That Prevent Uranium from Straying

At the Oak Ridge Y-12 Plant and other DOE sites, waste uranium in groundwater, streams, and ponds may be in the oxidized state. That’s a potential problem. Such uranium is soluble and mobile, increasing the risk that it might remain in water that flows off site. Because DOE wants to confine the uranium to its sites, it is interested in exploiting bacteria to change the chemical state of the uranium. The goal is to make the uranium stick to soil, rocks, and stream sediments to ensure that it stays on site.

Enrichments from site samples are used to isolate bacteria that digest different forms of organic phosphorus. Bacterial growth is obvious in media containing, from left, triethylphosphate (TEP) and glucose-6 phosphate (G6P) in comparison with the control, which has no added soil sample (right). The bacteria growing in the enrichments are used to obtain pure cultures. The resulting cultures from the TEP media are the first to be documented as users of TEP.

ESD researchers Tony Palumbo and Jizhong Zhou are studying bacteria that reduce uranium by adding an electron to each uranium atom, making it insoluble. As a result, the uranium should precipitate out of the water, drop into the sediments, and remain within the confines of the DOE site. The work is supported by the National Accelerated Bioremediation (NABIR) Program of DOE’s Office of Biological and Environmental Research.

Palumbo is working on a project with a group at the Georgia Institute of Technology to help meet DOE’s goal. One way to make uranium precipitate out of the water is to let it combine naturally with the phosphorus already in the water. The problem is that most phosphorus is unavailable for attachment to uranium because it is tied up with soil in and around the stream. One solution is to add to the soil an organic compound containing phosphorus that can move into the water. Palumbo and the Georgia Tech team genetically engineered a strain of bacteria that chops the organic compound from phosphorus in a high oxygen environment.

“We genetically engineered the *Pseudomonas* bacteria to rapidly metabolize organic phosphorus,” Palumbo says. “We isolated six to twelve bacterial strains that use triethylphosphate, or TEP, which is a very mobile organic form. We are identifying the genes responsible for the organism’s ability to break up the TEP. We do this by disrupting different sets of genes in various strains. We find which mutants do not metabolize TEP and then figure out which genes are disrupted in each mutant. The normal forms of those genes are linked to TEP metabolism.”

After they isolated two genes responsible for TEP metabolism, they identified the enzyme produced by these genes. Called phosphatase, this enzyme breaks down TEP, freeing phosphorus to combine with uranium in contaminated waters.

DOE is interested in an extremophile that is known to be able to make uranium insoluble. It is *Shewanella putrefaciens MR-1* bacterium. *Shewenella* is intriguing because it not only reduces metals (which may make it ideal for treating contaminated waters) but it also produces hydrogen and magnetite.

An intensive effort will be made by DOE in FY 2000 to completely sequence this bacterium to identify the genes that can change uranium’s chemical state. The genes from this microbial genome might be used to design microorganisms for advanced bioremediation of DOE’s contaminated streams.

Extremozymes and Hydrogen Production

Hydrogen may be the fuel of the future once hydrogen fuel cells for propelling cars are perfected. Combined with oxygen in a fuel cell, hydrogen provides electricity and a little heat. Its only waste product is water. The hydrogen car will be clean because it will not discharge nitrogen oxides and carbon dioxide.

But how can hydrogen be obtained cheaply? One approach may be to use special enzymes to (1) transform cellulose into glucose sugar, and (2) convert the glucose product and its by-product, gluconic acid, into hydrogen. Sources of cellulose are old newspapers, grass clippings, and other waste products of renewable resources.

In 1996 Jonathan Woodward and his associates in ORNL's Chemical Technology Division (CTD) reported an important advance. They learned how to produce a molecule of hydrogen from a molecule of glucose using two enzymes, both of which are "extremozymes." An extremozyme is an enzyme produced by an extremophile.

Because the glucose-to-hydrogen process is more efficient if run at a higher temperature, it makes sense to replace some standard enzymes with extremozymes. The reason: Standard enzymes will stop working when exposed to higher temperatures unless special, costly measures are taken to protect these proteins. Some extremozymes might eliminate the need for protective steps, increasing efficiency and reducing costs. In addition, extremozymes may be more stable and react faster than their "mesophilic" counterparts that prefer benign conditions.

In October 1999 CTD researchers Woodward, Mark Orr, and Elias Greenbaum and CTD student Kimberley Cordray reported that the CTD group had produced 11.6 hydrogen molecules for every glucose molecule in the substrate. The researchers achieved 97% of the maximum stoichiometric yield possible—12 hydrogen molecules for each glucose molecule. This is the highest yield of hydrogen ever obtained from glucose by a biological process.

This high stoichiometric yield of hydrogen from glucose was attained through an "oxidative pentose phosphate cycle" using 11 enzymes. In this cycle, glucose is oxidized completely to the compound NADPH and carbon dioxide. In the presence of hydrogenase, hydrogen is released.

This hydrogenase is produced by the extremophile *Pyrococcus furiosus*, a strain of bacteria from a deep-sea hydrothermal vent. It works most efficiently at a temperature of 85°C. This hydrogenase is also one of only two enzymes known to accept electrons from NADPH to produce hydrogen.

"We ran our hydrogen-producing reaction at 30°C because the yeast enzymes we used are inactivated above 45°C," Woodward says. "Thus, the activity of the hydrogenase was ten times lower than it would have been at 85°C. We could probably produce hydrogen much more efficiently from glucose if all eleven enzymes were isolated from thermophiles."

Woodward, CTD staff researcher Barbara Evans, and CTD students Cordray, Robert Emonston, Maria Blanco-Rivera, and Susan Mattingly showed that hydrogen could be obtained enzymatically from other biomass substrates. These substrates were lactose, sucrose, xylan, starch, and steam-exploded aspen wood.

Woodward, Evans, Gerard Bunick of the Life Sciences Division, and ESD's Jizhong Zhou and Tony Palumbo have been studying extremozymes obtained from extremophiles of the ORNL subsurface culture collections, the *Methanococcus jannaschii* genome clones available from the American Type Culture Collection, and biotechnology companies. Some enzymes are produced at ORNL by cloning purchased DNA sequences and inserting them into *E. coli* bacteria, which churn out the desired protein.

"We have identified, isolated, purified, and characterized extremozymes that might be useful for bioprocessing and energy production," Evans says. "To produce hydrogen fuel from cellulose, we must first break the cellulose down to its component sugar—glucose. We use the enzyme cellulase to hydrolyze the cellulose—that is, add water to the bonds connecting the glucose molecules that make up the cellulose polymer."

Converting the cellulose cheaply and efficiently to glucose continues to bog down the two-step process of producing hydrogen from cellulose. "The bottleneck in the cellulose-to-glucose process is the cellulase enzyme," says Woodward, who has long been experimenting with the fungal enzyme to increase its efficiency in breaking down cellulose into glucose. "We need a stable enzyme that works faster to catalyze production of glucose from cellulose. Right now it takes two days to produce glucose from cellulose. Our goal is to make cellulase work ten times faster to obtain glucose in 30 minutes to an hour."

If a reaction is run at higher temperatures, shouldn't thermophilic cellulases digest cellulose faster and be more stable than "mesophilic" cellulases, which works at moderate temperatures?

"That's not necessarily so," Evans says. "Mesophilic cellulases can break down cellulose in 30 minutes if you add enough enzyme to the cellulose. But the enzyme is too expensive to make this approach economically feasible.

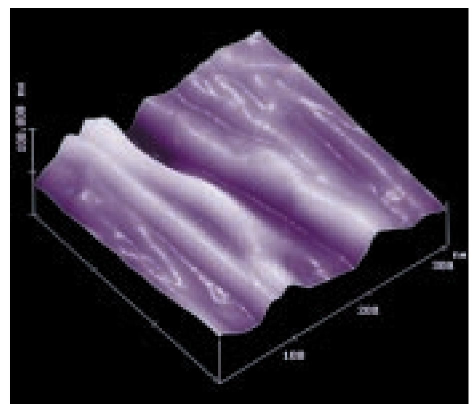
"We need a combination of cellulase enzymes that works effectively in very small concentrations. It must speed up the slow step of the process, disrupting the cellulose fibers and making them accessible so they can be digested into glucose. Even thermophilic enzymes appear to be slow in carrying out this initial step."

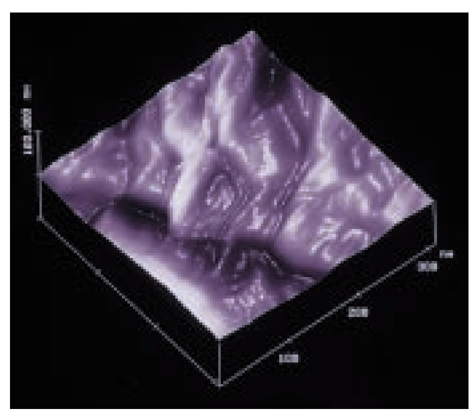
Evans is studying a variety of cellulases, including thermophilic ones, to determine their properties, such as stability and reaction speed, in the digestion of cellulose. She will be studying the interaction of various cellulases during the digestion process. Bunick uses X-ray diffraction to determine the structure of extremozymes, which could help explain why some are stable under extreme conditions.

Hugh O'Neill, a postdoctoral scientist in Woodward's group, is studying hydrogen-producing bacteria that prefer different temperature ranges to see which ones are the most efficient. He is looking at how efficient each microbe is at producing hydrogen from different substrates. He is studying psychrophiles (4–33°C), mesophiles (20–45°C), and thermophiles (45–70°C). He will then isolate the hydrogenase enzyme from the most efficient hydrogen producers.

If a psychrophilic hydrogenase is found, it could be useful for producing hydrogen for fuel cells in cold places, from Antarctica to outer space. The U.S. Defense Applied Research Projects Agency is funding this project because of its interest in producing hydrogen enzymatically for military fuel cells, using substrates from the environment, such as sucrose in tree sap. Such fuel cells could be used to power biosensors needed to detect biological and chemical warfare agents.

At ORNL, the X-10 files on extremophiles are expanding.





These atomic force microscopy images show, at top, control cotton fibers (cellulose) incubated in a buffered solution without enzyme and, at bottom, cotton fibers after treatment for 6 hours with the cellulase CBH I from the fungus Trichoderma reesei. *The image shows that the crystalline structure of the cotton fibers is disrupted by the cellulase enzyme.*

Illustration by Greg Lamb

Nuclear Winners

ORNL developments and ideas in the nuclear field have won a prestigious award, media attention, and new funding.

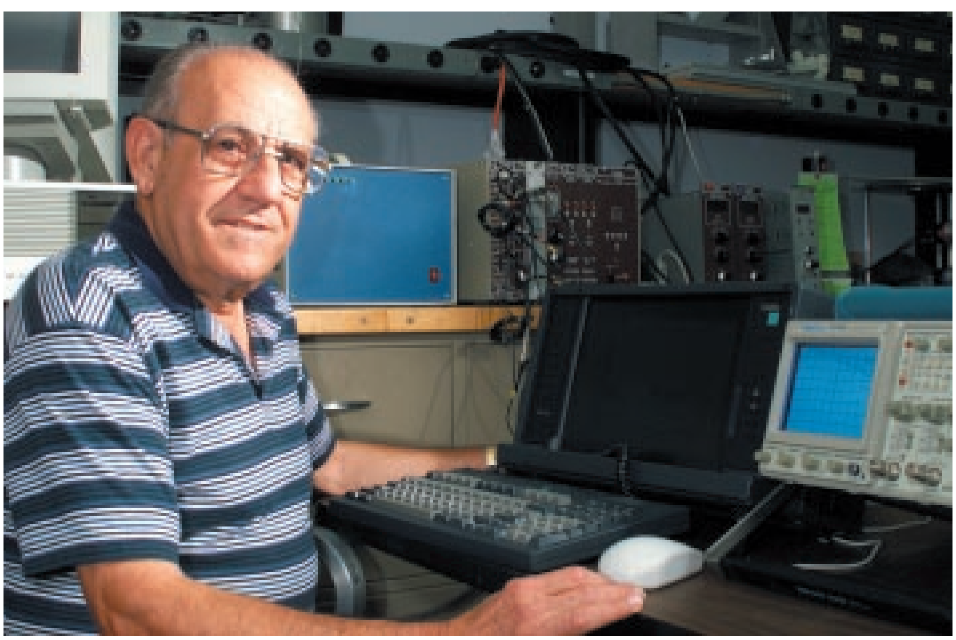
Wigner Award Winner

In 1999 Rafael Perez of the Advanced Nuclear Measurements Group in ORNL's Instrumentation and Controls Division received the American Nuclear Society's Eugene P. Wigner Reactor Physicist Award. He was cited for his outstanding contributions to the advancement of the field of reactor physics. Interestingly, the first two Wigner award winners (1990 and 1991 respectively) were Eugene Wigner and Alvin Weinberg, both of whom had previously served as ORNL directors. Wigner and Weinberg were pioneers in many fields of reactor physics, as well as in the design of nuclear reactors. They also co-authored the classic book *The Physical Theory of Nuclear Chain Reactors*.

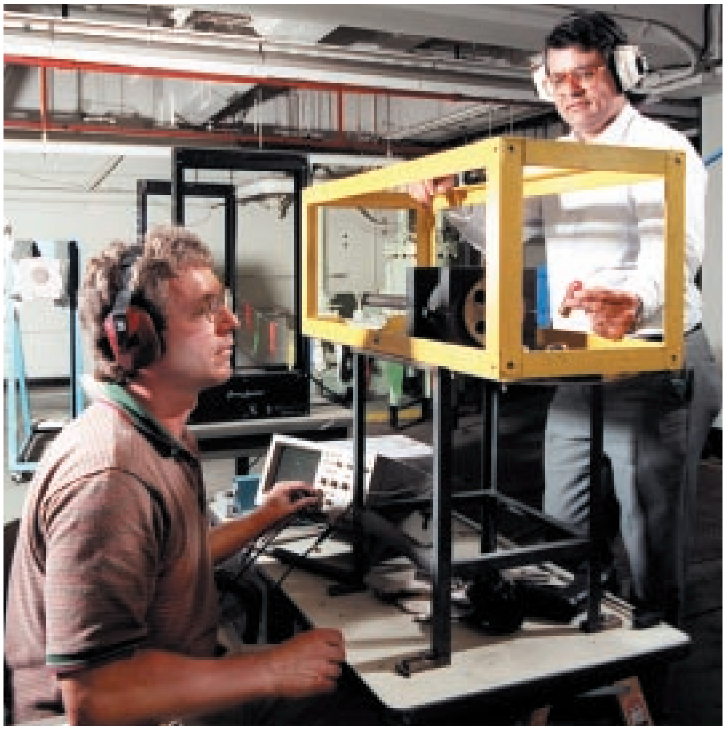
Perez, a native of Spain, contributed in several ways to reactor physics. From 1967 through the early 1990s, he worked with the late Gerard de Saussure on the theoretical interpretation and evaluation of neutron cross-section data resulting from measurements at the Oak Ridge Electron Linear Accelerator (ORELA). To determine the probabilities that various atomic nuclei will release neutrons by fission or capture neutrons of different energies, Perez applied a theory partly formulated by Wigner. In experimental research Perez, in collaboration with co-workers from the ORELA facility and physicists from abroad, measured the cross sections of thorium-232, uranium-235, uranium-238, protactinium-231, and protactinium-232. ORELA became a major source of "evaluated nuclear data files" for an international database that resides at DOE's Brookhaven National Laboratory. "These data," Perez says, "have been widely used by designers of nuclear reactors."

Working with ORNL's Felix Difilippo, and using neutron pulse and wave propagation, Perez also pioneered a way to measure reactor physics parameters. Since the early 1980s, he has taken an active part in the development and application of stochastic methods for the surveillance and diagnostics of commercial nuclear power plants. These methods, sometimes known as "neutron noise analysis," relate fluctuations of the neutron population in nuclear assemblies to their dynamics and operation, allowing the detection of abnormal occurrences and worn-out parts that should be replaced. In collaboration with members of the Advanced Nuclear Measurements Group, Perez has also applied stochastic methods to nuclear safeguards. More recently, he has focused on the nonlinear analysis of dynamical systems with applications to nuclear reactors.

Perez received his bachelor's degree from the University of Valencia in Spain, his master's



Rafael Perez, shown in his office, received the American Nuclear Society's Eugene P. Wigner Reactor Physicist Award.



Rusi Taleyarkhan (right) holds a variable-velocity bullet that has been shot at a target in tests at ORNL's melt-water-explosion-triggering analyzer. Seokho Kim adjusts the controls.

degree from the Massachusetts Institute of Technology, and his doctoral degree from the University of Madrid. He has conducted research at ORNL for 14 years and has held faculty positions at the University of Florida and the University of Tennessee, where he is currently professor of nuclear engineering. He is a fellow of the American Nuclear Society.

Reactor Research Leads to Variable-Velocity Bullet

For years, ORNL's Rusi Taleyarkhan studied the potential problem of steam explosions in water-cooled research reactors in which fuel elements are made of uranium-aluminum alloys sandwiched between aluminum plates. The concern was that an explosion might result from the interaction between heated molten aluminum and water in a research reactor, such as ORNL's High Flux Isotope Reactor, during severe accident conditions (an unlikely event that, nevertheless, has occurred in similar reactors elsewhere). Taleyarkhan led an investigation of the forces that could initiate, or trigger, an explosion and the nature of its propagation.

Further ORNL research demonstrated that introducing noncondensable gases into the protective steam film formed by aluminum-water contact would cushion external triggers, virtually eliminating the conditions that initiate melt-water explosions. This key finding is being confirmed by field tests of methods for preventing explosions in the aluminum industry.

Using such information, Taleyarkhan, Marshall McFee, and Joe Cunningham, all of the Engineering Technology Division, recently developed a variable-velocity bullet propelled by aluminum-water vapor explosions. Police officers using a gun based on this concept could dial up the velocity of the bullet to meet the needs of the situation. The bullet could be used to stun, disable, or kill. The weapon system currently has a cartridge based on a standard shotgun shell, and the variable-velocity projectiles can be steel, lead, or even fluid slugs.

The development won considerable attention in the media in the summer of 1999. It was mentioned in an Associated Press story and in articles in *USA Today, The London Times*, *Defense News*, *New Technology Week*, *Aviation Week and Space Technology*, *New Scientist*, and two local newspapers (*The Oak Ridger* and the *Knoxville News-Sentinel*). Radio listeners heard about it on National Public Radio, national radio shows starring Paul Harvey and Rush Limbaugh, the WIMZ radio station in Knoxville, Tennessee, and a New Zealand radio show. The technology was featured by ABC News on television and on the Internet (abcnews.com).

Nuclear Energy Research Initiative Projects at ORNL Win DOE Funding

DOE has started a new initiative that reflects increasing support for nuclear power development because of concerns about greenhouse gas emissions from fossil fuel power plants. Of the $19 million being provided by DOE to universities, private companies, and national laboratories for 45 nuclear reactor technology projects, $1.5 million came to ORNL in 1999 for 4 projects, as part of the new Nuclear Energy Research Initiative. More than 300 proposals were submitted to DOE. ORNL is expected to receive more than $5 million over three years for this work. The projects and ORNL participants are

- **Demand-driven nuclear energizer module** (D. G. O'Connor, P. J. Otaduy, F. C. Difilippo, T. D. Burchell, J. W. Klett). This advanced reactor concept will use a newly developed graphite with superb heat transfer properties and high-temperature mechanical properties to carry heat away from the fuel, avoiding the use of working fluids to cool the reactor core. The transferred heat could be used to generate hydrogen and increase the efficiency of electricity production. In addition, the reactor concept will use neutrons and gamma rays to produce certain radioisotopes and destroy others.

- **A new paradigm for automatic development of highly reliable control architectures for future nuclear plants** (T. L. Wilson and R. T. Wood). The goal for this research is to advance reactor control system design, diagnostic techniques, and information system design to provide a path leading to fully automated operation of reactors. For example, buttons, meters, and toggle switches of the 1970s will be replaced by the computer keyboards, joysticks, and touch screens of the 1990s.

- **Development of improved burnable poisons for commercial nuclear power reactors** (M. L. Grossbeck and J. P. Renier). The researchers will investigate the use of separated isotopes of rare-earth elements as substitutes for conventional burnable poisons, such as boron and gadolinium. Burnable poisons are neutron absorbers that are intentionally added to the reactor because they burn up at about the same rate as the fuel, permitting the use of a much smaller control system. The problem is that, because the conventional poisons don't completely burn up, they leave a residual negative reactivity that prevents some fuel from being used to produce additional energy. Use of a substitute material that would be totally consumed would cause the reactor to consume less fuel, reducing both waste generation and operating costs.

- **Mapping flow localization processes in the deformation of irradiated reactor structural alloys** (K. Farrell). Through study of plastic strains in irradiated reactor alloys, particularly dislocation channel deformation, deformation maps will be developed to help designers of new reactors select suitable materials, predict their performance, and avoid materials problems experienced in older reactors.

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Xudong Fan examines an image of an iodine-doped carbon nanotube that he obtained at ORNL's Z-contrast scanning transmission electron microscope (STEM), shown in the background. A computer model indicates that a charged iodine chain in a nanotube sucks its excess electrons from the tube wall, making the nanotube more electrically conductive. (See the cover story on nanotechnology starting on p. 2.)

The world's sharpest electron microscope image of a crystal was recorded recently at ORNL's Z-contrast STEM. This sub-nanoscale image of a silicon crystal has double the resolution of TEM images. ORNL physicist Steve Pennycook and Peter Nellist, now at the University of Birmingham in the United Kingdom, made this image showing columns of silicon atoms only 0.78 Angstrom apart. By contrast, typical TEM images show columns of atoms no closer than 1.6 Angstroms apart. One Angstrom is equal to one-tenth of a nanometer (or a billionth of a meter).