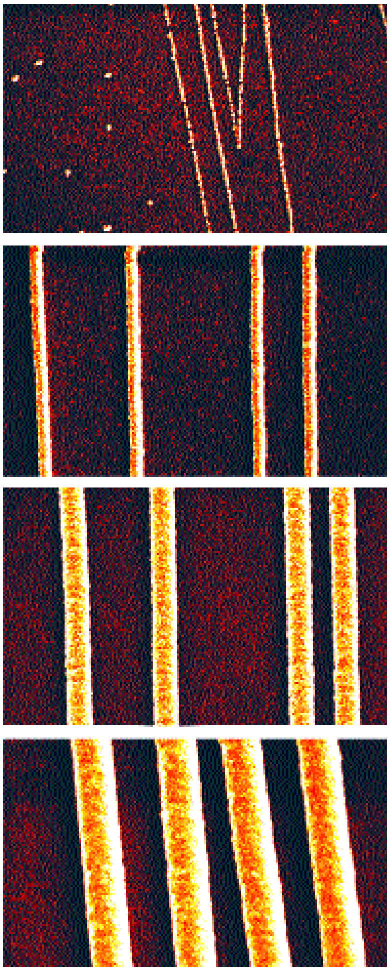
by Eric J. Lerner

Molybdenum as nanoconductor

Applied physicists are devoting considerable effort to developing materials for future nanometer-scale electronics. Some researchers still stick with silicon, with its vast industrial base; many others focus on the potential of carbon nanotubes, which, however, remain difficult to produce with highly repeatable characteristics. At the University of California, Irvine, chemists Reginald Penner, Michael P. Zach, and Kwok H. Ng have looked instead at molybdenum and have devised the first way to reliably produce nanoscale conducting wires (*Science* 2000, *290*, 2120).


University of California, Irvine

Colorized scanning electron micrographs of molybdenum nanowires with diameters of 13, 62, 130, and 210 nm.

Their method starts with a graphite surface that has molecular-scale steps. These steps act as nucleation sites for molybdenum oxides that are electrodeposited from an alkaline solution. In the past, attempts to directly deposit metal from the gas phase built wires only a few atoms thick, which bonded onto the graphite surface. By starting with a metal oxide deposited from a liquid solution, however, the UC Irvine team grew wires in a controllable fashion with diameters that ranged from 20 nm to 900 nm. Varying the duration of deposition controlled the diameter of the wires, with the smallest wires being grown in only 1 s of deposition. The wires were 500 μm in length.

Once the wires formed, they were reduced with hydrogen gas at 500 °C to form metallic molybdenum wires. In the process, the wires shrank by 30% in diameter, which loosened them from the graphite surface. They were then picked up by embedding them in a polystyrene film.

"We found the process would work as well for other base metals—cadmium and nickel, for example—but not for noble metals such as copper, platinum, and silver," Penner says. The noble metals formed particles but not connected wires. The disadvantage of molybdenum is that it rapidly reoxidizes back to an insulator in air. Penner, however, thinks the problem is easy to solve because the wires will be embedded in an insulating material in a chip and not exposed to air during manufacture.

Over the long run, Penner suggests that molybdenum could form the basis for not only conductors but also nanosized circuitry. Combinations of molybdenum and insulating molybdenum trioxide could be used to form the basis of nanotransistors as well. In the near term, Penner's group is looking for applications for the nanowires as sensors. One possibility is their use as chemical detectors, with tiny amounts of chemicals causing measurable changes in the wire conductivity.

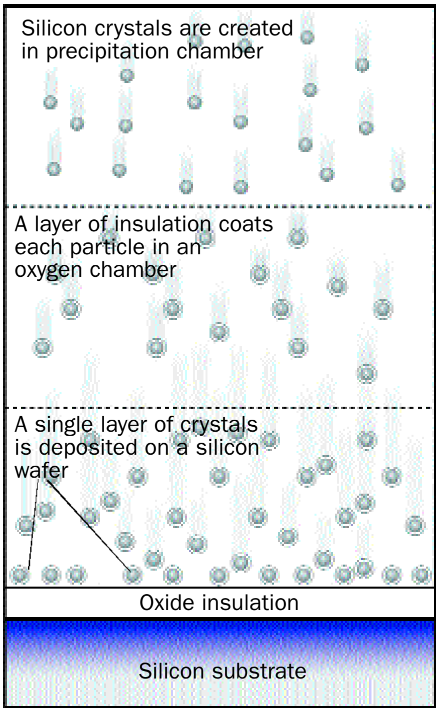
Memories from thin air

While awaiting the development of nanocircuits, researchers are shrinking those made of ordinary silicon. But shrinking the flash or nonvolatile memories (NVMs) that are a key part of many electronic devices is not easy. NVMs retain data when power is turned off, and they are vital to applications such as cellular phones, or indeed any device that does not have a disk drive. NVMs work by storing charge in a small cell of silicon that is insulated by a layer of silicon dioxide.

The insulator layer must be thick enough to prevent accidental leakage of the charge, even over long periods. To erase or record a bit, a voltage is applied across the insulator, causing the charge to tunnel in or out of the cell. But generating a tunnel current across a thick layer of insulator requires a relatively high voltage, around 10 V. This creates problems because the voltages needed by today's processors are only 1.8 V. Not only does this disparity make flash memories more expensive because they need separate voltage supplies, but it prevents them from shrinking in tandem with the processors. Such shrinkage would require lower voltages and thinner insulators, but unfortunately, with existing technology, this would create unacceptable levels of leakage.

To solve this problem and allow NVMs to shrink, a team of researchers at Agere Systems (part of Lucent Technologies, Murray Hill, NJ,) and the California Institute of Technology have devised a way to use nanocrystals of silicon—instead of a solid layer of silicon—to trap the charge. Their solution involves producing the nanocrystals not by the conventional lithographic process, but as an aerosol, and precipitating the crystals out of a gas like snow (*International Electron Devices Meeting 2000 Technical Digest*, pp.683-686).

The process starts with a mixture of nitrogen and silane (SiH_4) at 950 °C. At this temperature, the silane decomposes, leaving behind free atoms of silicon, which start to agglomerate into solid crystals. The nitrogen gas serves to dilute the crystals, keeping them apart so that they do not stick to each other in lumps. By controlling the time spent in the precipitation chamber, the team can create crystals as small as 3 nm in diameter.



Agere Systems

Nanocrystals of silicon are precipitated out of gaseous nitrogen and silane, coated with oxide, and deposited on a silicon wafer to create a nonvolatile memory cell.

Once the crystals are the right size, they are blown into a second chamber that has an oxygen atmosphere and a temperature of 1,000 °C. A 15-nm layer of insulator is then laid down on each of the particles, which are then deposited on a conventionally prepared silicon wafer to form the memory cells. Each cell typically has about 100 nanocrystals, which are arranged in a single layer. The nanocrystal layers are sandwiched between a 4-nm tunnel layer of oxide and another insulating layer laid down atop the crystals.

"The key advantage of the nanocrystals is that leakage is far less of a problem," explains Jan DeBlauwe of Agere, the lead researcher. "A conventional cell is like a bathtub—one leak and all the water flows out. With the nanocrystals, a leak just empties the charge from a single nanocrystal, and the cell still registers as having a charge." This means that thinner insulating layers and lower voltages can be used to tunnel the charge across the layers.

The experimental device generated by the researchers demonstrates the practicality of the idea because no leakage was observed, even after 100,000 record–erase cycles. The replication process is also simpler and less expensive than conventional lithographic approaches.

However, the critical output voltages are not yet low enough. "We are now experimenting with a high-dielectric-constant insulating layer, which we think will allow us to decrease the operating voltage to around 5 V," DeBlauwe says. This should make the next round of shrinking NVMs considerably easier.

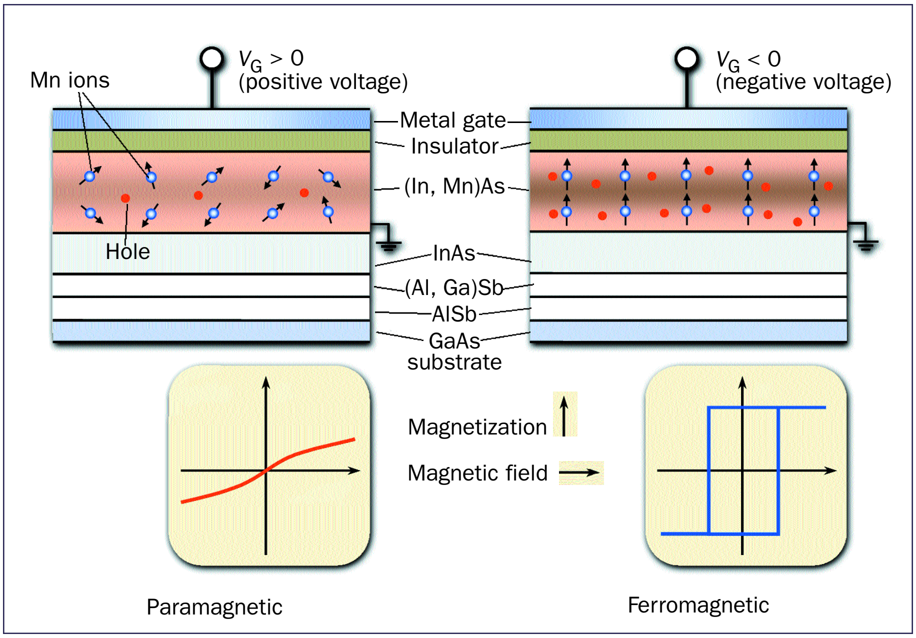
Ferromagnetics

Storing charge is not the only way to build NVMs. Another common technique is storing data in ferromagnetic fields, as on a disk drive. But for quick access, ferromagnetic elements and semiconductor processors would have to be on the same chip. As a result, semiconducting ferromagnetic materials have drawn a lot of interest. Such materials would be compatible with semiconductor-processor materials and, thus, could be integrated with them.

A big step in that direction was taken by the Laboratory for Electronic Intelligent Systems of the Research Institute of Electrical Communication at Tohoku University (Sendai, Japan). Researchers there demonstrated that they could use electric fields to reversibly turn on or off the ferromagnetism of a semiconductor material (*Nature* 2000, 408, 944). Such control would be extremely useful in any circuit that contained both ferromagnetic memory elements and semiconductor processors.

The experimental devices use indium manganese arsenide as the material in the magnetic channel. Below a critical temperature of around 30 K, the magnetic moments of the manganese atoms line up to create a ferromagnet, just as iron atoms line up at room temperature. The holes in the semiconductor material (places where electrons are missing) are vital to this process. In some way not yet understood, the holes couple the magnetic moments of the manganese atoms—the fewer the holes, the lower the critical temperature.

In the device built by Hideo Ohno and collaborators, the indium arsenide is placed in the gate of a field-effect transistor and kept at a temperature near the critical point. When a positive electric field is applied, the holes are repelled out, the critical temperature rises, and the material loses its ferromagnetism. When a negative



Research Institute of Electrical Communication, Tohoku University

An electric field can turn off (left) and on (right) the ferromagnetism of indium manganese arsenide in the magnetic channel of a semiconductor.

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The Web site for *The Industrial Physicist* has been redesigned with a new, cleaner functionality and new features, including easier ways to contact the staff. Most of the content back to February 1999 is online, and we are working to add all of the issues back to July 1995. Your comments are welcome (tip@aip.org).

field is applied, the holes are attracted back into the material, the critical temperature drops, and the material becomes a ferromagnet again.

The result is significant because Ohno and his team succeeded after other researchers failed many times using similar materials, such as gallium manganese arsenide. However, to produce a practical device, the operating voltage must be reduced far below its present level of 125 V and the operating temperature greatly increased. "Reducing the voltage is straightforward because it is the electrical field strength that is crucial," explains Ohno. "We were using a thick insulator layer of 800 nm. With a state-of-the-art layer 40 nm thick, our operating voltage should drop to 6 V."

Raising the temperature to room temperature will be trickier. Ohno's team is looking at doping manganese into zinc oxide or gallium nitrate to create potential room-temperature ferromagnetic semiconductors. However, before then, they want to use the existing material to gain a better understanding of how electric control of ferromagnetism really works. ◘

A nose comes of age

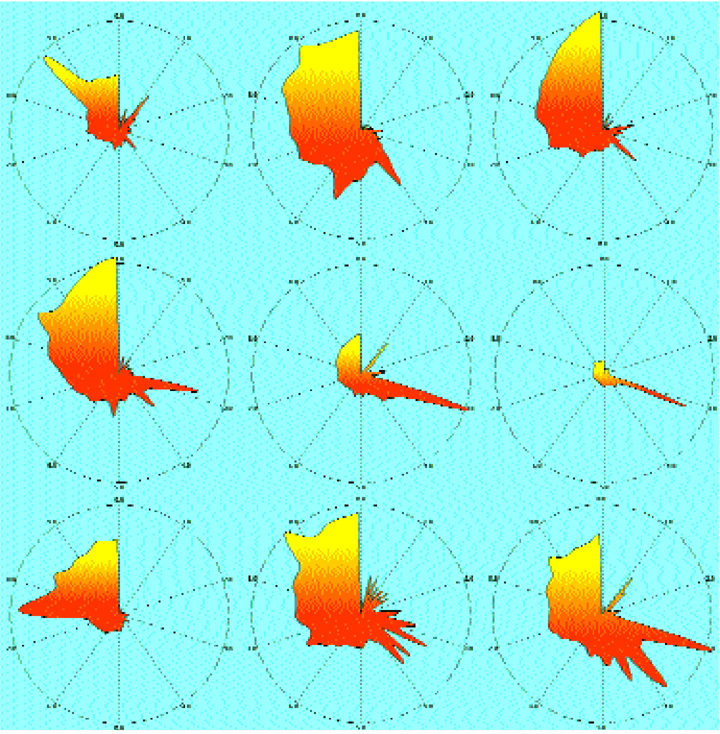
Sometimes a useful new technology emerges just by combining two existing techniques or devices. Often, however, even a simple idea takes years to move from concept to useful product. A recent example of both phenomena is the zNose, a new type of "electronic nose" capable of analyzing environmental pollutants, food components, and commercial fragrances in 10 s.

Researchers have long sought an electronic nose that can detect and classify chemicals in the field using tiny amounts of their vapors. Such noses could be used to detect drugs, monitor trace air pollutants, and provide quantitative quality control for foods and beverages. But most existing noses use an array of different sensors whose responses can be analyzed only by sophisticated pattern-recognition programs, which makes them impossible to understand physically or calibrate reliably with chemical standards.

Back in 1983, Edward Staples, now of Electronic Sensor Technology (Newbury Park, CA) thought he had a better idea. He knew that gas chromatography had been used for years in the laboratory as a standard and extremely sensitive method of detecting chemicals in vapor form. Gas chromatographs (GCs) work by slowly heating a sample of material and detecting the exact time at which each chemical arrives at the end of a tube. To detect the vapors as they condense out of the long separation tube, GCs use five or six different sensors, each optimized for different types of chemicals. With this variety of sensors, and capillary columns tens of meters long, traditional GCs were strictly laboratory, not field, devices.

Staples' idea was to develop a miniature GC and combine it with a surface acoustic wave (SAW) oscillator to create a single all-purpose sensor. A SAW sensor consists of a mechanical oscillator, often made from quartz, and frequency detection circuitry. When tiny amounts of any material are deposited on the oscillating crystal, its natural period of oscillation of around 500 MHz varies slightly, which allows an instantaneous measurement of the mass of the material that caused the change in frequency. Such a mass detector would be equally sensitive to all chemical components separated by the GC.

To get from this basic idea to a field-ready commercial product required overcoming several problems. First, the 0.5- to



Electronic Sensor Technology

Visual olfactory images of soup show radial amplitude proportional to fragrance intensity, with angular displacement (from the vertical) representing time. Images left to right, top to bottom, represent the following soups: cream of asparagus, bean bacon, chicken noodle, clam chowder, cream of mushroom, potato, beef consommé, vegetable, and cream of chicken.

1-h heating time used in GCs had to be radically reduced—eventually to 10 s—and the length of the capillary columns radically shortened, even at the expense of some resolution. To work on these problems, Staples began a firm in 1983 to produce an entirely new type of electronic nose, and a second firm in 1995 to commercialize the prototypes he had developed.

The zNose was first marketed in 1997 as a tool for law enforcement officers and environmental scientists. Currently it is the only electronic nose validated twice by the U.S. Environmental Protection Agency and once by the White House Office of National Drug Control and Policy. At the December 2000 meeting of the Acoustical Society of America, Staples presented evidence that the zNose can be used to monitor industrial processes involving various aromatic products and processes.

After years of development, the zNose has become an impressive field tool. It detects many substances at parts-per-billion levels and some down to parts per trillion. Even with reduced resolution, it distinguishes 500 different arrival times of chemicals in 10 s and has a dynamic range from highest to lowest concentration in a single run of 100,000. The briefcase-sized device also produces a graphic representation of its analysis—time is displayed as an angular measure and concentration as a radial measure. The resulting image allows operators to recognize certain key odors at a glance (see illustration on p. 17).

"We are getting new applications for the zNose almost every week," says Staples. A wine company is using zNose to detect a cork-produced contaminant called 2,4,6-trichloroanisole at the parts-per-trillion level, which is comparable to the sensitivity of a skilled wine taster. A zookeeper plans to use the device to detect pheromones given off by endangered animals in heat to optimally time their matings. "Because bacteria are known to give off characteristic odors, we hope that zNose will soon become a standard doctor's-office piece of equipment, able to diagnose infections without sending a sample to a lab," Staples says.