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Chemistry for the Future

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Chapter 9

Materials for Advanced Electronic Devices

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The typical integrated-circuit chip looks like an armored insect. It has a hard plastic or ceramic case from which an array of metal legs protrude. Inside this arthropodal packaging sits a remarkable collection of materials that are carefully engineered to control the movement of electrons.

The Structure of an Integrated-Circuit Chip

The key working parts of a generic chip are really too small to see with the naked eye. Only the packaging is readily apparent, but under a scanning electron microscope, you would see that the chip itself is made of a series of thin layers, with one material coated on top of another (*see* Figure 1). Each layer has a thickness that may be anywhere from a few atoms to several thousand atoms deep, depending on its function. These layers, carefully laid onto a chip's surface, then etched into vast arrays of microscopic electronic switches and gates, work together to shuffle electrons about. In place of the maze of separate wires and components typically associated with electrical circuits, the chip's wires and electronic devices are integrated as lines and channels on its surface. Today's integrated-circuit chips may carry hundreds of thousands of transistors, each measuring as little as a few micrometers across.

A typical chip starts off as a clean, polished wafer of silicon doped (deliberately contaminated) with a trace of either boron or phosphorus. Doping with phosphorus produces an ***n-doped semiconductor***, which provides electrons as current carriers. Boron produces a ***p-doped semiconductor***, which provides positive, electron-deficient

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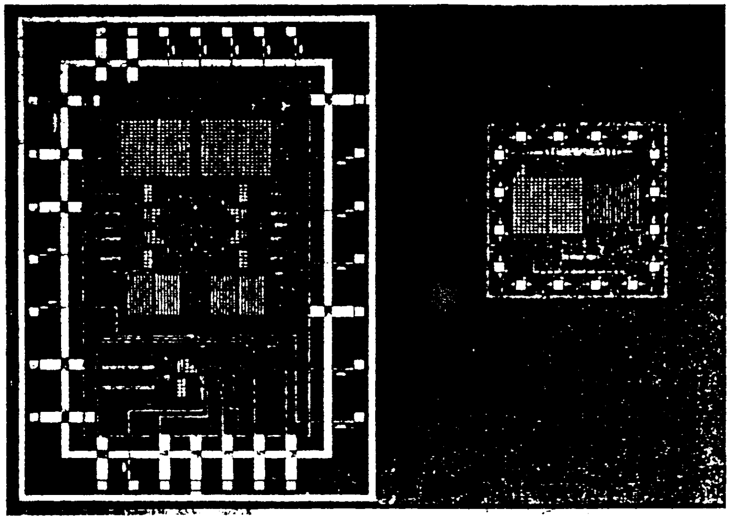

Figure 1. Scanning electron microscopic view of an integrated-circuit chip.

regions, called holes, as current carriers. Atop this silicon surface, chip fabricators deposit as many as a dozen layers, some of which, like silicon, are semiconductors, while others may be electrical insulators or conductors. Each type of material plays a role in pushing electrical charge through the chip's circuits. The conductor in an integrated-circuit chip may be a metal, such as aluminum, or silicon that is heavily doped with a conducting material. Strips of conductors form electrical connections within and between circuit elements. The insulator usually consists of silicon dioxide and is used to protect the silicon surface and separate conducting regions where no connections are desired. Figure 2 shows an integrated-chip cross section.

In the fabrication of integrated circuits, the layers are

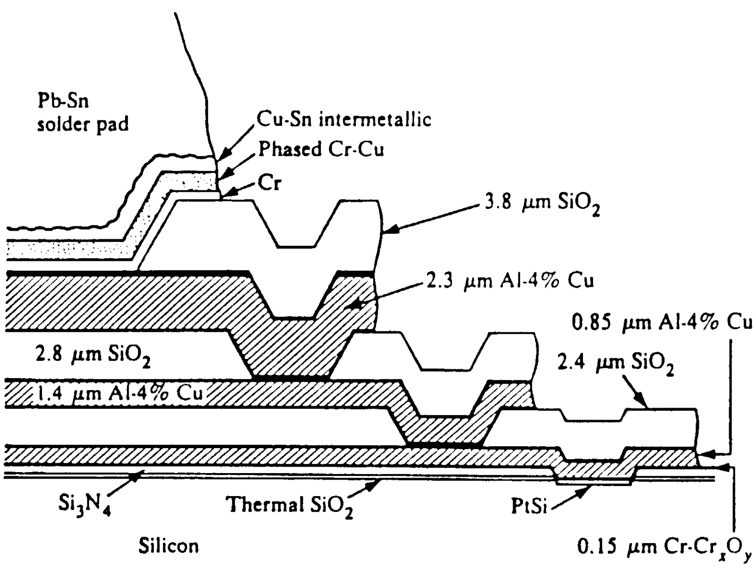

Figure 2. Cross section of an integrated-circuit chip.

added one at a time. A template called a "mask" determines the pattern for each layer. Fabrication takes place by various steps that combine oxidation, mask protection, etching, diffusion or ion implantation, and vapor deposition. Finally, the chips are sealed in a protective plastic or ceramic package. The package is what many people envision when they think of a computer chip, but the chip itself is actually a flat piece of silicon, no bigger than a fingernail.

These tiny chips, carrying an increasingly heavy load of transistors and other devices, have fueled the explosive growth in the electronics and computer industries. Every year, more and more everyday products, from toys and tape recorders to refrigerators and automobiles, rely in some way on integrated-circuit chips.

Competitive Choices

Microelectronic technology has evolved so quickly and has become the focus of such keen international competition that policymakers are now left wondering where the United States should focus its efforts and what role materials science should play in this research. On the commercial side, a very large fraction of the gross national product has come to depend, more or less directly, on electronics. More recently, from the perspective of national security, there is a growing perception and concern that many essential electronic systems in military applications use components that are available only from Japan.

The growth of microelectronics raises two important issues. First is the basic question of how best to try to defend the existing electronics industry, which relies heavily on silicon-based technology. Silicon itself will remain an important electronics material for the foreseeable future, especially as researchers achieve smaller feature sizes and three-dimensional structures. New technologies based on gallium arsenide and the construction of hybrid devices that combine the most promising characteristics of silicon and gallium arsenide will find their places. Technologies based on diamond or cubic boron nitride are also possible but much more distant. New superconducting materials will probably have a role in high-speed circuit connections.

The second issue is to determine in what directions the technology should be pushed. The electronics industry is continuing to move in the direction of miniaturization. Features on silicon chips are becoming so small that they are easily dwarfed by a human hair, and miniaturization can be carried further still. To achieve the next level of ultra-large-scale integration, chip designers are venturing into the realm of three-dimensional structures and exploring exotic approaches such as layered superlattices. New techniques of fabrication promise unprecedented densities and device geometries. The new generation of chips would have features that are less than a micrometer across; millions of transistors would be packed onto a scrap of silicon or some other semiconductor material. By studying the complete range of properties of electrons in all types of materials, scientists provide the fundamental knowledge essential for large-volume, reliable production of microelectronic devices.

As chip designers advance to the stage of ultra-large-scale integration, they will try at the molecular level to design the properties of chips. Then it will be especially important to be able to predict the response of a particular combination of materials and a particular circuit design. Chip designers will also need the ability to assess various strategies for growing the materials required for the microscopic structures they desire.

Packaging Semiconductors

The plastic or ceramic packaging that contains a chip's links with the outside world and protects it from damage is now becoming the bottleneck that restricts efforts to increase the speed and shrink the size of integrated-circuit chips. Although packaging has traditionally been much less exciting to work on than the chips themselves, new developments in packaging may be the key to breakthroughs in chip technology.

Most electronic devices are placed on alumina (aluminum oxide) supports, or substrates. A piece of alumina is made by compressing alumina powder into an appropriate form, and then sintering (heating without melting) it to create a dense microstructure (*see* Figure 3). There are important correlations between the form of the particulate alumina powder and the electrical properties

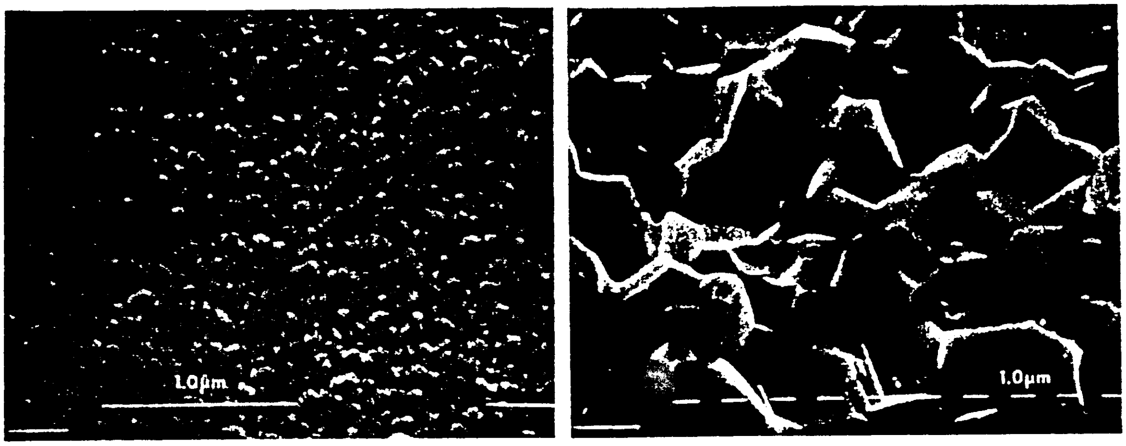

Figure 3. Sintering of alumina. Left, ideal packing; right, dense microstructure obtained at 1300 °C for one hour.

and dimensional stability of the final assembled product. One important goal is to perfect the final product by using the best available alumina powder, such as the highly regarded material provided by the Japanese company Sumitomo. That kind of perfection is likely to lead to fundamentally new processing technologies. Some researchers are also trying to fabricate more complicated alumina structures that not only support the functions in an integrated circuit, but also perform important functions of their own.

Atomic Views

To control the materials and the chemical reactions involved in fabricating sophisticated semiconductor circuits, scientists need the ability to detect surface details as small as individual atoms. To achieve this notoriously difficult task, chemists are beginning to adopt techniques developed in the field of vacuum physics. The scanning tunneling microscope enables researchers for the first time to image atoms directly, one at a time.

In a tunneling microscope, an extremely sharp, metal needle is brought within a few angstroms of the sample's surface. This distance is small enough for electrons to leak or tunnel across the gap and generate a minute current. As the gap between the tip and the sample increases, the current decreases. As the probe crosses the sample, moving back and forth across its surface, its vertical height is continually being adjusted to keep the current constant. In essence, the probe traces out a contour map of the sample's surface atoms.

The invention of the scanning tunneling microscope and subsequent refinements in its design have given scientists increasingly sharp views of atoms perched on solid surfaces. Most recently, the microscope has provided pictures not only of silicon atoms neatly arrayed on a silicon surface but also of the bonds holding the atoms in place (*see* Figure 4). Normally, the voltage applied between the sample and probe stays the same. To observe the bonds between atoms, scientists at the IBM Thomas J. Watson Research Center (*1*) held the probe still while varying the voltage. The result was a map of how the current varies at selected points over a surface. The information was then used to show where electrons bonded to surface atoms were likely to be.

It's amazing that scientists can make such minute observations and can begin to use devices like the probe to pick up individual atoms and move them to some other part of the substrate. Such a feat was inconceivable 20 years ago.

Speed and Gallium Arsenide

Since the early 1970s, scientists have been promoting gallium arsenide as a faster, more efficient substrate material than silicon for making integrated-circuit chips. (Figure 5 is a scanning tunneling micrograph of gallium arsenide.) However, the vast majority of chips are still made from silicon, which is abundant and cheap. The most important advantage of gallium arsenide is speed. Electrons travel about five times faster in gallium arsenide than they do in silicon. Gallium arsenide also has a high resistance to electrical current before it is doped with any impurities to form circuit elements. Consequently, a gallium arsenide wafer, or substrate, is semi-insulating, whereas a silicon wafer is semiconducting. That feature simplifies gallium arsenide circuit fabrication considerably. Gallium arsenide also offers a wider range of operating temperatures than silicon and much higher radiation hardness, which is a decisive advantage for military and space programs. Another major advantage is that gallium arsenide can be doped in such a way that it emits light, which makes it useful for lasers and light-emitting diodes.

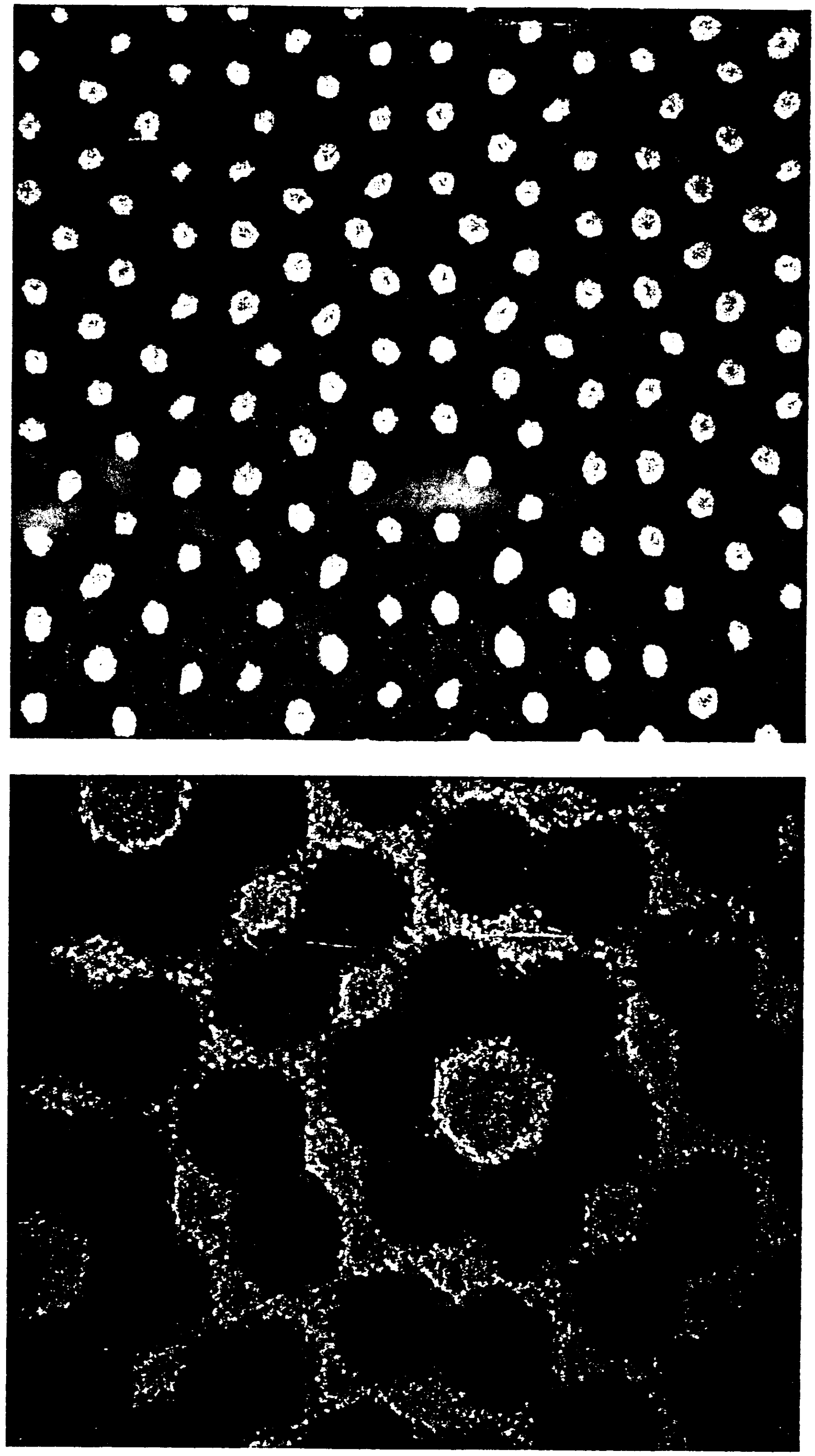

Figure 4. Two views of the silicon surface by scanning tunneling microscopy. The larger is a blow-up of the smaller.

Figure 5. Scanning tunneling micrograph of gallium arsenide.

The problem with gallium arsenide is that the material is exceptionally difficult to grow into large, defect-free crystals. Much care is needed to produce from the elements gallium and arsenic a very precisely tailored compound with just the right properties and the right proportions. Large silicon crystals, on the other hand, are relatively easy to produce, in part because only one element needs to be controlled. With gallium arsenide, two materials must behave properly. One of those materials—arsenic—is toxic and volatile at the high temperatures needed to grow crystals. It tends to bubble out of the high-temperature melt. Despite the development of various methods for overcoming these problems, high-quality gallium arsenide is still relatively expensive and hard to get. Furthermore, silicon is a better heat conductor, and it allows more transistors and other devices to be packed into a given surface area.

A Match for Silicon

Until now, silicon and gallium arsenide technologies have developed somewhat independently. One way of dealing with the silicon/gallium arsenide trade off would be to marry the two types of components. Putting gallium arsenide semiconductor circuits atop a silicon base is a bit like mating a Ferrari with a Honda. The components seem incompatible, but if the match were to work, the result would be an attractive combination of high performance and economy.

Hybrid integrated-circuit chips of gallium arsenide and silicon may now be feasible. Researchers at the University of Illinois at Urbana-Champaign have discovered a way to deposit gallium arsenide layers on top of silicon wafers without spreading the crystal defects that ruin the electronic properties of the materials.

The trick is to find a way of aligning the silicon and gallium arsenide crystal lattices. Normally, the structures do not quite match. For a row of 25 silicon atoms, only 24 atoms from a gallium arsenide layer are needed to fill the same space. Aligning the two materials produces a large number of defects where the two lattices meet. The mismatch can be overcome if the silicon base is slightly tilted. A gentle slope of about 4° provides, at the atomic level, tiny steps that take care of the problem. If these steps have the right orientation with respect to the silicon crystal lattice, then the inherent bumpiness of the slope does not produce dislocations that thread their way into the gallium arsenide layer.

The orientation is the key. For a square silicon chip with an upper surface parallel to a face of the crystal lattice, the slope needs to rise from its low point at one corner to its peak at the diagonally opposite corner. The combination of light-emitting gallium arsenide chips and complex, tightly packed silicon circuits could make it possible to connect circuits optically instead of using wires. In some of today's most advanced chips, far more power already goes into driving the wires that connect chips than in running the complicated silicon circuits themselves. With hybrid chips, the wires connecting one device to another could be replaced by an efficient optical system, perhaps using optical fibers.

Because all parts of an integrated circuit need not be equally fast, it may eventually be possible to deposit gallium arsenide at only the points on a silicon circuit where the chip must operate quickly. Recent work at the University of Illinois (*2*) will probably accelerate the pace of hybrid-chip research. Continuous lasers and optical interconnects may be developed soon. More and more research groups are active in the field, and several small companies have been established to develop the technology.

The use of materials that respond to light suggests the potential for a major shift in technology from computing and communications devices based on the movement of electrons to devices based on the transmission of light. Optical computation and communications are not yet a major commercial technology, although the communications part is becoming important. One major interest of researchers is to develop classes of materials that enable one to manipulate light with the speeds and characteristics that are required of new generations of chip-to-chip and continent-to-continent communications. Perhaps future computers will do their computations by manipulating light pulses instead of electrons. There is much opportunity for important inventions and major new applications.

Layers upon Layers

One interesting type of microelectronic device now being studied is a heterojunction device made up of multiple, alternating layers of gallium arsenide and gallium aluminum arsenide (*see* Figure 6). Each layer is only a couple of atoms thick. With such small structures, a host of remarkable phenomena begin to emerge. One is negative resistivity: When the voltage is increased, the current goes down rather than up.

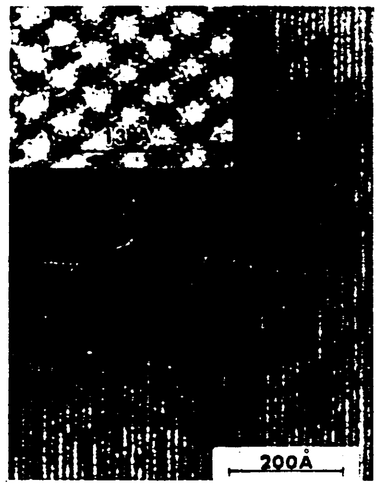

Figure 6. Heterojunction structure.

Another phenomenon evident in exceedingly thin semiconducting films is ballistic transport, which allows an electron to pass from one side of a barrier to another without striking any atoms in between, tunneling through the barrier like a ghost passing through a wall. Under normal conditions, electrons do not race from point to point like speeding bullets; they stumble along more like drunken sailors. Flowing through the circuitry of a chip, they constantly bump into impurities, rebound off walls, and slow down as they pass through the electronic gates that signify on or off in a microprocessor. Each collision costs distance and time. Ballistic transistors are designed to be so small that an electron can shoot right through the device with scarcely a single collision. The idea is to make the length of the region that electrons have to travel comparable to the average distance they go before colliding.

Over the last decade, there have been a number of spectacular advances in the construction of semiconductor heterostructures with a specified band gap. These have led to the discovery of the totally unexpected two-dimensional behavior of electrons, as well as to the development of novel electronic and optical devices. Many of the advances are a direct result of the development of new crystal growth techniques allowing the formation of layered semiconductors that are perfect on the atomic scale.

A number of technologies make possible these astonishing structures. One is metallo-organic vapor-phase deposition, also called vapor-phase epitaxy. It involves taking appropriately prepared organometallic compounds and allowing them to react in the vapor phase to deposit the desired inorganic structures on an appropriately prepared substrate. Epitaxy is the process of growing crystalline semiconductor films in which the substrate determines the crystallinity and orientation of the thin films grown on top of the substrate. Among the techniques that have been widely used are liquid-phase epitaxy, chemical-vapor deposition, and molecular-beam epitaxy.

In liquid-phase epitaxy, the epitaxial layer is grown by cooling a heated metallic solution saturated with the components needed to grow the layer, while that solution is in contact with the substrate. In chemical-vapor deposition, the epitaxial layer is grown from a heated stream of gaseous elements or compounds, which react at the surface of the substrate. Recently, researchers have made considerable progress in growing lasers and other quantum-well heterostructures, using metallo-organic chemical-vapor deposition for epitaxial growth.

The most advanced semiconductor heterostructures require special fabrication techniques under controlled, high-vacuum conditions. The process of molecular beam epitaxy is a bit similar to painting with spray guns containing different-colored paints. The materials to be layered are heated in separate ovens within a vacuum chamber until their atoms begin to boil off. A computer-controlled shutter then opens and closes at precisely timed intervals, releasing the proper quantity of atoms, first of one material then another, from each furnace. The atoms strike and adhere to the base plate, forming alternate layers.

Nevertheless, the precise control of the chemical reactions that take place at surfaces and especially the control of the purity of the materials is one goal that heterostructure fabricators have not yet attained. Whoever first learns how to achieve such control—whether it happens in Japan, the United States, or elsewhere—will dominate a substantial part of electronics processing in the future. The challenge shows a very real need for technological innovation.

Warmer Superconductors

For more than a decade, researchers have been toying with the idea of building integrated circuits for computers using superconducting Josephson junction switches. A *Josephson junction* consists of two thin layers of superconducting metals, such as lead or niobium, which act as electrodes, separated by an even thinner insulating layer. At liquid helium temperatures, the metal's electrical resistance drops to zero, and electron pairs can tunnel across the insulating junction. An externally applied voltage can stop the current flow, and thus this device can be used as a switch. Despite the disadvantage of having to work at temperatures close to absolute zero, Josephson junction circuits have appeared attractive for computer circuits because they switch on and off faster and emit only one one-thousandth as much heat as semiconductor transistors.

Until recently, however, researchers had had very little success in finding materials that become superconductors at higher temperatures. The best they could find were certain metal alloys that abruptly lose their electrical resistance at temperatures below 24 K. In 1987, the situation changed dramatically with the discovery of special ceramics that remain superconductors at temperatures now as high as 90 K. Because that temperature is greater than the boiling point of liquid nitrogen, though much lower than room temperature, much less costly refrigeration techniques can be used to cool the ceramic materials enough to turn them into superconductors. Therefore, the number of potential applications is greater.

. . . chemists and engineers have joined the exhilarating quest to understand high-temperature superconductors, improve their properties, and push them into practical commercial applications.

At the moment, scientists are optimistic for two reasons. They know they can shift the critical temperature at which a material becomes superconducting by varying the composition and the structure of these new superconducting ceramics. They are also certain that investigations of how these materials achieve a superconducting state will lead to the elucidation of fundamentally new mechanisms for superconductivity. Both advances will likely lead to devices—from electronic circuits to electromagnets—that operate at relatively high temperatures but pose no resistance to electric currents. For the world that we live in, these advances are potentially as important as advances in molecular biology.

From a materials point of view, the greatest amount of attention has been focused on yttrium-barium-copper oxides. However, these are not the only ceramic materials that show superconductivity. Researchers are beginning to look at other possibilities, especially as they learn what special electronic properties to seek in specific materials. A host of chemists and engineers have joined the exhilarating quest to understand high-temperature superconductors, improve their properties, and push them into practical commercial applications. One early application may be for magnetic field detectors and simple electronic devices.

Diamond's Sparkling Potential

A fiery sparkle isn't all that makes a diamond so eye-catching. Its hardness and its ability to conduct heat and to act as an electrical insulator make diamond an attractive material for electronic circuits designed to survive high temperatures or withstand intense radiation.

Although it is hard to imagine a way to fabricate diamond into thin sheets of the sort used for silicon-based devices, some researchers believe that a future generation of electronic devices may be based on diamond—if they can overcome certain problems. What is needed is an economical, practical method for laying down and then etching thin diamond films on silicon and other surfaces.

Diamond is attractive because it carries electrical pulses extremely quickly. Its transparency means that it can transmit optical signals. Because diamond is the best known thermal conductor, it could be extremely efficient in diamond-based electronic devices. Complete impermeability to oxygen and similar species gives diamond many of the properties one can hope for in an almost ideal device.

The basic process for generating diamond coatings involves passing a gaseous mixture of methane and hydrogen molecules at atmospheric pressure through a microwave bath. This process breaks up the molecules into hydrogen and carbon atoms, which can then settle onto a silicon surface. This chemical vapor deposition technique is not unlike that used for gallium arsenide structures.

The presence of hydrogen appears to be necessary to ensure that carbon atoms end up in a tetrahedral diamond crystal arrangement rather than in a planar graphite structure. Hydrogen atoms seem to pick up "dangling" bonds on a freshly laid carbon surface, which prevents the carbon's structure from collapsing into the form of graphite. Moments later, carbon atoms replace the hydrogen atoms, and the crystalline diamond film continues to grow.

It takes about an hour to lay down a 1-micrometer-thick diamond layer. Each film consists of a random array of individual diamond crystals about 200 angstroms across. Researchers are now trying to speed up the deposition rate and to build films that consist of a single diamond crystal. That accomplishment should make diamond fabrication very simple. The new process is potentially cheaper, cleaner and more versatile than high-temperature, high-pressure techniques now used to produce synthetic diamonds.

A diamond film's first application may be in microelectronics. Because diamond conducts heat like a metal, tiny diamond slabs could be used as bases for electronic circuits that need to survive high temperatures. Conventional silicon chips usually cannot withstand temperatures greater than 300 °C. However, diamond-based devices could be used as sensors in engines or nuclear reactors. Furthermore, because diamond does not overheat easily, more circuit elements could be packed onto a diamond-based chip than on a silicon chip.

In the United States, scientists at the Naval Research Laboratory in Washington, DC, and at MIT's Lincoln Laboratory have long worked on designs for diamond semiconductor circuits. Until recently, they lacked materials on which to test their designs. New research efforts to produce diamond films at Penn State; North Carolina State University in Raleigh; and at the Research Triangle Institute in Research Triangle Park, NC, will now provide the essential materials for that work (*3*).

Early in 1987, the Japanese company Sumitomo announced that it had succeeded in developing a diamond semiconductor. The diamond film is doped with a small amount of phosphorus, which turns it into an n-type semiconductor. The new process brings scientists one step closer to creating true diamond transistors and other electronic devices. Researchers working at the MIT Lincoln Laboratory (*4, 5*) have created authentic, though highly primitive, transistors in a thin diamond film by spraying ions in patterns in the presence of nitrogen dioxide trapping devices.

The Japanese company Mitsubishi has already come up with one commercial application for diamond in information systems. The company now manufactures a very fast Winchester drive in which the magnetic medium operates without a lubricant. With the head in very close proximity to the device, a diamond-film wear-resistant barrier prevents catastrophic crashes in the event of occasional, inadvertent contact between the head and the spinning disk.

Looking Ahead

Recent advances in high-temperature superconductivity and the fabrication of thin diamond films are two significant signposts pointing toward technologies that may someday play crucial roles in microelectronics. Microelectronic technologies are changing very rapidly, and any nation that expects to remain at the forefront of new technologies should invest broadly in investigating materials that have the potential for dramatically changing the world. The dividends may not come this year, or next year, but perhaps 25 years from now. Nevertheless, the investment is necessary to ensure a secure economic future.

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