Is Diamond the New Wonder Material?

American researchers growing diamond films are scrambling to catch up with their Soviet and Japanese counterparts with the help of money from the Star Wars office

BELATEDLY waking up to the evidence from the Soviet Union that began accumulating about 10 years ago and from Japan more recently, American researchers succeeded earlier this year in growing thin films of polycrystalline diamond on substrates such as silicon by the technique of plasma-assisted chemical vapor deposition.* The prospect of making high-quality material by a comparatively low-cost and straightforward process has predictably stirred a wave of interest in exploiting the many advantageous mechanical, thermal, chemical, optical, and electrical properties of diamond. "Diamond's natural properties are the driving force," says Jerome Cuomo of the IBM Yorktown Heights Laboratory, where researchers are just setting up equipment to make their own diamond films.

Amid rumors that Japanese firms will soon be marketing diamond products, including a tweeter manufactured by Sony with a diamond-coated cone for improving the fidelity of sound reproduction, two workshops held this past summer were aimed at stimulating academic and industrial activity in the area. At least one company whose researchers were reading the literature from overseas, Crystallume of Palo Alto, California, was formed 2 years ago to commercialize diamond films, with the first products projected to make use of the material's hardness and wear resistance. The largest chunk of research money, nearly $3 million per year, comes from the Strategic Defense Initiative Office's Innovative Science and Technology Office (IST). In addition, IST and the Office of Naval Research (ONR) have jointly launched a "diamond technology initiative" to look into optical and electronic applications.

Jewelry advertisements to the contrary, diamonds are not quite forever. In 1792, Antoine Lavoisier burned diamond in oxygen, transformed it entirely into carbon dioxide, and concluded that carbon was the only constituent of diamond. Ever since, a mixed bag of hopefuls ranging from charlatans to eminent scientists has tried to reverse the process and turn more ordinary forms of carbon into diamond. H. Tracy Hall (now at Brigham Young University) and his coworkers at General Electric finally succeeded in making synthetic diamond in 1954 in an apparatus that simultaneously applied high pressure and high temperature to graphite, which is the thermal equilibrium phase of solid carbon at room temperature and atmospheric pressure. Once formed, however, the metastable diamond phase persists in air until the material is heated to above 1100°C.

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Diamond's reputation for durability rests less on the technical details of its thermodynamic stability than on the simple fact that, under ordinary conditions, it is the hardest and most chemically inert of all known materials. The ability to coat tools and other items with a layer of diamond a few micrometers thick opens the way to a host of industrial applications, says Thomas Schultz of Crystallume. As a possibly flighty example that nonetheless illustrates the potential, one can anticipate that the "in" gift for gourmet cooks may one day be a diamond-coated carving knife that is as sharp as a razor blade and never wears out.

An important high-tech example of the benefits of diamond comes in computer hard-disk memories. Occasionally the head that transfers data to and from the rapidly spinning disk comes too close, with catastrophic results. At a workshop held last July in Durham, North Carolina, to introduce the diamond technology initiative, Max Yoder of ONR said that a diamond layer only 250 angstroms thick could protect against such "head crashes."

To those unfamiliar with diamond, it may come as a surprise that the high thermal conductivity of diamond, which at room temperature and above is better than that of any other material, including such metals as copper and silver, is one of the most compelling arguments for developing this material. Diamond is also unique in that no other material is simultaneously such a good heat conductor and electrical insulator.

A pervasive problem in electronics, for example, is heat dissipation, which limits how tightly transistors can be packed together on an integrated circuit chip and how closely printed circuit boards can be spaced in computers and other electronic equipment. At the diamond initiative workshop, Yoder addressed these issues, pointing out the possibility of a diamond printed circuit board without the ever-present cooling fins that now take up so much space.

Eventually, the transistors themselves may be made of diamond, which is a semiconductor with the same crystal structure as silicon. Four years ago, J. F. Prins of the DeBeers Diamond Research Laboratory in Johannesburg, South Africa, demonstrated a bipolar transistor made of natural diamond, although its performance was poor. For a bipolar transistor, one needs a material that can be both a *p*- and an *n*-type semiconductor. Some diamond is naturally *p*-type because of the presence of boron impurities, but making good *n*-type material has proved difficult. Prins transformed naturally *p*-type diamond into *n*-type by irradiating it with a high-energy beam of carbon ions.

A more promising result comes from Japan. According to an article a year ago in the *Japan Economic Journal*, researchers at Sumitomo Electric Industries, Ltd., in Hyogo have made both *p*- and *n*-type semiconducting diamond films by doping them with boron and phosphorus, respectively. Sumitomo plans on having a working transistor by next year. Diamond's electrical properties provide considerable motivation for the effort. At the workshop, Yoder obtained from different combinations of the properties of diamond figures of merit that ranged from 32 to 8200 times the values for the silicon upon which current semiconductor technology is primarily based.

One advantageous property of diamond is its large band gap, 5.45 electron volts as compared to 1.1 electron volts for silicon. The large band gap makes diamond comparatively insensitive to temperature and radiation damage. Sumitomo is said to be interested in diamond transistors for control systems in automobile engines, a particularly severe environment characterized by dirt and high temperatures, and for telecommunications systems in space, where radiation is hard to avoid. Although silicon electronics are now used for these applications, to protect them against temperature and radiation adds greatly to the cost.

*Crystalline diamond films are to be distinguished from diamond-like carbon films, which have an extensive history of their own.

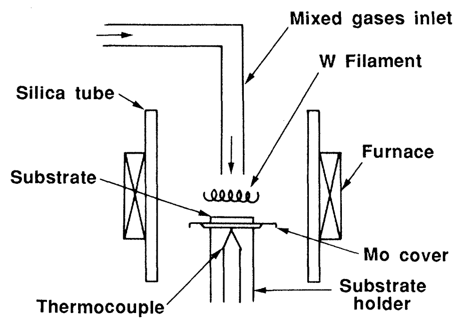
A second key characteristic of diamond is that the velocity of its current-carrying free electrons increases smoothly as the electric field that drives them grows, unlike many semiconductors in which the velocity reaches a maximum and then drops. In diamond, the electron velocity eventually reaches a value even higher than that of gallium arsenide, the current "king" of high-speed semiconductors. This feature combined with the ability of diamond to sustain a higher electric field than other materials before breaking down suggests the possibility of its use in high-power microwave and millimeter-wave electronics for telecommunications and electronic warfare applications. A group at North Carolina State University, including Jeffrey Glass and Robert Davis, is beginning to explore this opportunity.

Finally, diamond has enticing optical properties. Because pure diamond is transparent to photons having energies less than its large band gap, diamond is a candidate material for ultraviolet detectors. The strength and thermal conductivity of diamond combined with its transparency make it a potential window material for high-power lasers and radars in military systems. And, diamond could even be an ultraviolet laser.

If the hopes for diamond films are high, numerous practical obstacles remain to be overcome, including the difficulty of making large quantities of high-quality material economically. One of the attractions of chemical vapor deposition, notes J. Michael Pinneo of Crystallume, where researchers have successfully deposited polycrystalline diamond films, is that it is inherently scalable from a laboratory-sized operation to a production line, once the optimum growth conditions have been established. Moreover, large structures might be made of diamond "ceramics" sintered from smaller particles rather than deposited directly as thick layers.

Crystallume's operations are proprietary and the company has not released any details concerning its process. The only American group to submit results for publication so far is at Pennsylvania State University, where Andrzej Badzian, Barbara Simonton, Teresa Badzian, Russell Messier, Karl Spear, and Rustum Roy have deposited polycrystalline diamond films from a mixture of hydrogen and methane on silicon substrates with the aid of a microwave plasma. The first films were obtained last February. Penn State also sponsored a workshop in September with an eye toward signing up industrial affiliates whose financial support would help the group pursue diamond research.

Shortly after the Penn State success, Robert Markunas, R. A. Rudder, and their associates at the Research Triangle Institute in North Carolina succeeded with a somewhat different process. The group is also said to have made single-crystal films, which would be necessary for electronic applications, on inexpensive nondiamond substrates. All in all, sums up Messier at Penn State, diamond growth from the vapor has been demonstrated, but scientific understanding of the growth process needs to be accomplished.



Diamond grower. *Schematic diagram of thermal chemical vapor deposition apparatus used in Japan to deposit continuous films of diamond at rates up to 10 micrometers per hour.*

Interest in growing diamond from the vapor dates to at least 1911. An important advance came in 1958, when W. G. Eversole of Union Carbide patented a method for obtaining diamond films from the pyrolysis of methane. Unfortunately, substantial amounts of graphite were deposited along with the diamond, so that it was necessary to interrupt the growth periodically to etch away the graphite. The process was therefore impractically slow.

Success in preventing the formation of graphite is generally credited to a group headed by Boris Derjaguin at the Institute of Physical Chemistry in Moscow. In 1977, Derjaguin and D. V. Fedoseyev published an extensive account of the kinetics of the pyrolysis of hydrocarbons, in which they discussed the concept of a "solvent" that prevents the deposition of graphite but does not affect diamond. They suggested atomic hydrogen as the solvent and recommended several strategies for obtaining high concentrations of atomic hydrogen, which is not present in large quantities in thermal equilibrium. Eversole had used hydrogen gas as the etchant in his two-step process.

In 1981, B. V. Spitsyn, L. L. Bouilov, and Derjaguin reported the use of an electrical discharge to generate atomic hydrogen in the deposition zone of their reactor to grow epitaxial (single-crystal) diamond films on diamond substrates. With their method, the Soviet researchers could grow films at a rate of 1 micrometer per hour, about 1000 times the rate obtainable with a simple pyrolysis method. They also were able to deposit diamond crystallites (but not continuous films) on metal substrates. Published reports of further progress have been infrequent, although Penn State's Roy has visited Derjaguin's laboratory and was shown continuous films more than 1 millimeter thick on a polymer substrate.

Possibly because of the difficulty of characterizing diamond coatings with a high degree of assurance, American researchers were skeptical of the nonintuitive low-pressure process used by the Soviets and did not attempt to follow up these achievements. Japanese investigators were not so hesitant, and today almost 20 academic and industrial laboratories in Japan are working on diamond films. Much of the pioneering work has been done by Seiichiro Matsumoto and several co-workers at the National Institute for Research on Inorganic Materials in Ibaraki. Starting in 1982, these investigators demonstrated several methods for generating high concentrations of atomic hydrogen, thereby enhancing the effectiveness of the chemical vapor deposition process for the rapid growth of high-quality material.

It is the Japanese work that sparked interest in the United States. Roy, who helped spread the word, recalls a 1984 visit to the inorganic materials institute, "I saw a silicon substrate with thousands of little diamonds on it; that got my attention."

In their first publication, the Japanese researchers discussed the use of a tungsten filament heated to 2000°C to dissociate gaseous hydrogen just above a silicon, silica, or molybdenum substrate on which diamond was to be deposited. A mixture of methane and gaseous hydrogen flowed toward the substrate in a deposition chamber that was surrounded by a furnace. Although the process is not yet understood, carbon atoms from the pyrolyzed methane ended up on the heated substrate, where they built up diamond crystallites. Subsequently, the group reported on the use of microwave and radio-frequency plasmas to dissociate the hydrogen. Single-crystal films on diamond substrates have now been made, as have polycrystalline films on other types of substrates, by these techniques.

A publication last June by Yoichi Hirose and Yuki Terasawa of the Nippon Institute of Technology in Saitama suggests the current state of the nonproprietary art. These researchers used the tungsten filament method with silicon substrates but studied several gases of organic hydrocarbon molecules containing oxygen or nitrogen instead of restricting their attention to hydrocarbons. With acetone, for example, good quality polycrystalline films grew at a rate of 10 micrometers per hour. The investigators concluded that "this method may be promising for industrialization."

Opinion is divided over the question of how much further progress is dependent on solving the mechanism of the deposition process. The basic issue is the prevention of the formation of the double bonds between carbon atoms that are slightly favored energetically and that lead to the formation of graphite (the carbon atoms in diamond are linked entirely by single bonds). The presence of atomic hydrogen favors the breaking of double bonds and the formation of single bonds (sp^3 hybridized orbitals), which accounts for its solvent effect on graphite. The presence of the methyl radical with its sp^3 orbitals is also thought to be helpful, which effects the choice of starting material. Pinneo at Crystallume thinks, for example, that growth rates can be substantially enhanced if more efficient ways of generating the methyl radical are found. But the details of how all this fits together are not well understood.

Another growth method may also work better. There is some interest in a so-called remote plasma-enhanced chemical vapor deposition technique in which a molecular gas is dissociated in a location away from the substrate. The resulting monomers and an organic gas then flow through a heated region toward the substrate, where pyrolysis and deposition occur as before. Gerald Lucovsky and several colleagues at North Carolina State University and Markunas developed this method for the deposition of insulating materials, such as silicon nitride, on advanced semiconductor structures. It is said that the Research Triangle group used a variation of this method with plasma-excited helium to make its diamond films. That the method works without hydrogen suggests that it is the energy of the plasma-excited species rather than its chemical properties that facilitates diamond formation.

The development of techniques for the rapid manufacture of large quantities of diamond film is only one of the numerous tasks yet to be mastered before potential applications can be actualized. It is not certain, for example, how to bond diamond films to tools. Comparable issues arise in other applications. While the excitement over diamond may be merited by the potential of the material, so far it is only potential. ■ ARTHUR L. ROBINSON

ADDITIONAL READING

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Maleness Pinpointed on Y Chromosome

The sex-determining section of the Y chromosome is on the short arm—not where everyone thought it would be

No one really knows what makes a male a male or a female a female. But researchers thought they at least had a hint. Their hypothesis was that the mysterious H-Y antigen somehow determined maleness in mammals. Femaleness was determined by default; those who lack the H-Y antigen become females. Now, however, the H-Y antigen has fallen out of favor as new studies that use the sophisticated tools of molecular biology point to an entirely different chromosomal location for the sex-determining factor. The evidence was discussed on 9 to 10 October at a workshop sponsored by the National Institute of Child Health and Human Development.

There are practical as well as theoretical reasons for wanting to know how the two sexes exist. For instance, animal breeders want to establish the sex of embryos before transferring them to surrogate mothers. Reproductive specialists would like to understand the basis of sex determination because mutations or deletions of sex-determining chromosomal regions have been associated with human infertility.

Ernst Eichwald of the University of Utah, who first discovered the H-Y antigen in the 1950's, told the meeting participants that doctors call him virtually every month asking whether he does H-Y testing to establish the sex of babies born with ambiguous genitalia. Eichwald does not offer this service, and many researchers think that H-Y antigen testing would not resolve the question of sexual ambiguity anyway, since frequently what is wrong is an inappropriate amount of or response to sex hormones.

For decades, researchers have known that some sequence on the Y chromosome determines maleness, at least in mammals. In the 1950's, Eichwald serendipitously discovered the H-Y antigen when he tried to transplant the skin of male mice onto females of the same inbred strain. Ordinarily, mice of the same inbred strain accept skin transplants. But the female mice, Eichwald discovered, rejected the male skin, indicating that there is an antigen that is characteristic of males. He called it the H-Y antigen because it is a histocompatibility antigen and an antigen that seems unique to the Y chromosome. In fact, he suggested, it could actually be two separate antigens.

Years later, Ellen Goldberg of the University of New Mexico learned that the H-Y antigen, as defined by antisera rather than transplantation, is conserved in evolution and that it is present at the earliest stages of embryo development—in an eight-cell mouse embryo, for example. Finally, in 1975, Susumu Ohno of the City of Hope Research Institute in Duarte, California, proposed the H-Y hypothesis: The H-Y antigen is the diffusible substance that results in testes formation in mammals. It acts like a cell adhesion molecule for the formation of the testes cords.

A few years ago, however, Ann McLaren of the Medical Research Council in London reported some contrary findings. She found a mouse strain that had two X chromosomes yet was male because part of a Y chromosome was translocated onto one of the X chromosomes. These mice, however, do not make the H-Y antigen. McLaren concluded that the H-Y antigen does not determine testes formation but might instead have something to do with spermatogenesis because the mice do not produce sperm.

Michael McClure of the child health institute notes that some people still are trying to use the H-Y antigen to determine the sex of animal embryos. "Some say it works and some say it doesn't," he remarks. "But many people are nervous about using the H-Y antigen now." One difficulty, says David Page of the Whitehead Institute, is that the term H-Y antigen might convey different things to different people. Those, like Eichwald, McLaren, and himself, who define it as a transplantation antigen, are looking at a T-cell response. Those, like Goldberg and Ohno, who define it serologically, are looking at a B-cell response. "There is considerable debate about whether all these investigators are talking about the same thing," Page says.

Recently, Page brought molecular biology to the field. He began by searching for "cases in which the chromosomes and the gonads don't match or in which there is an abnormal Y chromosome." And he found