Diamond Films Sparkle As They Come to Market

High-fidelity tweeters, scratch-proof sunglasses, and fail-safe semiconductor devices are some of the potential applications

"DIAMONDS ARE A GIRL'S BEST FRIEND," sang Marilyn Monroe. Now, materials scientists are singing the same tune.

"It's the ultimate material," declares Jerome Cuomo, a materials researcher at IBM's T. J. Watson Research Center in Yorktown Heights, New York. "It is the hardest material known, it has the highest thermal conductivity at room temperature, it is totally inert, and it is an excellent insulator." Diamond is also transparent to visible light, infrared and ultraviolet radiation, and x-rays, and as a semiconductor it has several advantages over silicon for making electronic devices. What more could a materials scientist want?

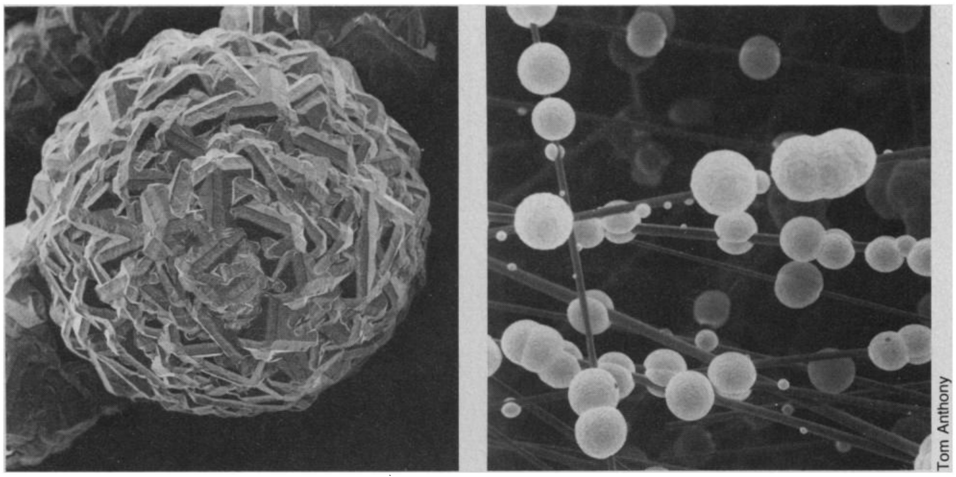
Just one thing: a practical, inexpensive way to make diamonds. And in the early 1980s, when Japanese scientists announced a way to make diamond films with a technique called chemical vapor deposition (CVD), it looked as if that last piece had fallen into place. The CVD method was not only more versatile than the existing high-pressure procedure for making artificial diamonds, but was expected to be less costly because it's simpler. Some enthusiasts predicted that CVD diamonds could eventually be made for as little as pennies a carat.

Now, half a decade later, products made with CVD diamonds are coming onto the market. And although the initial optimism about low prices has faded, enthusiasm over potential applications has, if anything, increased. The first products seem mundane—wear-resistant coatings for cutting tools and heat sinks to keep sensitive electronic components cool—but recent advances in processing are expected to lead to more interesting uses. Look for diamond films to show up on tweeters in stereo speakers, as windows in scientific instruments, as scratch-proof coating on sunglasses, and as masks for use in x-ray lithography.

The world market for diamonds made with the old high-pressure technique is now about $1 billion, most of it spent on abrasive grit and tool coatings, but that could be small change if the promise of CVD diamond technology is realized. A recent report by the National Research Council* concludes that "the ultimate economic impact of this technology may well outstrip that of high-temperature superconductors."

The attraction that diamonds hold for materials scientists is no mere infatuation—the affair goes back more than 35 years. In 1954, scientists at General Electric's Research & Development Center in Schenectady, New York, first showed that they could produce synthetic diamond by applying high temperature and pressure to graphite. Both graphite and diamond are pure carbon, but their atoms are arranged very differently. In graphite, the atoms line up in layers that are only weakly linked to one another; because the layers can easily slide past one another, graphite is soft and makes a good lubricant. Diamond, on the other hand, has a rigid three-dimensional structure that gives it hardness and strength.

In the current commercial method, which is a variation of the original GE discovery, graphite is heated in the presence of a metal catalyst, such as iron or nickel, to around 1500°C at a pressure of 50,000 to 65,000 atmospheres. Under these conditions, the carbon dissolves in the metal and begins to form diamond crystals along the metal. The result after several hours is a sheet of diamond on the metal substrate that can be a millimeter or more thick. Microscopic examination reveals that the diamond film consists of countless tiny diamonds, each only a few micrometers across.



Not your usual marquise cut. *CVD diamonds can take a variety of shapes, including a polycrystalline sphere (left) or tiny beads on silicon carbide fibers.*

But this method has a variety of disadvantages. The high pressures required limit the size of the growth chambers, for instance, so that the largest diamond sheets GE can make are only 2 to 3 inches across, says Tom Anthony, a physicist at GE's Schenectady lab. Using a metal catalyst creates metal inclusions and small voids in the diamond films that limit how smooth it can be, he adds, and the sheets of diamond inevitably consist of numerous tiny grains oriented at different angles. While this polycrystalline structure is good for tool coatings, Anthony notes, it is useless for such applications as making semiconductor devices.

So researchers began looking for a low-pressure method of synthesizing diamonds even before the GE discovery in 1954, but this has proved to be a much harder problem. In the 1960s, Boris Deryagin in the Soviet Union and John Angus, a chemical engineer at Case Western Reserve University in Cleveland, independently showed that diamonds could be formed from a high-temperature vapor of hydrocarbon gases, but both were stymied by the fact that after a short time graphite inevitably began to grow in place of diamond. In the late 1970s, Deryagin claimed to have surmounted the problem, but he released no details.

Finally, in the early 1980s, researchers from the National Institute for Research into Inorganic Materials in Japan learned how to grow pure diamond films at normal pressures fast enough to be of commercial value. Their process starts with a mixture of hydrogen gas and methane or other hydrocarbon, such as acetylene, inside a vacuum system. Heating the mixture to about 2200°C with microwaves or a hot filament breaks up both the hydrogen and hydrocarbon gas molecules, and carbon atoms begin

*"Status and applications of diamond and diamond-like materials: an emerging technology" (National Academy Press, Washington, 1990).

to condense on a plate of silicon or other material that is put in the chamber. A diamond film made of countless tiny diamond grains slowly builds up on this substrate.

Over the past 5 years, researchers in Japan and the United States have developed several related CVD methods, but having enough atomic hydrogen seems to be the key to all of them. The best results come from mixtures that contain about 99% hydrogen to 1% methane. In some way that is still not completely understood, the hydrogen prevents the carbon atoms from forming graphite and instead pushes the system toward a diamond structure.

The CVD diamonds have similar properties to synthetic diamonds made with high pressure, GE's Anthony says, but they have advantages over the high-pressure diamonds for some uses. "For one thing, we can make much larger sheets with CVD," he says. Instead of pieces that are 2 to 3 inches in diameter, GE has made sheets as large as 12 inches long by 1½ inches wide. The longer pieces of diamond are better, for instance, for certain cutting tools where the instrument must be several inches long and joining two diamond films is not practical. And the CVD diamonds are smoother than high-pressure diamonds, partly because with no metal catalyst there are no metal-caused defects in the diamonds; this extra smoothness makes them better for finishing applications, where a polished surface is important.

One of the potentially most valuable properties of the CVD diamonds is their high thermal conductivity. Pure single diamonds, with a conductivity at room temperature of about 21 watts per centimeter per degree centigrade, conduct heat better than any known material—five times better than copper, for example. The defects in high-pressure diamond films lower their conductivity to just slightly better than copper's, but CVD diamond registers twice that—from 8 to 12 watts per centimeter per degree centigrade. This makes CVD diamond a good candidate for making heat sinks to carry heat away from sensitive electronic components. One application might be in fiber optic systems where crowded laser diodes generate a lot of heat in a small space.

A number of obstacles still face CVD diamond films, however. For one, the expected cost advantage over high-pressure diamonds hasn't materialized. CVD diamonds cost well over $100 a carat to produce—much more than high-pressure diamonds, which sell for slightly over $1 a carat. Part of the difference in price is due to the fact that researchers have had 35 years to bring down the cost of high-pressure diamonds, Anthony notes, but some of it may be unavoidable. Angus at Case Western estimates that just the cost of energy to break up molecular hydrogen into atomic hydrogen adds between $1 and $100 a carat to the total price tag.

A variety of materials problems must also be overcome if CVD diamond is to live up to its promise—the diamonds must adhere better to cutting tools, for instance, and the deposition temperature will have to be lowered so that such substrates as plastic can be used. But for many researchers, one issue looms over the others, both for its scientific interest and its potential payoff.

"We need a breakthrough in hetero-epitaxial growth," says Andrzej Badzian at Pennsylvania State University in University Park. Epitaxial growth refers to producing a crystal whose atoms are lined up in the same direction as the atoms on the substrate, instead of having numerous individual grains oriented in different directions. "Hetero-epitaxy" means that the crystal and the substrate are two different substances.

Today's entire electronics industry is based on being able to grow silicon and other semiconductors epitaxially. With such growth, researchers can control the properties of the semiconductors completely, adding impurities or other defects only when desired. Diamonds would make excellent specialty electronics components—their heat resistance would be valuable in automobile engines, for example, and their radiation resistance would make them ideal for space applications—but first researchers must devise a practical way of growing diamond films epitaxially.

There's reason to hope that will be possible. Researchers in the United States and Japan have grown diamond films epitaxially on diamond substrates. And in just the past few months, several groups have shown they can grow diamond films on boron nitride, which has a crystalline structure almost identical to diamond. But neither substrate is suitable for widespread application, since there are few large single crystals of diamonds and none at all of boron nitride.

Instead, it would be best to be able to grow epitaxial diamond films on something cheap and plentiful, such as silicon, but no one has done this yet. "There is some doubt that it will ever work," Anthony says. "You need a process to grow diamond from a carbon-metal solution—the best crystals are always grown from a liquid." But the CVD method doesn't work above 1000°C, which is only about one-fourth of the melting point of carbon. Above that temperature, the hydrogen atoms leave the surface of the film and the carbon atoms arrange themselves as graphite instead of diamond.

But the promise of CVD diamond films is so great that materials scientists are not going to give up easily. They, like Marilyn Monroe, know a good friend when they see one. ■ ROBERT POOL

Ultra Diamond from Pure Carbon-12

Isotopically pure diamond has startling material properties that are even more extreme than those of normal diamond, according to work done by researchers at General Electric Research & Development Center in Schenectady, New York, and Wayne State University in Detroit. The results, which are due to appear in the 13 July *Physical Review*, were described briefly in *Physical Review Abstracts*.

Natural diamonds contain about 99% carbon-12 and 1% carbon-13, but the researchers were able to make synthetic diamonds that were 99.9% carbon-12 by using starting materials that contained almost no carbon-13. The resulting 1-carat single crystal showed some remarkable properties. It conducted heat 50% better at room temperature than normal diamond, and its "laser damage threshold went up by an order of magnitude," says GE's Tom Anthony. And the changes in a diamond's properties should become even more pronounced as a diamond becomes increasingly more pure. The researchers' calculations indicate that a 100% carbon-12 diamond could have a thermal conductivity of up to 48 watts per centimeter per degree centigrade, Anthony says—more than double that of normal diamond.

The researchers also expect that diamonds made with pure carbon-13 will be harder than other diamonds, Anthony said, but they have not yet done those experiments.

Although isotopically pure carbon is much more expensive than normal carbon, the price is very volume-sensitive, Anthony says, and should come down quickly if companies begin to order it in large quantities. Eventually, he guessed, synthetic carbon-12 diamond could be sold for only a couple of dollars more per carat than normal high-pressure diamonds. That would make them a bargain for such applications as heat sinks, whose usefulness is directly related to their thermal conductivity.

■ R.P.