Diamond Fever

New ways of coating just about anything with diamond may spawn a sparkling new industry

By IVAN AMATO

In late 1955, Robert H. Wentorf Jr. achieved something close to alchemy. He bought a jar of peanut butter at a local food co-op, brought it into his lab, and then turned a glob of the bread-spread into a few tiny diamonds.

At about the same time, Wentorf and three co-workers at the General Electric Research and Development Center in Schenectady, N.Y., also transformed roofing pitch, coal, wood and other carbon-containing materials into diamond grains — some as fine as flour and others as large as sesame seeds. These spectacular experiments showed that almost anything could serve as a diamond-in-the-rough, as long as it contained enough carbon atoms. Wentorf recalls receiving anxious letters from gem speculators who envisioned the value of their natural-diamond investments deflating into peanuts.

The trick to making diamonds from peanut butter, or, more reasonably, from graphite — diamond's all-carbon mineralogic sister — initially lay in recreating the high temperatures and gargantuan pressures that produce diamond within the earth. Since its commercialization by GE in 1958, this rugged and expensive high-pressure process for synthesizing diamond has become the basis of a half-billion-dollar per year abrasive-grit industry whose end-products include diamond-coated cutting tools for drilling, mining, quarrying, precisely machining automotive parts and producing dies used by wire makers.

Yet even before the diamonds from GE's high-pressure technique infiltrated a number of industries, some researchers had their eyes on growing diamond with cheaper, low-pressure processes known as chemical vapor deposition (CVD). In these techniques, carbon-containing gases like methane decompose under an intense heat source within a chamber maintained at pressures ranging from 1 atmosphere to less than a thousandth as much. The carbon atoms then deposit onto surfaces of materials also placed within the vacuum chamber but held at lower temperatures.

Though this less brutish approach to growing synthetic diamond costs far less than GE's original process — which involves pressures at least 50,000 times those used in CVD — that's not its primary advantage. CVD now offers the prospect of coating far more materials with a substance that holds more world records than any other in the materials game.

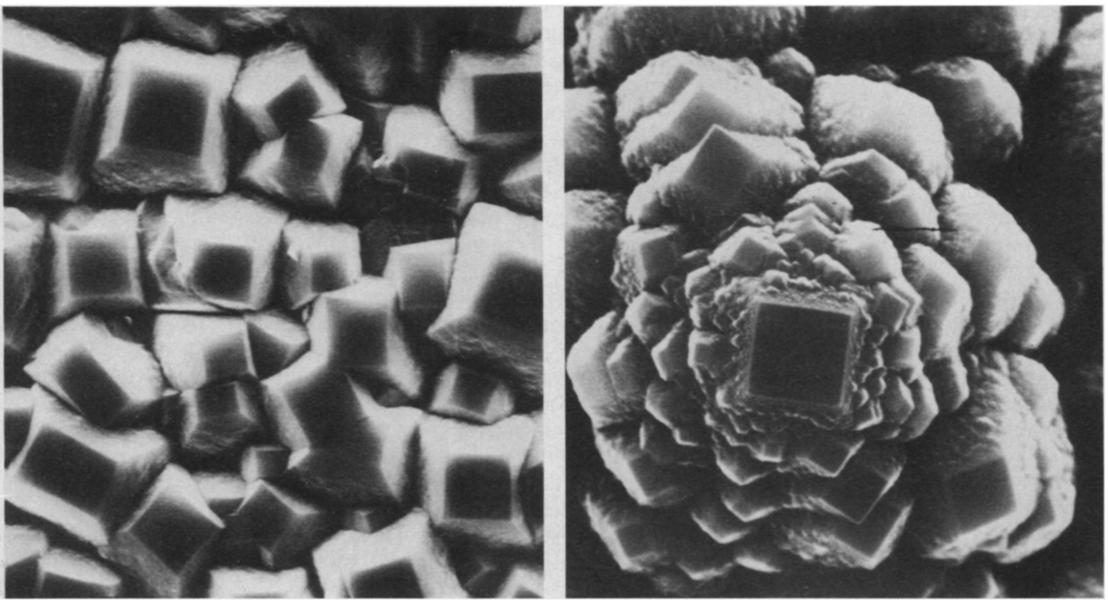
In work reminiscent of Wentorf's high-pressure peanut-butter alchemy, researchers using these and related new techniques reportedly have turned out diamond films from whiskey, although swamp gas — also known as methane — remains their carbon source of choice.

"Diamonds are going to be everywhere," predicts John C. Angus, a chemical engineer at Case Western Reserve University in Cleveland and a leader in the field since the 1960s. "They'll be in pots and pans, on drill bits and razor blades, in copying machines and on hard discs."

Materials scientist Rustum Roy, of Pennsylvania State University in State College, concurs. Low-pressure diamond synthesis "is a much wider discovery than high-pressure techniques, in that you can coat virtually any material with diamond," he says. That means engineers can add diamond's superlative properties — including scratch resistance and the ability to draw away heat — to materials that may lack these traits.

Despite publicized claims of lab-made diamonds in the 19th century, the first commercially promising account of synthetic diamond made news in July 1955, when Wentorf and his fellow diamond-makers published a groundbreaking paper in NATURE. They described a process for turning graphite — the sooty, all-carbon stuff of pencil "leads" — into the all-carbon crystal symbolic of perfection and purity in nature and of elegance and love in matters more exclusively human. The feat so impressed government officials that they temporarily imposed a gag order on the project.

The GE process required hell-on-earth conditions: 1,400°C temperatures and



Butler et. al

Researchers have found that they can grow diamond on surfaces held in the flames of an oxy-acetylene torch. As these scanning electron micrographs show, the resulting diamond can vary from carnation-like shapes (right) to more uniform cubic ones (left).

GE

Chemical vapor deposition (CVD) techniques yield thin polycrystalline sheets of diamond, which looks like dirty sand when crushed up. Its uses include superhard abrasive coatings and a starting material for growing gem-sized diamonds like the one shown on the cover.

pressures equivalent to 50,000 or more stacked atmospheres (roughly 1 million pounds per square inch). That's an environment the GE scientists knew would be comfortable for diamond and intolerable for graphite. The squeeze of the presses first used to synthesize diamond proved so severe that the team had to design especially rugged vessels that could withstand the stress.

At more familiar temperatures and pressures, carbon generally prefers to take on graphite's structure: hexagonally arranged and covalently linked carbon atoms that form stacked layers – each layer resembling a sheet of molecule-scale chicken wire.

But graphite simply can't hold together under the extreme conditions of GE's high-pressure process. In the presence of a metal catalyst and a tiny seed diamond held at submelting temperatures, graphite's carbon atoms disengage from each other, migrate through the now-melted metal to the seed, and reconfigure into a sparkling new arrangement. Instead of stacked chicken wire, diamond's carbon atoms covalently bond into a super-uniform tetrahedral pattern.

The early GE process didn't quite duplicate nature's own top-line carbon crystal. "These weren't what you ordinarily think of as diamonds," Wentorf recalls. Though the crystals were superhard and sparkling, impurities and defects made them dark and opaque like black sand. The peanut-butter diamond grains had a greenish tinge due to nitrogen atoms formerly locked within protein molecules.

GE subsequently refined its process to make beautiful, clear diamond grains ranging from microns to millimeters in size. In 1970, its scientists even learned how to make large gem-quality diamonds by using diamond grit instead of graphite as a starting material. But these were so expensive to produce that jewelry stores selling natural diamonds could easily underprice them.

That still holds, but CVD's milder and easier-to-maintain conditions appear to have brought diamond to the brink of new industrial and economic stardom.

"Recent success in deposition of diamond and diamond-like coatings on a variety of substrates at practical growth rates is one of the most important technological developments in the past decade," concludes a technology-assessment report released in June by the National Research Council (NRC) in Washington, D.C. "Indeed, the ultimate economic impact of this technology may well outstrip that of high-temperature superconductors," the report asserts.

The world's synthetic diamond production – predominantly by companies in the United States, South Africa, Japan and Soviet Union – totals more than 300 million carats yearly. This translates into more than 60 tons of abrasive diamond grit, the NRC report says, and by some accounts, a $500 million-per-year industrial market. (Natural rough-diamond production weighs in at about 19 tons a year.)

But that dollar figure will rise dramatically if predictions by some material scientists and business analysts prove correct. Market researchers at Gorham (Maine) Advanced Materials Institute expect a low-pressure synthetic diamond industry to reach sales of $1 billion annually by century's end, and a Japanese firm multiplies this estimate 16-fold.

These predictions rest on the growing finesse and reliability with which researchers can deposit films of diamond and diamond-like materials onto surfaces as diverse as paper and silicon.

Since diamond is the hardest material known, transparent diamond coatings would perpetually protect eyeglasses, wristwatch crystals and other surfaces. Diamond coating a computer's hard disc, which spins at high speeds, would protect it from the occasional crash of the read-head as it hovers barely overhead.

Because it absorbs almost no light, diamond offers ideal protection for optical fibers and space-based radiation sensors. But here, the less perfect diamond-like materials might be preferable, since they deposit as a smooth layer rather than as a multifaceted, light-scattering landscape. For the same reason, engineers eye diamond-like coats as lifelong lubrication for such things as ball bearings.

Diamond carries heat away at rates second to none, almost never reacts with anything – and then only at high temperatures – and serves as an excellent electrical insulator. So diamond coatings and heat sinks could enable engineers to make faster electronic chips that operate well at high temperatures. Some scientists even envision semiconducting forms of diamond that might supersede silicon as the materials basis for a faster generation of electronic chips.

"Diamond would be the best semiconductor if you could make it work," notes Roy. By growing synthetic diamond in the presence of boron, several laboratories already have made crystals that behave like semiconductors. But these crystals contain too many defects, and they cannot yet be reliably integrated with other materials used in electronic components.

Indeed, no one seems at a loss for ways to use diamond coatings. Even singer Paul Simon, in "Diamonds on the Soles of Her Shoes," suggests a possible – though perhaps unlikely – wear-limiting application.

The new wave of interest in synthetic diamond as an engineering material stems from diamond-making techniques so simple and mild that, until the mid-1980s, most materials scientists didn't believe they would work.

CVD, developed even before the GE scientists announced their breakthrough in the mid-1950s, is now a family of techniques ushering in a new era of low-pressure synthetic diamond production. Though these techniques can involve temperatures several times greater than those of high-pressure diamond-making processes, they also feature easily achieved pressures, most often in the thousandth-of-an-atmosphere range.

As early as 1952, William G. Eversole of Union Carbide Corp. reported he had created CVD-grown diamond, but at hopelessly sluggish rates. He heated small diamonds to at least 600°C in a partial vacuum and allowed methane to decompose, coating these hot rocks with new layers of diamond.

Four years later, the Soviets launched a sustained effort in low-pressure diamond making. Boris Deryagin, who won fame for this venture, also won eventual notoriety over the polywater drama – a classic example of mistaken science. (In the early 1970s, Deryagin and a few other researchers temporarily believed they had discovered polymeric forms of water that not only held promise as a cheap and abundant material even for furniture, but also posed a global environmental threat since the liquid oceans might convert into polymeric water.)

In the 1960s, researchers in the U.S. and the Soviet Union began empirically discovering conditions conducive to diamond growth at low pressures. But their crystals grew very slowly, typically at 0.01 micron per hour. It would take more than 11 years, at that rate, to lay down a diamond layer as thick as a worn dime.

In 1976, Deryagin's group announced it had grown diamond films at low pressure – and tantalizingly fast, at up to 1 micron an hour. Because the Soviets kept their processing conditions secret, however, most researchers paid little attention, Angus notes. He suspects Deryagin's involvement with the polywater fiasco added to people's skepticism. But Roy points out that widespread preconceptions about the need for high pressures in diamond synthesis also slowed acceptance of the Soviets' claim by most materials scientists.

However, some did take the Soviet report seriously. "The Japanese got real busy," notes John D. Venables, who chaired the committee authoring the NRC report. Beginning in 1982, he notes, a series of "remarkable papers" by researchers at Japan's National Institute for Research in Inorganic Materials (NIRIM) convincingly demonstrated micron-per-hour, low-pressure growth of diamond films and outlined the conditions required to achieve such rates.

Researchers elsewhere quickly reproduced the Japanese results. "The current worldwide interest in the new diamond technology can be directly traced to the NIRIM effort," Angus says. In a project reminiscent of Wentorf's peanut-butter diamonds, one Japanese researcher even reportedly made CVD diamonds from sake, the Japanese rice wine.

And the Japanese maintain the pole position for commercializing the technology, remarks Roy, who co-heads Penn State's diamond-research effort. After touring NIRIM's diamond-making laboratories in 1984, he convinced the U.S. Office of Naval Research to begin supporting basic CVD diamond research. Funding this year by federal agencies and industry falls between $10 million and $15 million dollars, Roy says. In comparison, he points out, $220 million a year now goes into research on high-temperature superconductors, a technology he believes shows less industrial and economic promise than CVD diamond.

The detailed physical and chemical mechanisms underlying the CVD process remain mysterious. But that hasn't discouraged researchers from discovering reliable conditions the hard way: trial and error, eased by an admixture of intuition and theoretical insights.

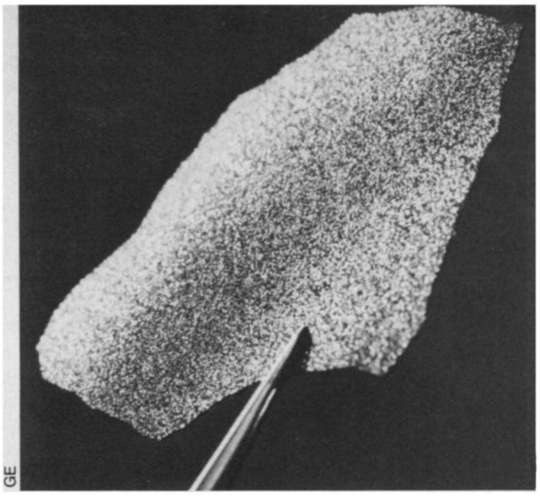
"You really only have to know a few concepts about how crystals are put together and then make some intuitive guesses," notes Robert C. DeVries, a retired GE diamond-research veteran who worked on the NRC report. "Most of these advances are not made by theoreticians, they're made by intuitive materials scientists playing around in a sandbox."

Carbon-containing gases represent CVD diamond-making's "sand." A vacuum chamber serves as the "box." Inside this box, a localized source of intense heat – a tungsten filament or microwave-generated plasma, for example – decomposes a carbon source, usually a small dose of methane gas carried in a steady flow of hydrogen gas. Carbon fragments from the methane then deposit as diamond films on target surfaces also in the chamber but kept in the 600°C to 900°C range.

By regulating the hydrogen-hydrocarbon ratio, the pressure inside the chamber and the temperature of the target materials, researchers have succeeded in growing diamond films at rates as fast as 100 microns per hour onto relatively large and intricate target areas. Thousands of tiny diamonds nucleate on the deposition surface and then grow together into a continuous polycrystalline film.

Researchers now routinely produce diamond films or diamond-like coatings. The latter lack true diamond's broad-scale crystalline order, either because they contain lattice-disrupting hydrogen atoms or because their carbon atoms bond in more random ways. Though less perfect than true-diamond films, diamond-like coatings can deposit on materials at temperatures approaching room temperature and form smoother surfaces.

The first commercial CVD products have already hit the market. Audiophiles with fat wallets can buy tweeters with diamond diaphragms made by Sumitomo for Sony. Seiko plans to market watches with scratch-proof diamond-coated crystals. Crystallume in Menlo Park, Calif., sells diamond-coated windows for infrared-scanning systems, important in analytical instruments and missile guidance. IBM scientists use a CVD process to fashion light-filtering masks made of patterned diamond films, which they hope to use for making smaller electronic components. Last month, GE announced it was combining CVD diamond synthesis with its high-pressure technique to make synthetic diamond that exceeds natural diamond's ability to dissipate heat and withstand laser irradiation without damage (SN: 7/21/90, p.37).



GE

Thousands of tiny diamond crystals grew together to form this free-standing diamond film created through the low-pressure CVD technique.

The seemingly alchemical dream of turning baser materials such as peanut butter and sake into diamond now has been realized over and over again. Two years ago, a Japanese researcher even reported being able to deposit diamond films onto cooled metal surfaces held in the flame of an oxyacetylene torch – a $250 welding tool. That work has been repeated by James E. Butler at the Naval Research Laboratory in Washington, D.C. He's betting that the oxyacetylene route will become a big player in the coming era of CVD diamonds.

Whatever the exact CVD technique, materials scientists generally agree that diamond films made with the low-pressure techniques seem poised to become a mega-scale industry.

But swelling to larger industrial scales won't be easy, especially for the U.S research community, the NRC report concludes. That's why the report recommends that theoreticians, chemists, optical scientists, electrical engineers and materials scientists pool their talents for getting small-scale laboratory technology up to industrial speeds. It calls for expanding funding to "turn this emerging technology into a national pivotal technology." Since such a scaling up requires production of films with predictable and reproducible properties, the report also recommends a coordinated effort to understand fundamental physical and chemical mechanisms underlying diamond and diamond-like film growth.

For early diamond makers such as Wentorf and Angus, the resurgence of interest in synthetic-diamond research feels like a pat on the back. "But luckily, no one has ever asked us to make peanuts out of diamond," Wentorf says. "That would be much more difficult."

And bad business, no doubt. ☐