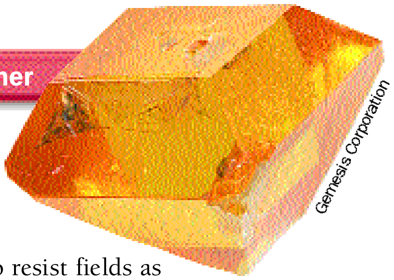
NEWS

by Eric J. Lerner


Gemesis Corporation

Industrial Diamonds Gather Strength

Superlatives stick to diamonds, if nothing else does. Diamonds are the hardest, most thermally conductive materials known, their atoms more densely packed than in any other substance. They can be excellent insulators or good conductors, and they are transparent to wide swaths of the electromagnetic spectrum, from ultraviolet (UV) to microwaves. In gem form, they are also among the most costly of materials, their ancient mystique and value enhanced in recent decades by catchy slogans and massive advertising campaigns.

But in the past few years, that mystique has started to break down as the quality of manufactured diamonds has increased and allowed industry to harness the material's remarkable properties (Figure 1). Perhaps most dramatically, small but growing numbers of manufactured gem-quality diamonds have begun to enter the market in the past year to challenge the far-flung DeBeers organization, which held a near monopoly on natural gem-diamond sales. More important for industry, advances in chemical-vapor-deposition (CVD) diamond films are opening up new applications in electronics, pollution control, and energy technology.

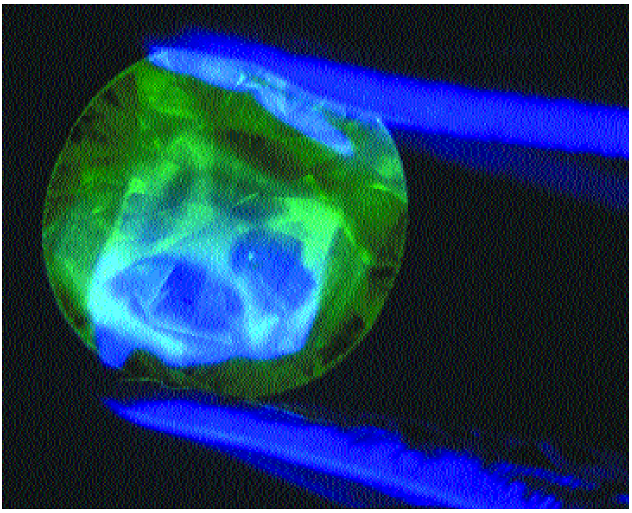

Gemological Institute of America/Photo by Nicholas DelRe

Figure 1. When exposed to short-wave ultraviolet radiation, this diamond shows a fluorescence pattern typical of synthetic diamonds—a square with extensions from the four corners.

Extreme properties

The key to diamond's extreme properties lies in the closeness of its atomic bonds. In diamond, each carbon atom is only 0.15 nm from each of its four closest neighbors. As a result, at all but the highest pressures, diamond has the highest atomic density—number of atoms per unit volume—of any known substance. (Strictly speaking, isotopically pure carbon-13 diamond holds this title because it is slightly more densely packed than diamond with a natural isotope mix.) And because diamond's bonds are so short, they are extremely strong, leading to its hardness and chemical inertness.

The strength of the bonds, combined with the relative lightness of the carbon atoms, is responsible for diamond's thermal properties. Because vibrations can travel extremely quickly through the lattice, diamond has the highest thermal conductivity of any substance at room temperature—six times that of copper. At the same time, the strength of the bonds resists disruption, giving diamond the highest melting point—more than 4,200 K, some 500 K higher than that of tungsten.

Strong bonds mean not only that the carbon atoms are bound tightly to each other, but also that their electrons are bound tightly, leading to a large bandgap of 5.5 eV. That is, it requires that much energy to knock an electron into the conduction band. In turn, this means that photons with an energy of less than 5.5 eV cannot dislodge electrons, making diamond transparent to radiation from 225-nm wavelength in the UV to deep in the microwave region (except for a narrow absorption band in the infrared). Diamond's refractive index of 2.42, among the highest known, also results from its large number of atoms per unit volume and accounts for diamond's beauty as a gemstone.

In addition, diamond's high bandgap makes it a first-class insulator, with an ability to resist fields as strong as 10 MV/cm before breaking down, a far better performance than common insulators. Yet when doped with boron, or when exposed to radiation more energetic than 5.5 eV, diamond can conduct electricity, although not as well as a metal. This property makes it into a semiconductor—one with an unusual, wide bandgap.

High pressure

The first property of diamond exploited by industry was its hardness, and for decades diamond abrasives have been vital to cutting tough metals. As a result, when World War II threatened the diamond supply to the United States, the government started a secret project to produce diamonds industrially. However, attempts to duplicate the enormous pressures and high temperatures that form natural diamonds deep within Earth failed until the mid-1950s, when teams at Sweden's ASEA and at General Electric (GE) dissolved carbon in a metal and precipitated out diamond crystals. GE scientists used a 1,000-ton press to generate a pressure of 50 tons/cm^2 and an electric current to heat the solution to 1,400 °C.

The crystals produced initially were less than 1 mm across, which made them suitable for diamond grit. In the 1970s, researchers found a modified technique that could grow large, gem-quality crystals. By placing a heating unit at one end of the pressure chamber and diamond seed crystals at the other end, experimenters could dissolve graphite or diamond grit into a metal at the hot end and precipitate it out on the seeds at the other as diamonds as large as several carats (1 carat = 200 mg).

However, given the slow growth of the crystals and the expense of the huge presses, production of gem-quality diamonds was not economical. Nor did General Electric actively pursue the cost reductions needed to produce synthetic gems. In part, the company may have wanted to avoid another bruising battle with DeBeers, which had fought GE over the diamond-grit market before agreeing to buy a license for the technology from GE.

Soviet researchers, however, picked up the challenge and in secret defense work developed much smaller presses that could deliver the same pressure for far less cost. The GE presses delivered pressure from either two or four directions. The Soviet presses, no larger than washing machines, had a spherical geometry that evenly distributed the pressure. In post-Soviet Russia, these efforts became public, and by 1995, several Russian laboratories were trying to reliably and economically produce gem-quality diamonds (Figure 2).

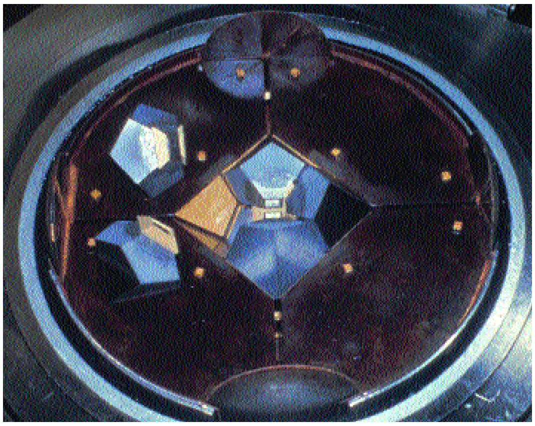

Gemological Institute of America/Photo by Maha Tannous

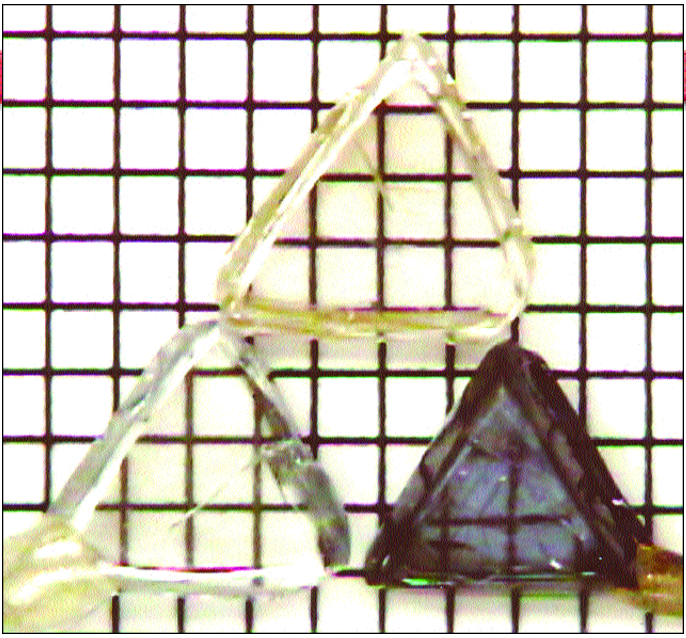
Figure 2. Sample chamber of a BARS apparatus in Novosibirsk, typical of the split-sphere presses commonly used to manufacture Russian synthetic diamonds.

Process control is the key to making gem diamonds. The temperature and pressure of the process must be carefully controlled to prevent metal from entering the diamond and creating metallic inclusions.

In 1996, an American entrepreneur, retired U.S. Army general Carter Clarke, got involved. "A scientist in St. Petersburg told me about the diamond-making and, of course, I was interested," he recalls. He contracted with University of Florida scientists led by Reza Abbaschian to work with the Russian team to develop the essential process-control systems. After much work, the combined American–Russian team learned how to control the process to eliminate the metal inclusions—an important achievement because they could be seen under a standard gem microscope, which hurt the value of any synthetic gemstone.

To reduce the color, the researchers used aluminum as a nitrogen "getter," which attracted much, but not all, of the nitrogen. The result was a golden yellow diamond, virtually identical in appearance to relatively rare, and thus highly valued, natural yellow diamonds. Starting last year, Clarke's company, Gemesis (Longboat Key, FL), began small-scale commercial diamond production. "We are producing a diamond every four days with each of 24 machines, but we are building more machines and ultimately hope to have 700 in our new facility," says Clarke.

Gemesis is working on developing a colorless diamond as well, but Clarke admits that the problem is a tough one. "The nitrogen not only colors the stones, it helps



Chemical Engineering Department, Case Western Reserve University

Figure 3. Natural diamonds on a 1-mm grid (top) have been thin-coated with boron-doped p-type-semiconductor synthetic diamond by chemical vapor deposition (left) and thick-coated (right) for use as electrodes in electrochemistry.

the crystallization process to go faster. So, at the moment, the less nitrogen, the slower the growth,” he explains.

Meanwhile, Gemesis is selling rough yellow diamonds, up to 3 carats in weight, to diamond cutters who produce finished stones weighing up to 1.3 carats (Figure 4). The gems—labeled as lab-grown, synthetic, or cultured diamonds—retail for about $3,000 a carat, about half the price of comparable mined yellow diamonds.

“They are really very nice gem-quality stones,” comments Thomas Moses, vice president for identification of the Gemological Institute of America (GIA). Consequently, the diamond industry is scrambling to decide what to do about the new challenge to its market, which also includes production from Russian laboratories. The main response of industry and the GIA has been to develop ways to distinguish natural from synthetic diamonds. One purpose is to prevent synthetic diamonds from being deceptively sold as natural gems, which remain higher-priced. Of course, such tests can also be used to convince consumers of ways in which natural diamonds are “superior” to synthetic and, thus, deserving of premium prices.

Information for jewelry dealers from the GIA still emphasizes the detection of metallic inclusions, which can be seen with ordinary jewelers’ microscopes and pointed out to consumers. But the latest synthetic diamonds no longer have such inclusions. More sophisticated tests, developed by De Beers and the GIA, include exposing the diamonds to short-wavelength UV radiation and observing the phosphorescent colors. Synthetic diamonds fluoresce more strongly than natural stones. In addition, the mix of cubic and octahedral crystallization patterns in synthetic diamonds contrasts in fluorescence tests with the octahedral patterns of mined diamonds.

Several Russian laboratories are experimenting with methods to further reduce the differences between natural and laboratory-grown diamonds, including trying to grow pure octahedral-symmetry crystals. But Gemesis’s Clarke is unconcerned about subtle differences that can be observed only with specialized equipment. “We don’t think that consumers are going to be impressed with these tests. We intend to brand our diamonds clearly with ion beams, so there is no question of someone presenting them as natural. Our surveys indicate that women will choose a larger diamond for the same price over a smaller one, if they both are the same quality, and that favors us.”

Some retailers selling Gemesis diamonds have gone further and marketed them as better than natural diamonds, pointing out, accurately, that synthetic diamonds, with fewer flaws than mined diamonds, tend to be harder and less brittle. (Whether jewel buyers are truly worried about chipping or scratching their diamonds is another question.)

What impact manufactured gem diamonds will have on the mined-diamond market once hundreds of thousands of carats a year are produced is still uncertain. If laboratory-grown diamonds are seen as closely equivalent to natural diamonds, the price of mined diamonds may start to fall. “But that did not happen with rubies, emeralds, or sapphires,” points out Moses. “Synthesized rubies are as beautiful as mined ones, but they bring prices only one-tenth as high and have had no real impact on the natural ruby market. People still want the rarity of the natural rubies. Once the novelty of manufactured diamonds wears off, that fall-off in price could happen to them, too.” However, whether consumers consider the more-common diamonds in the same way they do rubies will only become clear in the next few years.

Low pressure

Although high-pressure processes produce large gem diamonds, low-pressure techniques yield diamond films with a wide range of applications. In CVD, a mixture of methane and hydrogen at about 0.05 atm is heated and ionized by microwaves. The carbon ions begin to deposit as a film on a substrate, frequently silicon wafers seeded with diamond dust or other nucleation materials. The individual crystals formed are tiny, less than 100 mm across, but CVD diamond films made up of the crystals can be grown up to 10 cm across and 1 mm in thickness.

Scientists do not fully understand the process by which diamonds form at low pressure and moderate temperature (800 °C), but it is driven by surface chemistry interactions that first bind hydrocarbons to the growing diamonds and then expel the hydrogen atoms. CVD techniques are progressing rapidly as researchers improve film quality and increase the rate of growth. For example, recent work at Tsinghua University (Beijing) has demonstrated that using carbon nanotubes instead of diamond microparticles as nucleation sites could produce higher-quality films.

Other than its long-time use as a hard coating for machine tools, perhaps the most widespread use of CVD diamond film is for heat conductors in high-performance microcircuits. Such circuits produce a high level of heat that must be rapidly conducted away

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Figure 4. The 3-carat rough diamond shown at the top of page 8 can be produced synthetically in four days and then cut and polished to a 1.3-carat gemstone like the one shown here.

to cooling fluids or gases. But with smaller and smaller circuits, copper no longer has the thermal conductivity needed to do the job, which CVD diamonds, with sixfold higher conductivity, can.

On a more specialized level, windows made from CVD diamond have found application in short-wave UV, infrared, and high-power microwave sources because of diamond's transparency across a wide band of the spectrum. Another research application is for radiation detectors. X-rays and gamma rays can bounce electrons into the diamond conduction band, which allows collection of the electrons as a measure of radiation intensity. Diamonds are far more resistant to radiation damage than any other detector materials, so they are suitable for high-energy flux detectors in particle-physics experiments.

Other uses

One of the most intensive areas of research is in the use of diamonds as coatings for electrodes (Figure 3). Diamond doped with boron is a good enough conductor that a thin film covering an electrode has little resistance but conveys great benefits.

On the surface of diamond, water is extremely stable, so high potentials that would break water apart at graphite electrodes do not do so with diamond-coated electrodes. Such high potentials are useful for detecting dissolved compounds, such as pollutants, which reveal their presence during electrolysis. High potentials can also be used to destroy pollutants. Organic compounds can be oxidized at diamond electrodes to carbon dioxide, and these electrodes withstand weeks of operation without damage. In addition, such electrodes can produce ozone as a means of destroying microorganisms in water supplies.

Another intense effort is in the development of diamond switches for pulsed-power technology. Devices that release energy in microseconds are used in fields with large potential impact, such as fusion-energy research. But the switching of high-voltage, high-current pulses has generally required the use of gas-based switches, such as rail switches, which are difficult to use and contribute to the reputation of pulsed-power work as a "black art."

Diamond switches could change that. Alameda Applications Science Corp. (Alameda, CA), among others, has developed switches based on undoped CVD diamond films. When exposed to UV radiation from a laser, diamond films generate conduction electrons and can conduct current at densities as high as 12 kA/cm^2. But when the laser is switched off, within a few nanoseconds, the diamond becomes an insulator, capable of fending off 200- to 300-kV fields. Such diamond switches could replace rail switches in capacitor banks. In the future, if pulsed-power fusion machines, such as dense-plasma-focus or inertial-confinement devices, ever produce net energy, fast diamond switches could also be essential in energy collection and processing.

Further reading

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