NOTES
· AND ·
NEW TECHNIQUES

A PRELIMINARY GEMOLOGICAL STUDY OF SYNTHETIC DIAMOND THIN FILMS

By Emmanuel Fritsch, Laurie Conner, and John I. Koivula

To evaluate possible problems in separating gem materials coated with a synthetic diamond thin film from their uncoated equivalents, we examined one sample of a free-standing, polycrystalline diamond film about one micron (0.001 mm) thick. This film could be easily recognized by standard microscopic examination, especially in surface-reflected and polarized light. The potential problems related to detecting thicker, monocrystalline, or colored synthetic diamond thin films and coatings that might be encountered in the future on faceted stones are also briefly discussed.

One of the most significant developments in gemology in the 1980s has been the commercial growth and production of gem-quality synthetic diamonds. All of the samples—both commercially grown and those for research only—described in the gemological literature to date, however, have been synthesized using high pressure and temperature. Because of this mode of formation, they exhibit characteristic features that allow a skilled gemologist to separate them from natural diamond by means of conventional testing techniques (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986 and 1987).

Within the past few years, a completely different type of process has been developed to grow a thin layer of synthetic diamond on a substrate at low pressure and moderate temperature. Based on the well-known technique of chemical vapor deposition (CVD), this new technology involves the deposition of tetrahedrally bonded carbon atoms from a carbon-containing, hydrogen-rich gas (Angus and Hayman, 1988). Variations of this technique have been used successfully to grow both synthetic diamond films and a new class of materials called diamond-like carbon (DLC), in which the carbon atoms are present in both diamond-type and graphite-type bonding arrangements. Although the physical and chemical properties of the diamond-like materials can be noticeably different from those of diamond, they seem to be easier to manufacture than synthetic diamond and yet offer many of its advantages. This new growth technique suggests the possibility that a synthetic diamond or DLC coating several microns thick could be placed on various materials to improve their resistance to wear, enhance some other property of the material, or even create new types of devices for many useful technological applications.

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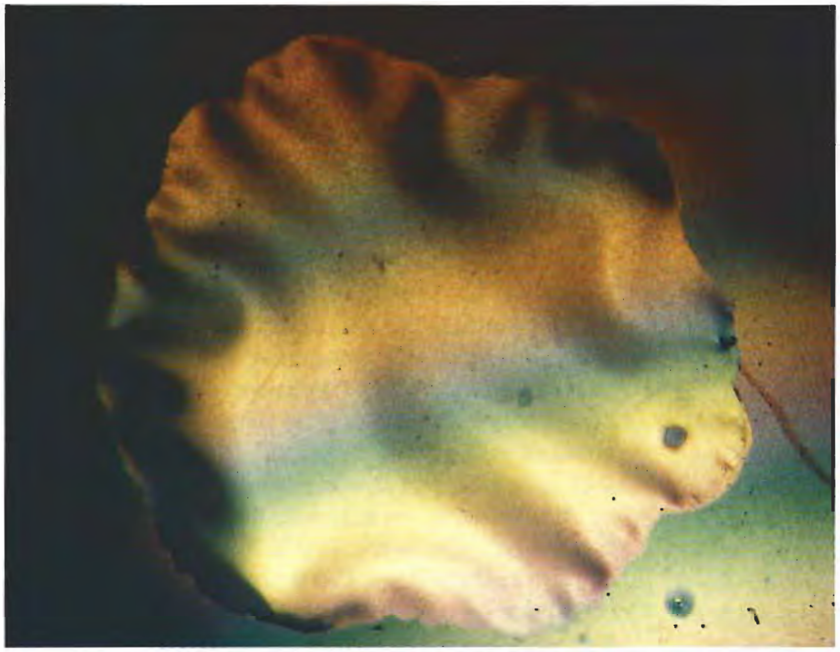


Figure 1. The synthetic diamond thin film studied measures approximately 6.8 × 6.8 mm. One of the reasons interference colors are evident here is the fact that the thickness (1 μ) of this film is of the same order of magnitude as the wavelengths of visible light. Note the warped aspect of the free-standing part of the film, which measures about 4 mm in diameter. Without the tension imposed by the silicon base, the film relaxes and wrinkles. Photomicrograph by John I. Koivula; magnified 6×.

With few exceptions, the synthetic diamond and DLC films grown today are polycrystalline; that is, they are made up of many tiny crystallites. To date, only limited experimental work has been done (e.g., by Sumitomo Electric Industries) to deposit single-crystal synthetic diamond films on a substrate of a crystal of synthetic diamond (Hara and Fujimori, 1989).

Even so, there has been some concern that this technique could be used in the jewelry industry, for example to coat faceted stones of various diamond simulants so that they would show a high thermal conductivity and might then test as diamond on a thermal inertia probe. These films might also show some other gemological properties that would make the simulant behave more like a diamond. One jeweler has already reported encountering a diamond simulant that was allegedly coated in this manner (Koivula, 1987).

To investigate the potential problems that such a product might pose, we examined a polycrystalline synthetic diamond thin film, about one micron (1 μ) thick, that had been deposited on a silicon substrate (figure 1). The particular technique used to grow this thin film, plasma-enhanced chemical vapor deposition (PECVD; see figure 2), is one of the most common methods currently used to grow such materials. The sample we studied was manufactured by Crystallume of Menlo Park, California. The center part of the silicon square was chemically etched away, so that part of the thin film would be free standing. This allowed us to examine the film by transmitted light, as would be done if it were deposited on a transparent substrate such as a diamond simulant.

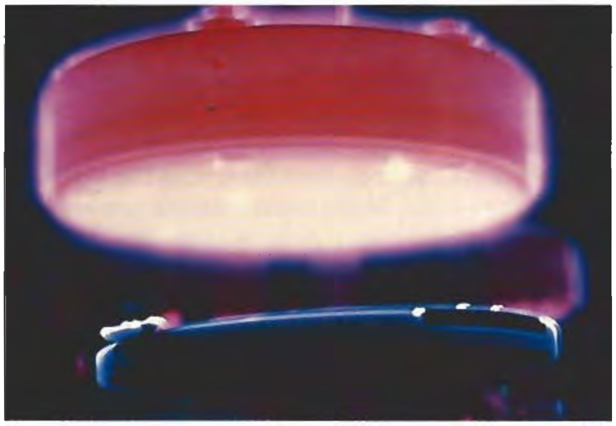


Figure 2. The thin film studied was grown from this gas plasma, using a technique known as plasma-enhanced chemical vapor deposition (PECVD). Photo courtesy of Crystallume.

This thin film was tested by classic gemological methods and instrumentation to document ways by which it could be detected. The results are reported below. Although some background on the history of synthetic diamond thin films is provided, this article will not present a detailed explanation of the various and sometimes complex growth processes used to produce such films. Readers interested in learning more about this technology and its expected industrial applications outside of gemology are referred to DeVries (1987), Spear (1987), Angus and Hayman (1988), and Bachmann and Messier (1989).

HISTORY OF DIAMOND THIN FILMS

It is difficult to tell from the published scientific literature who was first to grow synthetic diamond at low pressure. W. Eversole received a patent in 1962 to produce diamond by a low-pressure process, but his methodology is very different from the techniques used presently (Eversole, 1962). The low-pressure CVD diamond technology in greatest use today got its start in the Soviet Union in the early 1960s. Not until 1968, however, did crystal growth scientist Boris Derjaguin and his coworkers report their success in depositing synthetic diamond at low pressure (Derjaguin et al., 1968). Although many Western scientists were aware at that time of Derjaguin's work, they questioned the validity of the material's identification as diamond.

In the late 1970s and early 1980s, however, Japanese researchers indicated that they had duplicated Derjaguin's earlier work, and proved that the deposition of a synthetic diamond thin film at low pressure was technically feasible (see, e.g., Matsumoto et al., 1982 a and b; Kamo et al., 1983). These reports made a major impact in the world of materials science. Many organizations worldwide, such as the Royal Signal & Radar Establishment in the United Kingdom (Lettington, 1988) and companies like Sumitomo, Kobe Steel, Fujitsu, and Toshiba in Japan, started research and then production of synthetic diamond or DLC thin films. In 1988, for example, approximately US$20 million was spent on CVD synthetic diamond research in Japan (M. Yoder, pers. comm., 1989).

Individual researchers in the U.S. began work on growing tiny synthetic diamond crystals by the CVD method in the 1960s (Eversole, 1962; Angus et al., 1968). Not until the early 1980s, however, was a major collective effort directed toward the growth of synthetic diamond and DLC thin films. Prominent organizations such as General Electric, IBM, Pennsylvania State University, the Massachusetts Institute of Technology, and the Naval Research Laboratory, among others, began significant research programs in this area, supported for the most part by grants from the Department of Defense Strategic Defense Initiative ("Star Wars"). One company, Crystallume, was created in 1984 for the sole purpose of developing "engineered" products coated with synthetic diamond or diamond-like thin films.

Although most of the interest in diamond thin film production to date has focused on the many industrial, scientific, and military applications, organizations with significant interest in the gem market worldwide are following this new technology closely. Kyocera, a Japanese company well known for the many synthetic gem materials grown by its subsidiary Inamori, has submitted several patents on the manufacture of synthetic diamond by CVD, including one claiming the production of a 1.2-ct "inclusion-free, flawless and blemish-free" single crystal (Hiroshi, 1986). When contacted, Kyocera admitted that "work in this area is still in the developmental stage." De Beers is also "closely monitoring developments in the CVD area" (De Beers, 1988).

Why all the fuss? Until now, diamond's unique combination of superior hardness, very high thermal conductivity, and optical transparency was unavailable in the form of a film or coating over large surface areas on a three-dimensional object with good adherence to the substrate. Although adherence problems have not been solved completely, this new CVD process does allow synthetic diamond to be deposited on a variety of surfaces in thin coatings, thereby opening up a wide variety of applications, including the possibility of a synthetic diamond coating on diamond simulants or other gem materials.

A BRIEF DESCRIPTION OF THE CVD PROCESS

A schematic illustration of a typical CVD diamond reactor is given in figure 3. Quite simply, the process involves the use of hydrocarbon (typically methane) and hydrogen gases and a source of energy. The energy is most commonly derived from microwave, radio frequency (RF), or direct current (dc) sources, or from a heated tungsten filament. This energy serves to ionize the input gases, creating a carbon-rich gas "plasma" of charged particles. Typically, a pressure of 50 to 150 Torr and a temperature of 700° to 1000°C are needed for a gas composition of 0.1 to 1 vol.% methane (CH_4) in hydrogen. Under these conditions, the hydrocarbon gas breaks down, and carbon atoms are deposited on the substrate material as a thin film of synthetic diamond. Atomic hydrogen is believed to be necessary near the deposition area to maintain the carbon atoms in the proper type of tetrahedral bonding and thereby minimize the formation of graphite. The resulting coated surface can have all the inherent properties

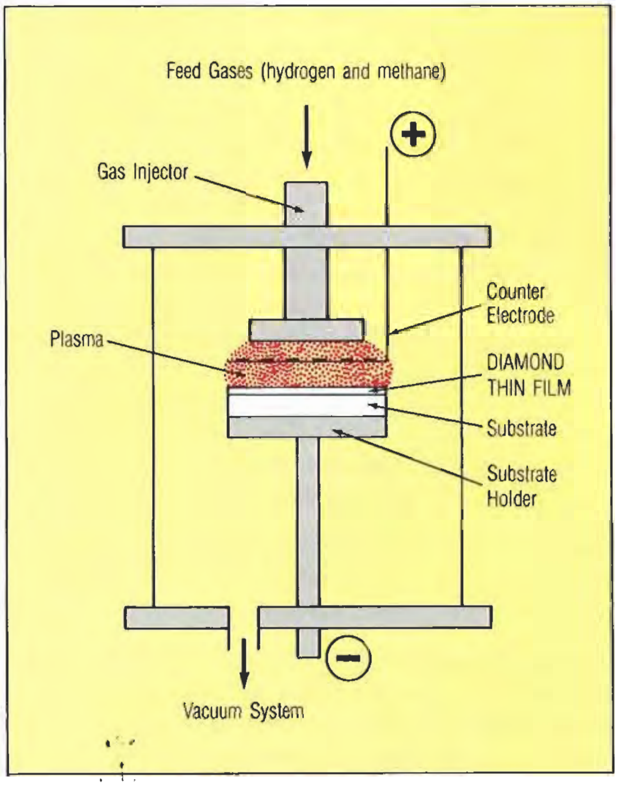


Figure 3. This schematic diagram illustrates the PECVD process used to grow synthetic diamond thin films similar to that studied by the authors. Drawing by Robin Teraoka.

of diamond. DLC films are produced with variations of CVD technology that use a higher methane concentration in the gas, a much lower temperature (down to room temperature), or ion beam sputtering.

GEMOLOGICAL EXAMINATION OF THE DIAMOND THIN FILM

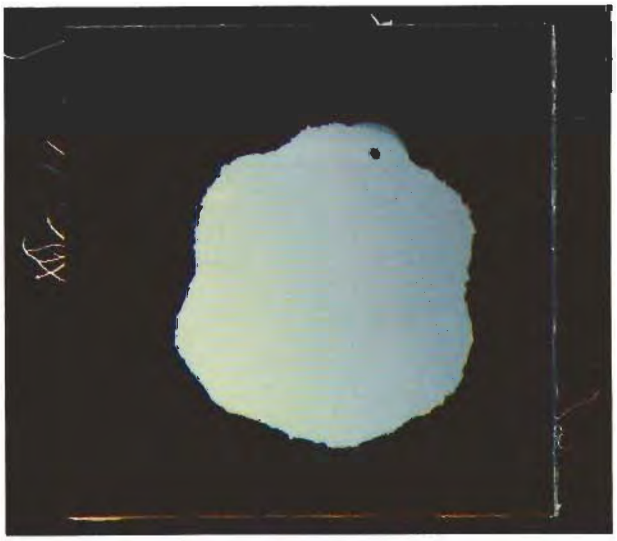
The film we examined was deposited on a square silicon substrate that is 6.8 mm on each edge and 0.55 mm thick. The central free-standing portion is about 4 mm in diameter (again, see figure 1). This film (Crystallume sample EASI 23K), approximately 1 µ thick, was determined by Raman spectroscopy to be crystalline diamond with one part per thousand of a "graphitic" component. It would, therefore, be readily considered a synthetic diamond film rather than a diamond-like carbon film (see Williams and Glass, 1989).

General Appearance. The film can be easily recognized either on the silicon substrate or free standing in air because it gives rise to interference colors (like an oil slick on water—again, see figure 1). This results from factors such as the contrast in index of refraction between diamond and the underlying silicon (or air, for the free-standing part) and a film thickness close to the wavelengths of visible light. Also, the smoothness of the silicon-diamond film interface might have an influence.

Haziness. In darkfield illumination, the thin film appears to be hazy rather than transparent (figure 4). Because the film is polycrystalline and the individual synthetic diamond crystallites are uniformly approximately 1 µ (again, comparable in size to wavelengths in the visible range), the material scatters visible light. This scattering results in a hazy appearance.

Color. When viewed against a white background in diffused light, this film has a brownish appearance that is barely visible to the naked eye (figure 5). We could not detect any absorption features with a hand-held spectroscope. However, the optical absorption spectrum obtained by transmission mode with a Pye Unicam 8800 spectrophotometer shows a gradual rise in absorption toward the ultraviolet, which is what would be expected from a brownish material. For the most part, this color is probably due to an intrinsic absorption of the film material,

Figure 4. In darkfield illumination, this synthetic diamond film is not transparent but somewhat hazy. This is due to light scattering at the grain boundaries of this polycrystalline material. Photomicrograph by John I. Koivula; magnified 3×.



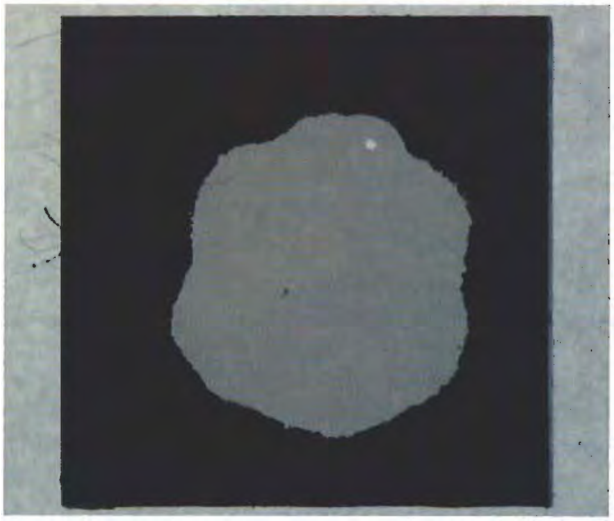


Figure 5. When viewed against a white background in diffused light, this synthetic diamond thin film appears light brown. Photomicrograph by John I. Koivula; magnified 3×.

resulting from the peculiar electronic structure of the minor "graphitic" component (Koidl, 1989). Also, a thin-film interference phenomenon could give rise to a brown interference color evenly distributed on the film (as is commonly observed on camera lenses with optical coatings).

Reaction to Polarized Light. When examined between crossed polarizers, the thin film is not extinct. Although diamond is singly refractive, an aggregate reaction is shown by polycrystalline thin films because of light scattering at the grain boundaries and also possibly strain.

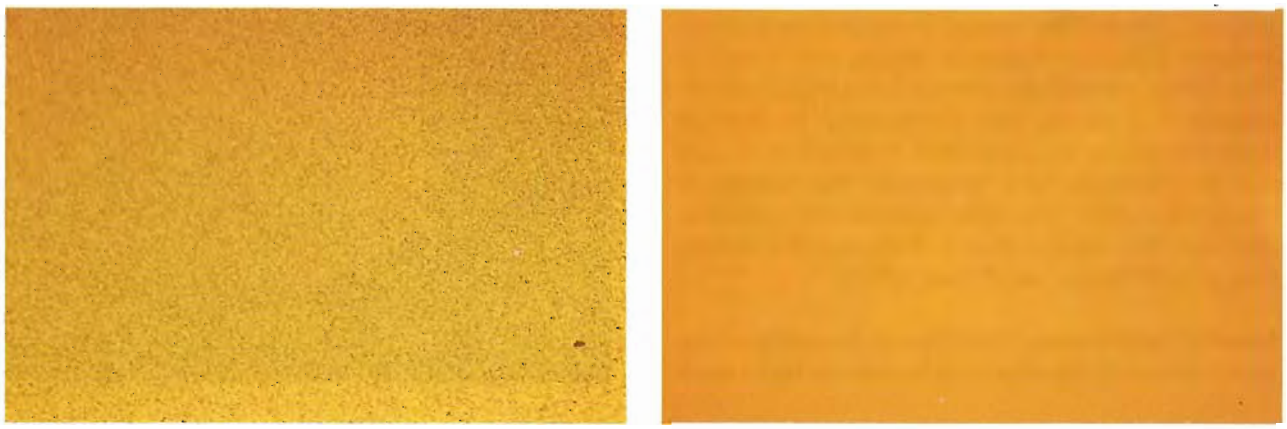
Nomarski Differential Interference Contrast Microscopy. This examination technique (McCrone et al., 1978) highlights very small details on a surface, down to 1 nm or so, by means of different interference colors (thus the orange color of the illustrations in figure 6). Not only is the granular nature of the thin film readily visible with this technique (figure 6, left), but one can actually measure the approximate diameter of the individual grains, 1.25 μ on average.

The surface of the table of a natural polished diamond, examined with the same technique at the same magnification, has a very different appearance (figure 6, right). The few lines visible are surface graining, features inherent to the underlying structure of this particular diamond.

Luminescence. No luminescence to either shortwave or long-wave ultraviolet radiation was observed on this particular film.

Thermal Conductivity. Using a GIA-GEM Duotester, we tested several spots on the synthetic diamond thin film for thermal conductivity. The readings on the diamond tester fell in the range 60 to 80 on the scale, which is at the lower end of the green zone labeled "diamond." However, the silicon substrate gave the exact same readings. Therefore, we believe that the film is too thin to test as diamond with this instrument (on which the value should really be between 90 and 110), and that the measured readings actually correspond to the thermal conductivity of the substrate, since diamond has a higher thermal conductivity than silicon. This film (at this thickness) could not be used to "disguise" a diamond simulant.

Figure 6. With Nomarski differential interference contrast, the graininess of the surface of the synthetic diamond thin film is readily apparent (left). The only observable features on the surface of the table of the natural cut diamond (right) are grain lines. Photomicrographs by John I. Koivula; magnified 80×.



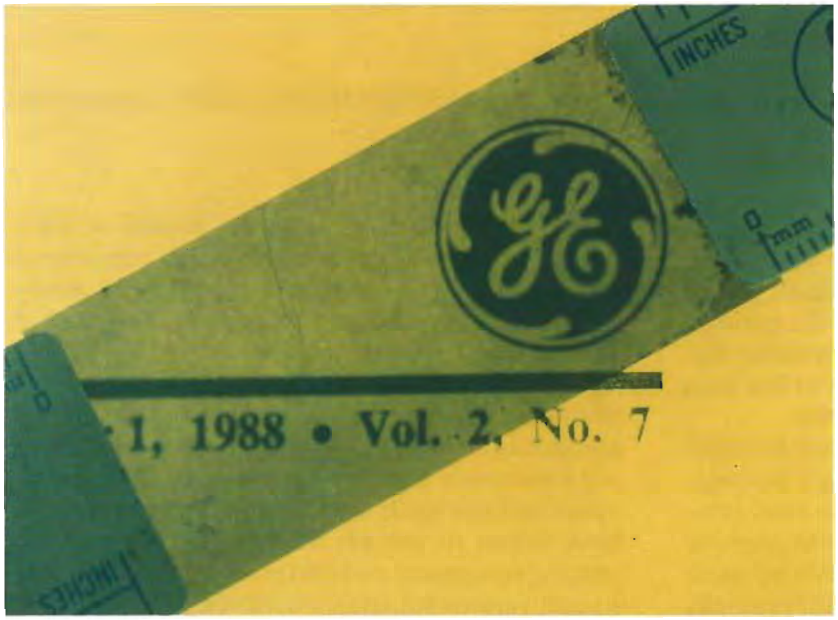


Figure 7. Thin-film technology has advanced to the point of producing this 500-μ (0.5-mm) thick transparent synthetic diamond film. Because this film has been polished on one side only, there is some residual haziness and color caused by impurities from the substrate on the unpolished surface. Photo courtesy of Thomas Anthony, General Electric Co.

Electrical Conductivity. Two steel electrodes were applied to different points of the film still on the substrate to test for electrical conductivity. A very weak conductivity was detected in certain areas (readings around 1 or 2 compared to 130 when the two electrodes are put in contact with each other). This might be due to minute amounts of a more "graphitic" phase at the grain boundaries, as graphite is a good electrical conductor.

DISCUSSION

From this restricted set of observations, one can still predict that as long as a synthetic diamond or DLC film grown by the CVD technique is thin, the thermal tester remains the fastest instrument to separate diamond from a synthetic diamond-coated simulant. According to Michael Pinneo (pers. comm., 1988), the film would have to be at least 5 μ thick to test as diamond with the diamond thermal probe. This thickness requirement could be even greater; the fact that the film is polycrystalline makes its thermal behavior very unpredictable. Currently, this behavior is even more uncertain for DLC.

Interference colors also readily reveal the presence of a very thin film such as that examined for this study, although they disappear on a film 3–4 μ thick (M. Pinneo, pers. comm., 1988). General Electric's Thomas Anthony announced at the April 1989 Materials Research Society Short Course on Diamond and Diamond Thin Films that a transparent, near-colorless polycrystalline synthetic diamond thin film 500 μ thick—one-third the thickness of a Sumitomo synthetic diamond slice—has been grown on a silicon substrate (figure 7). While this material currently is not commercially available, it does indicate the speed with which this technology is progressing.

The most identifiable feature of the synthetic diamond thin film we studied is its granular texture, the result of its polycrystalline nature. What if, one might hypothesize, someone developed a monocrystalline synthetic diamond film thick enough to give the thermal conductivity of diamond that could be deposited on a transparent substrate? There should be no haziness and no aggregate reaction in polarized light. The case most feared by the gem trade would be a monocrystalline film on cubic zirconia. It is highly improbable, however, that such a synthetic diamond film would adhere to this particular substrate, since the crystal structures of the two materials are very different. Although similar adhesion problems also exist with polycrystalline thin films, an intermediate layer of DLC as thin as 10 nm could be used to improve adhesion, as it has in a variety of industrial applications requiring a nonsilicon substrate.

Another possible application of a synthetic diamond thin film would be to modify the apparent color of a faceted diamond. Sumitomo Electric Industries is already able to deposit a blue synthetic diamond coating as thick as 20 μ on a natural near-colorless diamond octahedron (N. Fujimori, pers. comm., 1989). The resulting blue product is electrically conductive. One can imagine that this type of coating might be easy to detect by immersion of the diamond in methylene iodide.

The color in a natural blue diamond is distributed in a slightly nonhomogeneous patchy pattern, whereas the sharp edges of the coating would be readily visible, as they are on a diffusion-treated sapphire with immersion in methylene iodide. Currently, it is unclear whether this technology could provide a new way to balance a small yellow component in a faceted near-colorless diamond by depositing small amounts of blue synthetic diamond in certain areas of the cut stone, as has been done in the past with metallic fluorides.

Many more applications of synthetic diamond and DLC coatings in the gem trade can be imagined. Perhaps the most obvious is to coat gemstones that have a low scratch hardness to improve their resistance to wear. A patent already exists in Germany for this very application on, for example, apophyllite and kyanite (Streckert et al., 1988). Also, DLC thin films could potentially be used to "seal" water in natural opals to prevent crazing. Should diamond coating evolve into a very inexpensive technology, it might even be economical to add a point of weight to push a 0.99-ct stone over the 1.00-ct barrier.

CONCLUSION

The polycrystalline synthetic diamond or DLC films commercially available today, as represented by the sample we examined, appear to be easily detectable and should not be a source of concern at this time to the jewelry industry.

However, even scientists intimately familiar with the subject are in strong disagreement about possible future developments. There is, therefore, a need to closely monitor the progress of this developing technology. It is interesting to note that we have begun to see advertisements for diamond-coating equipment and also for companies offering to coat various substrates with synthetic diamond or DLC thin films (both of which are often—and erroneously—referred to simply as "diamond films"). At this time, however, we are not aware of the commercial availability of any synthetic diamond- or DLC-coated gem material.

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