

# GEM-QUALITY SYNTHETIC DIAMONDS GROWN BY A CHEMICAL VAPOR DEPOSITION (CVD) METHOD

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Brown-to-gray and near-colorless single-crystal type IIa synthetic diamonds grown using a chemical vapor deposition (CVD) technique by Apollo Diamond Inc. have gemological properties that are distinct from those of both natural diamonds and HPHT-grown synthetic gem diamonds. The tabular crystals typically range up to 1 ct or more and a few millimeters thick, and consist of an overgrowth on a natural or synthetic diamond substrate. Faceted CVD synthetic diamond usually cannot be separated from natural diamond with standard gemological techniques; although when portions of the substrate are still present, an experienced gemologist may be able to recognize differences in luminescence or color between the overgrowth and substrate. In all cases, however, the CVD synthetic diamonds examined to date could be identified in a gemological laboratory by the combination of a strong orangy red fluorescence seen with the De Beers DiamondView deep-ultraviolet imaging system, a characteristic anomalous birefringence (strain) pattern, and distinctive features in their infrared absorption spectra (e.g., at  $3123\text{ cm}^{-1}$ ) and photoluminescence spectra (strong 575 and 637 nm emissions, a doublet at 596 and 597 nm, and a line at 737 nm).

Apollo Diamond Inc. of Boston, Massachusetts, has succeeded in growing facetable, single-crystal type IIa synthetic diamonds using a patented chemical vapor deposition (CVD) technique (Linares and Doering, 1999, 2003). For characterization of this material, the company has provided a number of brown-to-gray and near-colorless gem-quality crystals and faceted samples, which represent what is intended to become a commercial product for use in high-technology applications as well as for jewelry purposes (figure 1). Because of the growth conditions and mechanisms used, the gemological properties of these CVD-produced synthetic diamonds differ from those of both natural diamonds and synthetic diamonds grown at high pressures and temperatures. For the same reasons, the brown coloration of CVD synthetic diamonds may not react in the same way, or as efficiently, as most natural type

IIa brown diamonds, which can be decolorized at high pressure and high temperature (see box A). Preliminary notes on GIA's examination of some of these Apollo samples were published by Wang et al. (2003) and appeared in the August 8, 2003 issue of the *GIA Insider* (GIA's electronic newsletter: [http://www.gia.edu/newsroom/issue/2798/1842/insider\\_newsletter\\_details.cfm#3](http://www.gia.edu/newsroom/issue/2798/1842/insider_newsletter_details.cfm#3)). Spectroscopic analysis of an Apollo CVD synthetic diamond also was performed recently by other researchers (Deljanin et al., 2003). The purpose of the present article is to provide a more complete description of this material and its identifying features.

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GEMS & GEMOLOGY, Vol. 39, No. 4, pp. 268–283.  
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Figure 1. This jewelry is set with CVD synthetic diamonds from Apollo Diamond Inc. The pendant contains an HPHT-annealed 0.2 ct CVD synthetic diamond with a color equivalent to “K” on the GIA diamond grading scale (sample no. 57687). The 0.31 ct sample (no. 56924) in the ring on the left is equivalent to Fancy Dark brown in color. The Fancy Light brown 0.45 ct CVD synthetic diamond (no. 57688) in the ring on the right was HPHT annealed, but no change in color was observed (see box A). Composite of photos by Elizabeth Schrader.



## BACKGROUND

Synthetic diamonds have been produced by the high pressure/high temperature (HPHT) technique since 1955, with the growth of crystals of a size and quality suitable for jewelry first announced in 1970 (Crowningshield, 1971; Burns and Davies, 1992). HPHT-grown synthetic diamonds have distinctive physical features, such as a cuboctahedral crystal form and a related arrangement of internal growth sectors, as a result of growth at high pressures and temperatures from a molten metal or metal alloy flux/catalyst. The crystals produced in this manner typically weigh 1–3 ct; when faceted for jewelry use, they occasionally exceed 1 ct. The vast majority of crystals are yellow, although limited numbers of blue and colorless synthetic diamonds have also been produced (other colors, such as pink or red, are the result of post-growth treatment of material that is yellow as grown). Shigley et al. (1995) summarized the distinctive gemological properties of both colored and colorless HPHT-grown synthetic diamonds.

A diamond crystal, which is composed solely of carbon atoms, has a structure in which each carbon atom is symmetrically surrounded by four other carbon atoms. Because of this structure, diamond has unique physical and chemical properties that make it highly desirable for a wide range of applications (see, e.g., Field, 1992; Davies, 1994; Spear and Dismukes, 1994; Wilks and Wilks, 1994). Specifically, diamond:

- Is the hardest known natural material
- Is the best thermal conductor of any material near room temperature
- Has the lowest coefficient of thermal expansion

- Is resistant to heat, acids, and radiation
- Is a good electrical insulator, but can be doped to act as a semiconductor
- Is transparent to visible and almost all infrared radiation

Given these many notable properties, it is hardly surprising that diamond not only is the most important gem material, but it also has extensive industrial applications in thermal management, cutting tools, wear-resistant coatings, optical components, and possibly semiconductor electronic devices. An increasing proportion of these applications use synthetic diamond. The resulting demand has, in turn, supported active research and development programs on synthetic diamond growth worldwide.

Most of the techniques currently used to produce gem-quality synthetic diamond employ high pressures and temperatures—similar to those under which diamonds form in nature—to transform elemental carbon into diamond. Recently, however, the growth of gem-quality synthetic diamond by one of several new chemical vapor deposition (CVD) techniques, which do not require high pressure, is drawing increased attention worldwide (Hunter and Paparella, 2003). In contrast to the conventional HPHT synthesis process, CVD techniques involve gas-phase chemical reactions that deposit layers of a synthetic diamond film on a solid substrate (Butler and Woodin, 1993; Davis, 1993; Spear and Dismukes, 1994—see figure 2). If a natural diamond or a synthetic diamond is used as the substrate, single-crystal CVD diamond can be produced; however, if another material (such as silicon) is used, com-

## BOX A: PRELIMINARY NOTE ON CHANGING THE COLOR OF CVD-GROWN SYNTHETIC DIAMONDS BY HPHT ANNEALING

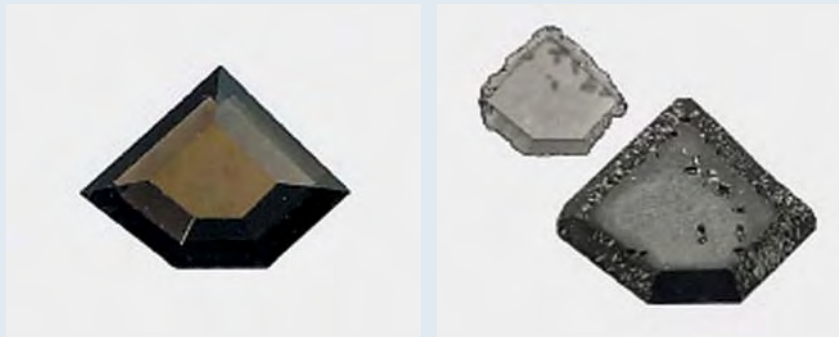
The as-grown CVD synthetic diamond samples examined for this study were type IIa, and for the most part their color varied from light to dark brown. It is now well-known in the jewelry industry that the brown coloration of natural type IIa diamond can be changed to near-colorless or colorless by annealing at high pressures and temperatures. Therefore, we conducted a preliminary study to determine whether HPHT treatment could lighten the brown color of some of our samples, and also to determine any gemological and spectroscopic variations related to HPHT annealing.

Three samples were selected for HPHT treatment at pressure and temperature conditions initially in the graphite-stable region (similar to those commonly used in HPHT treatment; see, e.g., De Beers Industrial Diamonds et al., 2001) using a belt-type press. After annealing, only one sample showed a clear improvement in color.

In one instance (sample no. 57608), the color changed from Fancy Dark brown to Fancy black (figure A-1). In the second sample (no. 57688), the

Fancy Light brown color did not show any perceptible change after treatment. When this second sample was annealed again at a temperature and pressure in the “diamond-stable region,” there was still no improvement in its color (figure A-2). The third sample was cut into two pieces, with the as-grown portion (no. 58768) retained as a control while the other portion was HPHT annealed. The color changed from brown to light gray (figure A-3) after HPHT annealing. Significant color improvement after HPHT annealing was also observed in sample no. 57687 (see table 1 and figure 1) by one author (RCL); unfortunately this sample was not color graded or analyzed before HPHT annealing.

Although our HPHT-treatment experiments were limited, they do indicate that, unlike natural type IIa diamonds reported to date, different CVD synthetic diamonds will react differently to HPHT treatment, with no improvement in some cases. This can perhaps be explained by the fact that the cause of color in natural brown diamonds is different from that in these CVD-grown synthetic diamonds.



*Figure A-1. The color of this 1.11 ct faceted CVD-grown synthetic diamond (no. 57608) changed from Fancy Dark brown as-grown (left) to Fancy black (right) after HPHT annealing in the graphite-stable region. The sample broke into two pieces after treatment, and now exhibits dissolution features along its edges. Photos by Elizabeth Schrader.*

monly polycrystalline CVD diamond is created.

The first successful, reproducible growth of synthetic diamond as a thin film was achieved by W. G. Eversole in 1952 using a CVD technique (Angus, 1994, p. 21; it is interesting to note that this event predated General Electric’s 1955 announcement that its researchers had created single-crystal synthetic diamonds). Goodwin and Butler (1997) reviewed the important features of the growth environment and critical aspects of the growth process. As illustrated in figure 2, the CVD method involves bringing together the needed gaseous reagents—typically a small amount of methane ( $\text{CH}_4$ ) in hydrogen ( $\text{H}_2$ )—in a chamber with a substrate. A reaction

among these components is initiated at high temperatures and low pressures (between 10 milli Torr [0.000013 atm] and 1 atm). The reactants, products, and reactive species are transported throughout the chamber by diffusion and convection. Over the substrate surface, various reactions (adsorption, diffusion, and desorption) occur among the chemical species, leading to the deposition of synthetic diamond and, ultimately, the growth of a continuous layer of synthetic diamond. A number of variations of the CVD growth technique have been developed (see, e.g., Spear and Dismukes, 1994), and it is now possible to grow a colorless, high-purity, single-crystal layer of material to a thickness of a



Figure A-2. As grown, this 0.45 ct CVD synthetic diamond (no. 57688) was light brown (left). After HPHT annealing, first at the graphite-stable region and then at the diamond-stable region, the sample showed virtually no change in color (right). Photos by Wuyi Wang.

The brown color of type IIa natural diamonds is generally thought to result from the diamonds' having been subjected over geologic time to high stresses deep in the earth's mantle, resulting in plastic deformation (see, e.g., Wilks and Wilks, 1994). This deformation produces an atomic-level defect (i.e., an internal extended defect) by moving carbon atoms slightly away from their normal positions in the diamond lattice. HPHT treatment can remove brown coloration related to this defect in natural type IIa diamonds, and this is the basis of the diamond decolorization process announced in 1999 by scientists at General Electric Co. (see, e.g., Fisher and Spits, 2000).

In contrast, the brown color in the type IIa CVD-grown samples from Apollo Diamond Inc. results from precipitation of non-diamond carbon and/or internal extended defects such as dislocations. It appears that these defects in CVD synthetic diamonds do not react to HPHT annealing in the same way as plastic deformation in natural diamonds, and thus they do not always produce similar decolorization. This may help explain the diversified results we observed.

It should be noted that the HPHT annealing strongly affected some other defects in the CVD-grown diamonds. The H-related absorptions in the mid- and near-infrared regions described in the pres-

ent article disappeared entirely after treatment. However, little variation was detected in the Si-related emission lines. In addition, the hardness of the CVD diamond seems to have been enhanced by the treatment, as gauged by the cutter during re-polishing (M. Witriol, pers. comm., 2003). Further experimental work is needed to explore the potential for HPHT treatment of CVD-grown synthetic diamonds to remove their brown color, and to identify these HPHT-treated CVD synthetic diamonds.

Figure A-3. A CVD synthetic diamond crystal was sawn in two, and the 0.18 ct as-grown portion on the left (no. 58768) was retained as a control sample while the 0.36 ct portion on the right was HPHT annealed. The brown as-grown sample became light gray after HPHT annealing. Photo by Wuyi Wang.



few millimeters on a diamond substrate.

Recent successes in the coating of relatively large surface areas (up to 100 cm<sup>2</sup> or more) with a continuous layer of diamond have created a whole new range of potential applications for polycrystalline CVD synthetic diamond products in other industries (see, e.g., Ravi, 1994). More than a decade ago, Fritsch et al. (1989) discussed some possible uses of this technique to coat gemstones with polycrystalline CVD synthetic diamond. So far, however, the application of CVD growth in the jewelry industry has remained negligible due to the problem of coating a polished gem with a synthetic diamond layer of sufficient thickness and the difficulty of growing sin-

gle diamond crystals of a sufficient size and thickness to be faceted. This situation has now changed.

In the first quarter of 2004, Apollo Diamond Inc. will start commercial production of CVD synthetic diamonds for jewelry use. Brown to near-colorless type IIa crystals up to 1 ct or more are anticipated, with some experimental production of colorless type IIa and blue type IIb synthetic diamonds scheduled to start in 2005. A total annual production of 5,000–10,000 carats of faceted synthetic diamonds is planned initially, with expanded production in the future. Faceted samples will be mainly 0.25–0.33 ct, but they could reach 1 ct in mid-2004. Apollo Diamond Inc. is negotiating with a wide range of



jewelry industry distributors to develop possible marketing relationships, and the products will be sold with proper disclosure.

## MATERIALS AND METHODS

A total of 13 CVD-grown synthetic diamonds were provided by one of the authors (RCL) for this study (see table 1). These samples are representative of the material currently produced by Apollo. Eight of the samples were crystals, and five were faceted. (Two of the crystals were subsequently faceted, and these faceted samples also were examined.) The largest crystal weighed 0.87 ct, and the largest faceted sample weighed 1.11 ct. Substrates and poor-quality exterior portions of some as-grown crystals were removed using a laser before examination in this study.

The visual features of the studied samples were observed with a gemological microscope. Reactions to ultraviolet radiation were checked in a darkened room with conventional four-watt long-wave (366

nm) and short-wave (254 nm) lamps, and also with the De Beers DiamondView deep-ultraviolet (<230 nm) imaging system (Welbourn et al., 1996). The faceted samples were examined by experienced diamond graders and given color and clarity descriptions equivalent to those used in the GIA diamond grading system.

Many of the studied samples were characterized by various spectrometric methods (again, see table 1). Certain data on some samples could not be obtained due to time constraints. Infrared absorption spectra were recorded on all samples in the mid-infrared range (6000–400  $\text{cm}^{-1}$ ) and nine samples (four crystals and five faceted) in the near-infrared range (11,000–4000  $\text{cm}^{-1}$ ) at room temperature with a Thermo-Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer, with a resolution of 1  $\text{cm}^{-1}$  for the mid-infrared range and 4  $\text{cm}^{-1}$  for the near-infrared range. A total of 1,024 scans per spectrum were collected to improve the signal-to-noise ratio. A KBr beam splitter was used

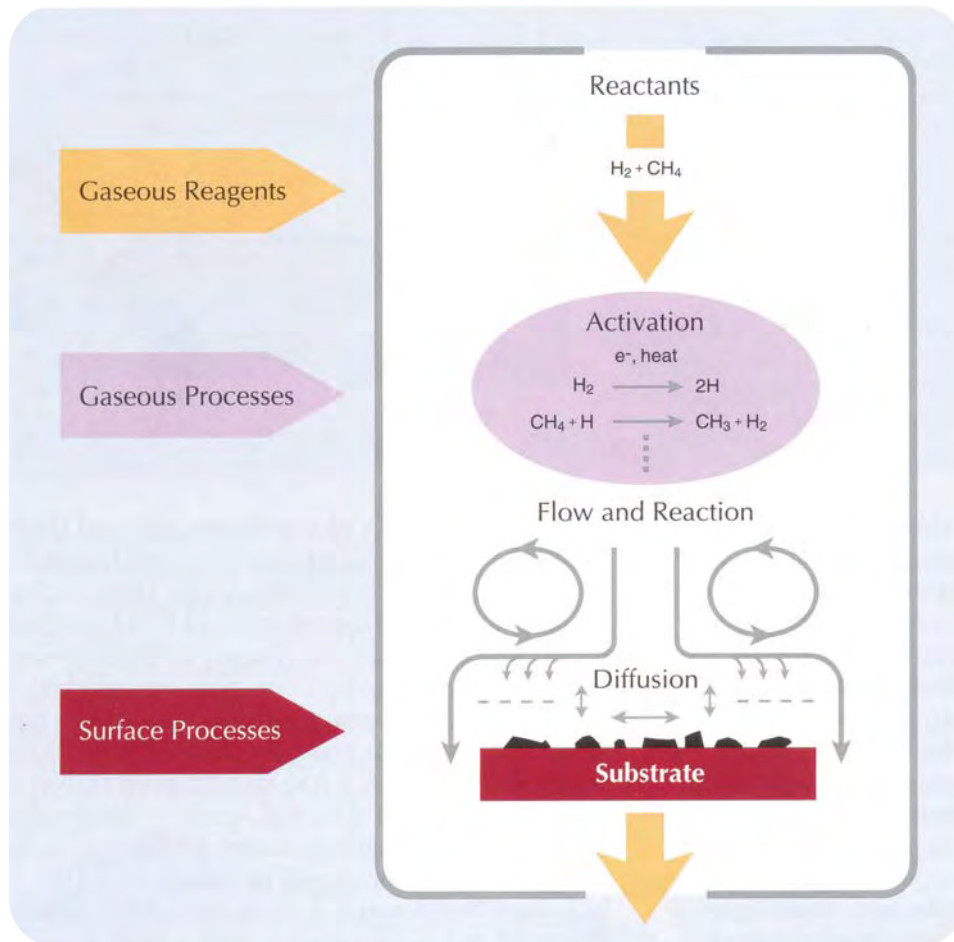


Figure 2. This schematic diagram shows the complex chemical reactions and transport processes that occur during the CVD growth of diamond layers on a substrate (modified after Butler and Woodin, 1993).

for the mid-infrared range, and a quartz beam splitter for the near-infrared range. A 6× beam condenser focused the incident beam on the sample. For comparison purposes and for calculation of absorption coefficients, each infrared spectrum was normalized according to its absorption in the two-phonon region (2664–1500  $\text{cm}^{-1}$ ).

A Thermo-Spectronic Unicam UV500 spectrophotometer was used to record absorption spectra on eleven samples (eight crystals and three faceted) over the range 250–850 nm with a sampling interval of 0.1 nm. For these analyses, the samples were held in a cryogenic cell cooled by liquid nitrogen. Photoluminescence spectra were recorded on all samples with a Raman Renishaw 1000 microspectrometer using two different lasers. The range 520–900 nm was recorded using an Argon-ion laser providing excitation at 514.5 nm operating at an initial power of 40 mW, while a He-Ne laser (632.8 nm) was used to record the range 650–850 nm in order to obtain better emission intensity and spectral resolution for some specific point defects. The samples were again held in a cryogenic cell cooled by liquid nitrogen. For all photoluminescence spectra, five scans were accumulated to achieve a better signal-to-noise ratio. Raman spectroscopy also was employed to identify some inclusions at room temperature.

## RESULTS AND DISCUSSION

The characteristics of the CVD-grown synthetic diamond crystals and faceted samples are reported in table 1 and discussed below.

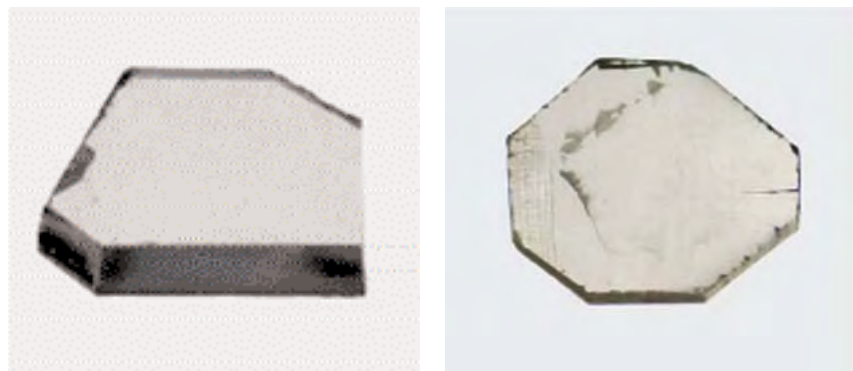
**Crystals.** CVD-grown diamond crystals from Apollo Diamond Inc. are very different in appearance from natural diamonds, as well as from traditional HPHT-grown synthetic diamonds; this is due to the dramatic differences in their formation environments and



*Figure 3. Due to the dramatic differences in their formation environments and growth mechanisms, CVD synthetic diamond crystals differ in appearance from natural diamonds, as well as from traditional HPHT-grown synthetic diamonds. HPHT synthetic diamonds (left) usually show well-developed {111} and {100} faces, and the flat surfaces have characteristic growth features. CVD-grown diamond crystals (center, no. 48922) usually have a tabular form, and {111} and {110} are poorly developed. Natural diamond crystals (right) may occur in any of several shapes that are very different from those of either CVD or HPHT synthetic diamonds. The octahedron is a very common form. Many natural diamonds display resorption features on their surfaces. Photo by Elizabeth Schrader.*

growth mechanisms (figure 3). Five of the eight crystals showed evidence of a substrate. In four of these, the substrate was type Ib HPHT synthetic diamond; in the fifth, it was CVD synthetic diamond. On the remaining three crystals, this substrate appeared to have been entirely removed. Without the substrate, the crystals were transparent with a light brown or gray to near-colorless appearance.

The crystal form of a CVD synthetic diamond is dependent on the conditions under which it is grown. As is typical of the material Apollo Diamond has grown to date, our crystals exhibited a tabular shape with two near-parallel surfaces (which correspond to cubic {100} crystal faces; see figure 4). In addition, small but distinct octahedral {111} and dodecahedral {110} faces were present on



*Figure 4. These CVD-grown synthetic diamond crystals illustrate the typical tabular shape of this material. The crystal on the left (no. 48921a) weighs 0.34 ct, while the one on the right (no. 56923) weighs 0.57 ct. The large, flat upper faces on both are the growth surfaces where new diamond material crystallized by chemical vapor deposition at high temperatures but low pressures. Photos by Elizabeth Schrader.*

**TABLE 1.** Characteristics of Apollo Diamond Inc. CVD-grown synthetic diamonds, listed by GIA sample number.<sup>a</sup>

Property	48922	56923	57595	57597	58060	58768 <sup>b</sup>	48921a
Weight (ct)	0.50	0.57	0.57	0.37	0.40	0.18	0.34
Description	Crystal	Crystal	Crystal	Crystal	Crystal	Crystal	Crystal
Shape	Tabular	Tabular	Tabular	Tabular	Tabular	Tabular	Tabular
Dimensions (mm)	5.6 × 4.5 × 1.5	8.5 × 8.2 × 0.6	7.1 × 7.1 × 0.8	6.1 × 6.4 × 0.6	5.0 × 4.5 × 1.4	3.6 × 2.9 × 1.1	4.9 × 3.7 × 1.3
Substrate	Type Ib HPHT synthetic diamond	None	Type Ib HPHT synthetic diamond	Type Ib HPHT synthetic diamond	Type Ib HPHT synthetic diamond	None	None
Color	Light brown	Light brown	Light brown	Very light brown	Light gray	Brown	Light brown
Clarity	nd	nd	nd	nd	nd	nd	nd
Fluorescence:							
Long-wave UV	Inert	Inert	Inert	Inert	Inert	Inert	Very weak orange
Short-wave UV	Very weak orange-yellow (chalky)	Very weak (color uncertain)	Strong, chalky green-yellow due to type Ib synthetic diamond substrate	Strong, chalky green-yellow due to type Ib synthetic diamond substrate, only at a small corner	Tiny region of chalky green-yellow due to type Ib synthetic diamond substrate, only at a small corner	Inert	Weak orange
DiamondView luminescence	Orangy red	Orangy red	Pink to orange (+greenish yellow from substrate)	Orangy red	Orangy red	Orangy red	nd
Infrared spectra (cm <sup>-1</sup> )	1344 3123 nd	1344	1344 3123 8753, 7354, 6856, 6425, 5564 group of features	3123 8753, 7354, 6856, 6425, 5564 group of features	1344 3123 8753, 7354, 6856, 6425, 5564 group of features	3123 8753, 7354, 6856, 6425, 5564 group of features	nd 3123 nd
UV-Vis-NIR spectra (nm)	Increasing absorption below 500	Increasing absorption below 500 Broad feature centered at 520	Broad 270 band Increasing absorption below 500 Broad feature centered at 520 268, 271	Broad 270 band Increasing absorption below 500 Broad feature centered at 520 268, 271	Broad 270 band Increasing absorption below 500 268, 271	Broad 270 band Increasing absorption below 500	Increasing absorption below 500 Broad feature centered at 520 271
	591, 596	591	591, 596	591, 596	591, 596	591, 596	591, 596
Photoluminescence spectra (nm)	575 637 596–597 doublet 737 543, 546, 589	575 637 596–597 doublet 737 534, 543, 563, 589, 591, 592	575 637 596–597 doublet 737 543, 563, 591, 592, 604	575 637 596–597 doublet 737 543, 563, 588, 591, 592, 604	575 637 596–597 doublet 737 543	575 637 596–597 doublet 737 <sup>d</sup> 543, 559	575 637 596–597 doublet 737 543, 545, 546

<sup>a</sup> nd = not determined.<sup>b</sup> HPHT annealed for this study. Properties for pretreated material only are listed.<sup>c</sup> HPHT annealed by Apollo Diamond Inc. Examined after treatment only.<sup>d</sup> Very weak in intensity, detected only by using 632.8 nm laser excitation.

one of the eight crystals. In several cases, these faces around the edges of the examined crystals had been removed from the samples.

Figure 5 illustrates a CVD diamond grown on a substrate of type Ib HPHT synthetic diamond. Because of the trace amounts of isolated nitrogen impurity in the substrate, this crystal appeared slightly yellow (although the CVD-grown portion is light brown as viewed from the side). A sharp boundary between the two portions of the crystal was visible to the unaided eye. When the sample was observed from the side with a strong ultraviolet radiation source (De Beers DiamondView), the two

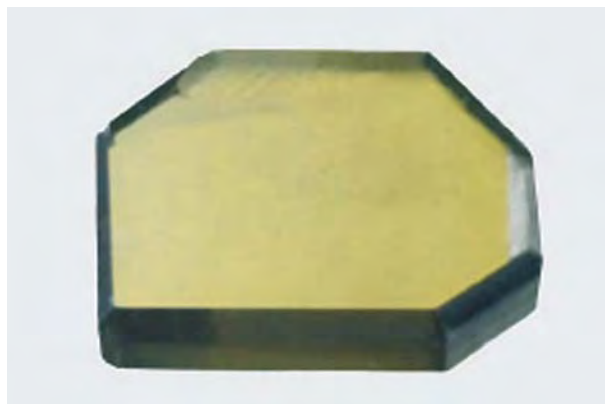
layers could be clearly distinguished due to their different luminescence (figure 6). Although the substrate in this sample was eye visible, in some instances it is very thin (less than 100 μm) and thus hardly detectable even with an optical microscope. However, even when a sample with such a thin substrate was observed with a DiamondView, it showed the strong green-yellow fluorescence and growth-sector pattern characteristic of HPHT synthetic diamonds (figure 7).

Figure 8 shows the growth of CVD synthetic diamond on a CVD synthetic diamond substrate. Initially, high-quality synthetic diamond was

48921b	49806a	49806b	45441	56924	57608 <sup>b</sup>	57687 <sup>c</sup>	57688 <sup>b</sup>
0.14	0.87	0.28	0.23	0.31	1.11	-0.2	0.45
Faceted from 48921a	Crystal	Faceted from 49806a	Faceted	Faceted	Faceted	Faceted	Faceted
Cut-corner rectangular modified brilliant	Tabular	Square modified brilliant	Pear-shaped brilliant	Cut-corner square modified brilliant	Kite modified brilliant	Round brilliant	Portrait cut
4.0 × 1.8 × 3.6	nd	3.6 × 3.5 × 2.5	nd	4.1 × 3.8 × 2.5	6.7 × 6.8 × 2.2	nd	7.6 × 3.9 × 1.2
None	Type IIa CVD synthetic diamond	None	None	None	Type Ib HPHT synthetic diamond	None	None
Fancy Light pinkish brown	Near-colorless	Fancy brownish yellow	Fancy brown	Fancy Dark brown	Fancy Dark brown	K (faint brown)	Fancy Light brown
VS <sub>2</sub>	nd	VS <sub>1</sub>	nd	SI <sub>2</sub>	SI <sub>1</sub>	SI <sub>2</sub>	SI <sub>1</sub>
Very weak orange	Very weak orange-yellow	Very weak orange-yellow	nd	Inert	Inert	Very weak orange	Very weak yellow
Weak orange	Moderate orange-yellow	Moderate orange-yellow	nd	Moderate chalky orange-yellow	Tiny region of chalky green-yellow due to type Ib synthetic diamond substrate, only at a small corner	Moderate yellowish green	Very weak orange
Orangy red	Orangy red	Orangy red	nd	Orangy red	Orangy red	nd	Orangy red
nd	1344 3123 nd	nd	1344 3123 8753, 7354, 6856, 6425, 5564 group of features	1344 3123 8753, 7354, 6856, 6425, 5564 group of features	1344 3123 8753, 7354, 6856, 6425, 5564 group of features	3029	3123 8753, 7354, 6856, 6425, 5564 group of features
nd	Increasing absorption below 500 Broad feature centered at 520	nd	nd	Broad 270 band Increasing absorption below 500 Broad feature centered at 520 268, 271 419, 447, 625, 637	Broad 270 band Increasing absorption below 500 268, 271 301, 305, 447, 625, 637, 653 591, 596 737	nd	Broad 270 band Increasing absorption below 500 271 591, 596 737
575 637 596–597 doublet 737 543, 545, 546	575 637 596–597 doublet 737 543, 563, 589, 591, 592	nd	575 637 596–597 doublet 737 543	575 637 596–597 doublet 737 543, 563, 591, 592	575 637 596–597 doublet 737 543	575 637 596 737 532, 533, 535, 543, 544, 546, 764, 765, 792	575 637 596–597 doublet 737 543, 546, 563

deposited on the substrate. After this initial precipitation, the growth process tended to deposit a grayish black phase—best described as “non-diamond carbon”—around the edges of the crystal, which is removed during faceting. However, with this sub-

*Figure 5. Depending on the intended application, synthetic diamond can be grown on various substrate materials by the CVD process. This 0.50 ct light brown CVD synthetic diamond (no. 48922) was produced on a substrate of yellow HPHT synthetic diamond. Photo by Elizabeth Schrader.*





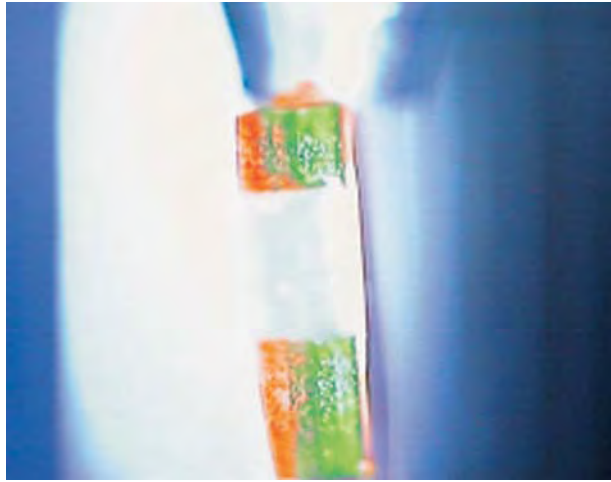


Figure 6. The two layers in the sample shown in figure 5 exhibit different reactions to UV radiation when observed with the De Beers DiamondView imaging system (CVD-grown diamond on the left and HPHT synthetic diamond substrate on the right). Photo by Wuyi Wang.

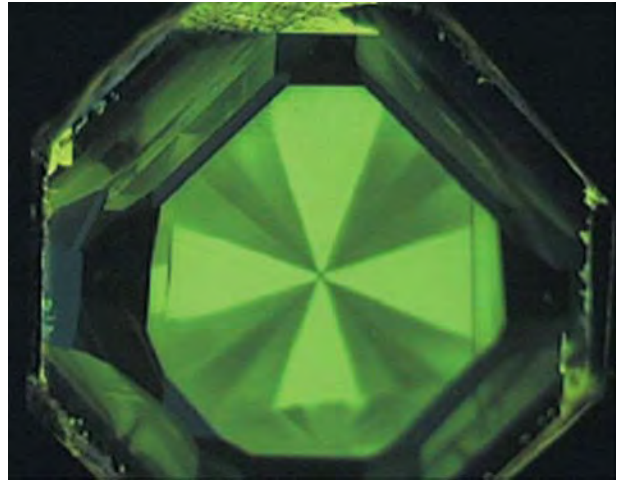


Figure 7. Although what remains of the HPHT synthetic diamond substrate on this 0.57 ct CVD crystal (no. 57595) is so thin it is almost undetectable with an optical microscope, the DiamondView reveals the strong green-yellow fluorescence and growth-sector pattern typical of HPHT synthetic diamond. Photo by Wuyi Wang.

strate the synthetic diamond overgrowth is relatively thick (here, 2.5 mm). The substrate and the overgrowth appear to be continuous—no physical boundary between them could be seen with an optical microscope up to 100× magnification.

**Faceted Gems.** All of the faceted samples were cut to optimize the yield from the tabular crystals (see, e.g., figure 9). In general, they displayed an evenly distributed brown coloration, which varied from faint to Fancy Dark brown; one was near-colorless. The near-colorless crystal (no. 49806a) became Fancy brownish yellow (no. 49806b) after faceting. It is likely that this change in color was due to the heat of the faceting process, much the same way natural rough or a partially polished diamond will change color in the course of faceting. Unlike some

natural and HPHT-grown synthetic colored diamonds, no graining or color zoning was seen in the CVD samples when they were examined with magnification through the table facet. However, when observed through the girdle (which is perpendicular to the growth direction of the tabular crystals), at least one sample displayed more than five faint brown planes oriented parallel to {100} (figure 10). These represent short disruptions or changes in deposition, such as a fluctuation in temperature.

We believe that these brown planes reflect the deposition of relatively more non-diamond carbon and/or the presence of internal extended defects such as dislocations. This is different from the banded coloration seen in natural brown diamonds, which is due to plastic deformation of the diamond



Figure 8. In this 0.87 ct sample (no. 49806a), shown here from two different views, near-colorless CVD synthetic diamond has been grown over a CVD substrate, resulting in a much thicker crystal than would have been produced with an HPHT synthetic diamond substrate. Note the precipitation of graphite and non-diamond carbon around the crystal that gives rise to the dark gray to black rim. Photos by Elizabeth Schrader.

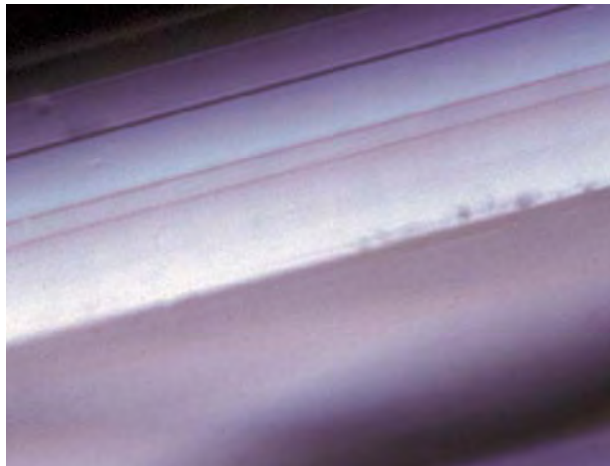


Figure 9. As these samples illustrate (left, no. 48921b at 0.14 ct; right, no. 49806b at 0.28 ct), the CVD-grown diamonds were faceted to get the best yield from the tabular crystals. The sample on the right, which was equivalent to Fancy brownish yellow, was cut from a near-colorless crystal (see table 1). It is likely that the color changed during faceting, as has been known to occur with natural diamonds. Photos by Elizabeth Schrader.

while in the earth. In the CVD material, the brown planes seem to be narrow, and they exhibit a sharper boundary, than the slip bands typically seen in natural brown diamonds (e.g., Fritsch, 1998). The overall brown color of the material, like the brown planes mentioned above, could be attributed to the presence of non-diamond carbon and/or internal extended defects such as dislocations.

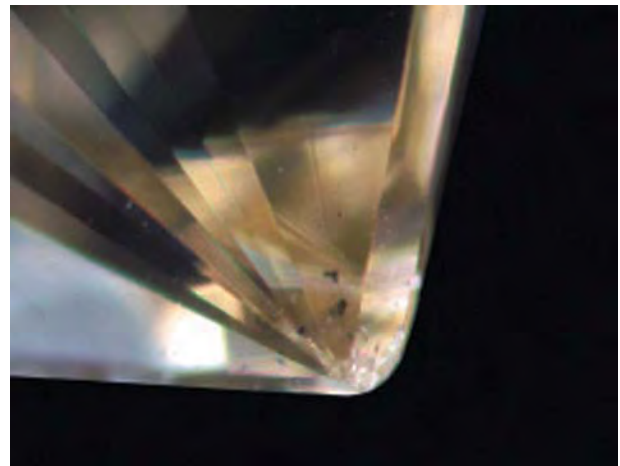
Relative to the GIA diamond grading system, the samples ranged in clarity from VS<sub>1</sub> to SI<sub>2</sub>. We observed only a few small inclusions—they were

Figure 10. When viewed perpendicular to the growth direction and the table facet {100}, this CVD-grown diamond (here, no. 57688) exhibited brown graining parallel to {100}. Photomicrograph by Wuyi Wang; magnified 30×.



opaque and irregularly shaped, possibly due to deposition of non-diamond carbon (figure 11). In addition, tiny pinpoints were common in many samples, and these were principally responsible for each sample's resulting clarity grade (figure 12). Since no metal flux/catalyst is used in the CVD growth process, the metallic inclusions that commonly occur in HPHT-

Figure 11. On occasion, CVD-grown synthetic diamonds (here, no. 49806b) display small, opaque, irregular inclusions that are thought to be particles of non-diamond carbon on the basis of Raman spectroscopy. Opaque inclusions in natural or HPHT synthetic diamonds might look similar in appearance, so these non-diamond carbon inclusions may be of little diagnostic value for identification purposes. Photomicrograph by Wuyi Wang; magnified 15×.





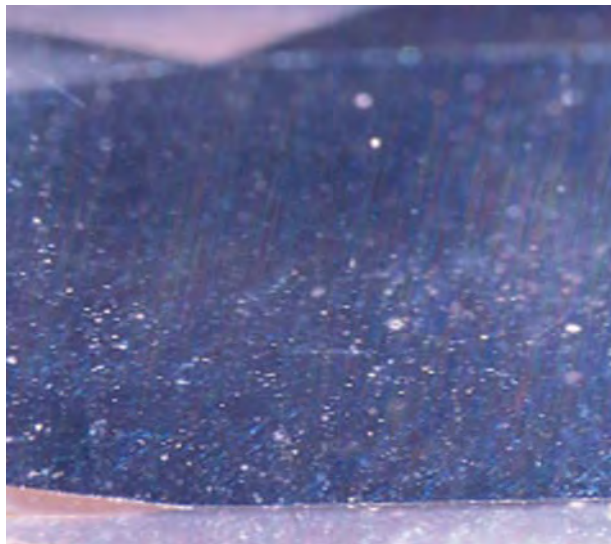


Figure 12. Pinpoint inclusions of uncertain identity were seen in some of the CVD-grown diamonds (here, no. 57688). Photomicrograph by Christopher P. Smith; magnified 30 $\times$ .

grown synthetic diamonds are absent in the Apollo material. In rare cases, small fractures were seen.

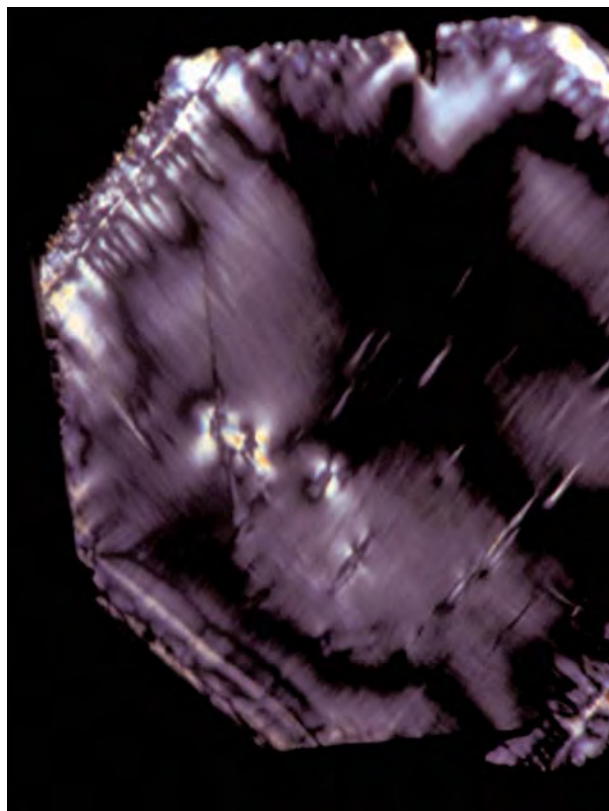
Anomalous birefringence, a typical feature of diamond, is formed due to residual internal strain. All the CVD-grown synthetic diamonds examined in this study displayed cross-hatched bands of low-order interference colors (when viewed through the table facet perpendicular to the {100} face), probably due to an uneven rate of deposition in growth. Although the table-facet orientation in a natural diamond varies according to the shape of the rough, the strain pattern is typically a much more well-defined cross-hatch pattern with higher-order interference colors, especially in type IIa diamonds. We also saw small, localized strain areas with relatively higher interference colors surrounding tiny defect centers as well as small inclusions or fractures in some of our samples (see, e.g., figure 13). Observation of such strain patterns could be considered as a strong indication of CVD-grown synthetic diamond.

**Luminescence.** As detailed in table 1, the reaction to ultraviolet radiation emitted by a standard gemological UV lamp varied among all the samples we examined. Eight were inert to long-wave UV, and the balance of those tested fluoresced a very weak orange, orange-yellow, or yellow. However, all except one (no. 58768) of the as-grown CVD samples tested showed some reaction to short-wave UV, ranging from very weak to moderate in orange to orange-yellow. In those samples where some

HPHT-synthetic diamond substrate remained, the substrate fluoresced more strongly, with a chalky green-yellow color (figure 14). In general, no phosphorescence was observed.

A characteristic feature seen in nine of the 10 CVD-grown diamonds tested is a strong orange red fluorescence when they were exposed to high-energy UV radiation in the DiamondView imaging system (figure 15). In our experience, this fluorescence is related to the emission from N-V centers (mainly 575 nm) and is very rare in natural type IIa diamonds. Note that, depending on its size, a remnant of HPHT synthetic diamond substrate in a faceted CVD diamond could have a strong impact on the DiamondView fluorescence image. In sample no. 57595, for example, the HPHT synthetic diamond substrate covers the whole {100} face, so it could entirely shield the emission from the CVD-grown diamond if the UV radiation hit the {100} face direct-

Figure 13. This crystal (no. 57595), measuring 7.1 mm across, displays the characteristic strain pattern of a CVD-grown diamond when viewed perpendicular to a cubic crystal face {100}. Photo by Wuyi Wang; crossed polarizers.



ly. When the CVD side was faced to the UV radiation, pink to orange fluorescence was observed.

**Spectroscopy. Infrared.** The infrared absorption spectra shown in figure 16 are representative of the as-grown CVD synthetic diamonds examined. Most samples displayed little absorption around the one-phonon region ( $<1332\text{ cm}^{-1}$ ; again, see table 1). Eight samples displayed a very weak absorption peak at  $1344\text{ cm}^{-1}$ , demonstrating the presence of trace amounts of isolated nitrogen impurity (typical of type Ib diamond).

Analysis of those diamonds that did not have an HPHT synthetic diamond substrate, or of selected regions where the substrates had been removed, showed that the strongest absorption at  $1344\text{ cm}^{-1}$  corresponded to an absorption coefficient of  $0.14\text{ cm}^{-1}$  (no. 56924), and the second highest was  $0.06\text{ cm}^{-1}$ . No absorption at  $1344\text{ cm}^{-1}$  was detected in four samples. These observations indicate that the nitrogen concentration differs from sample to sample, and thus the purity of CVD synthetic diamond depends on the specific conditions under which it was grown. Using the calibration of Lawson et al. (1998), we see that the highest concentration of isolated nitrogen in the studied CVD diamonds should be less than 5 ppm.

Based on a working definition of diamond types (Wilks and Wilks, 1994, pp. 75–77), all the CVD samples we examined were type IIa. Traces of hydrogen also were detected in 11 samples, as a sharp absorption peak at  $3123\text{ cm}^{-1}$  with full width at the half maximum (FWHM) varying from  $3.58$  to  $1.81\text{ cm}^{-1}$  (figure 17; also see Zaitzev, 2001, p. 32) and an absorption coefficient ranging from  $0.08$  to  $0.01\text{ cm}^{-1}$ . In all the as-grown CVD synthetic diamonds examined, only one sample (no. 56923), which was light brown, did not show this H-related

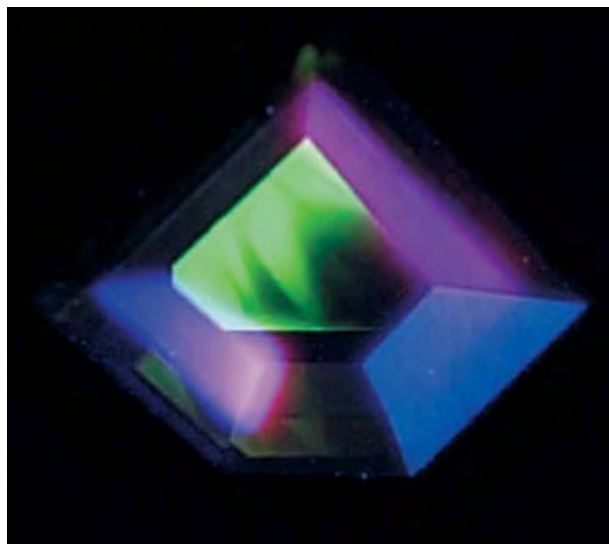
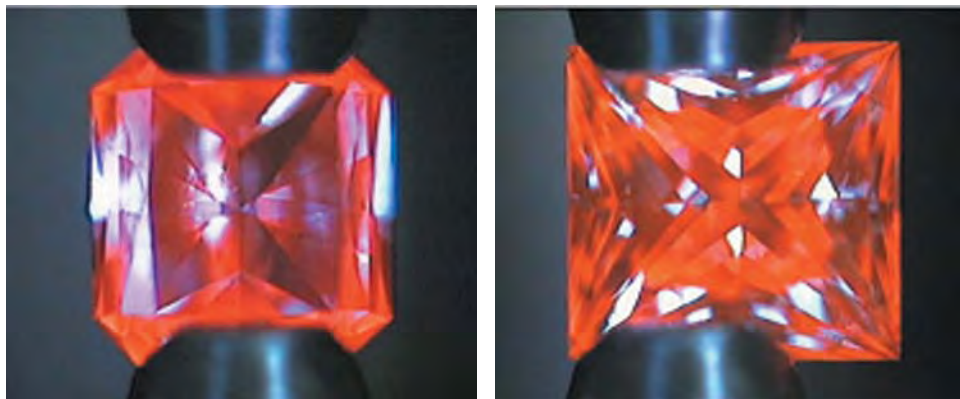


Figure 14. The CVD synthetic diamond portion of this 1.11 ct faceted sample (no. 57608) is inert to short-wave UV radiation, but the small area of HPHT-synthetic diamond substrate that remained after cutting fluoresces a strong green-yellow color. Photo by Elizabeth Schrader.

absorption. The fact that the strongest  $3123\text{ cm}^{-1}$  absorption was observed in Fancy Dark brown sample no. 56924 does not necessarily mean the coloration is due to hydrogen, since the color may be due to non-diamond carbon and/or internal extended defects while coincidentally more hydrogen was captured during growth. Hydrogen is a common impurity in natural diamond; however, the position of the fundamental C-H stretching vibration is almost always at  $3107\text{ cm}^{-1}$ .

In the near-infrared region (again, see figure 16), one or more distinct absorptions of unknown origin were observed at  $8753$ ,  $7354$ ,  $6856$ ,  $6425$ , and  $5564\text{ cm}^{-1}$  in all eight as-grown CVD synthetic diamonds analyzed, with the one at  $7354\text{ cm}^{-1}$  commonly

Figure 15. The CVD-grown diamonds examined during this study displayed a strong orangy red fluorescence when they were exposed to UV radiation in the De Beers DiamondView imaging system. The sample on the left is no. 48921b (0.14 ct); on the right is sample no. 49806b (0.28 ct). Photos by Wuyi Wang.





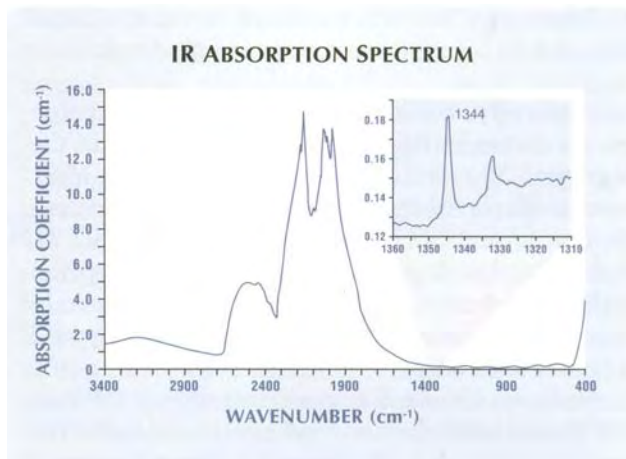
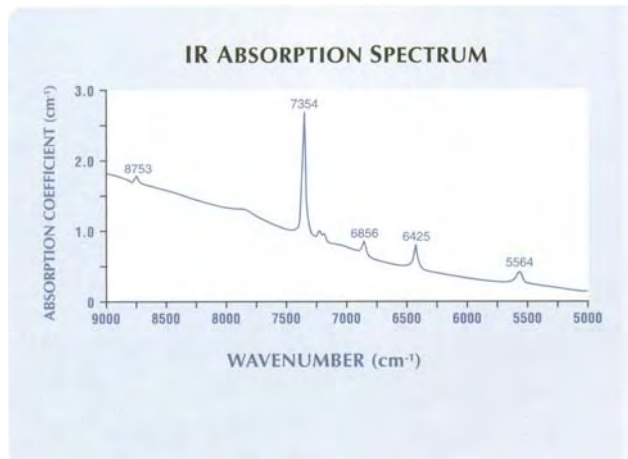


Figure 16. These infrared absorption spectra (left, sample no. 57608; right, no. 49806a) are typical of those recorded from the as-grown CVD synthetic diamonds. All samples examined were type IIa, but a few contained trace amounts of an isolated nitrogen impurity (at concentrations of less than 5 ppm, with most less than 1.0 ppm). Absorption bands at 8753, 7354, 6856, 6425, and 5564  $\text{cm}^{-1}$  were observed in all tested as-grown CVD synthetic diamonds.

showing the strongest intensity. In two samples (nos. 57595 and 57597), the peak at 6856  $\text{cm}^{-1}$  was the strongest absorption in the near-infrared region. These absorptions in the NIR range have been attributed to hydrogen impurities in as-grown CVD diamond (Fuchs et al., 1995a,b).

**UV-Vis-NIR.** Most of the samples tested displayed a smooth, gradual increase in absorption from about 500 nm toward the blue end of the spectrum. In general, the stronger brown coloration corresponded to an increase in this absorption.

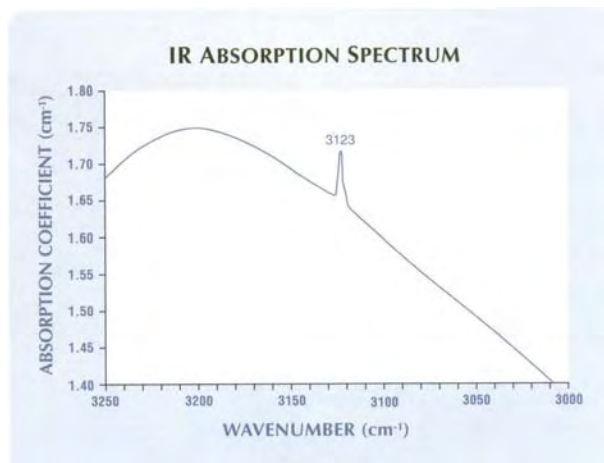
A few of the samples also showed distinct absorption lines (again, see table 1). For example, the spectrum of a dark brown CVD synthetic diamond (see figure 18, sample no. 57608) exhibited a broad band around 270 nm and two sharp absorption lines at 268 and 271 nm, all of which are related to traces of isolated nitrogen (Zaitsev, 2001, pp. 342–344). Weak but sharp lines at 447, 591, 596, 625, 637, 653, and 737 nm were also detected in this sample. In addition, a broad band around 520 nm occurred in two other samples. Among the tested samples, the FWHM of the 271 nm absorption peak varied from 0.60 to 0.85 nm.

Weak absorptions at 591 nm and/or 596 nm were detected in 11 samples. These two peaks were relatively broad, with a FWHM around 3 nm. The FWHM of absorptions at 447 nm and 625 nm is generally less than 1.0 nm. Also as described in Zaitsev (2001, pp. 197–203), the 637 nm peak is

caused by the nitrogen-vacancy (N-V center). Causes of the other peaks remain unknown, but some of them could be related to traces of hydrogen in the lattice. A weak absorption line at 737 nm, due to traces of silicon (Zaitsev, 2001, pp. 174–181), was observed in four samples.

**Photoluminescence (PL).** Despite a large variation in coloration, all the as-grown CVD synthetic dia-

Figure 17. This expanded portion of the infrared spectrum from sample no. 56924 shows a weak absorption at 3123  $\text{cm}^{-1}$  due to hydrogen as an impurity in the crystal lattice. This sample had the strongest absorption at 3123  $\text{cm}^{-1}$  of all those tested.



monds in this study showed similar PL spectra (again, see table 1 and also figure 19). When a green 514.5 nm laser was employed, the CVD samples displayed strong N-V emission lines at 575 and 637 nm. The relative intensities of these two lines varied, but in general the 575 nm was more intense. All but one of the samples also showed a doublet at 596 and 597 nm, the cause of which is uncertain. Although these two peaks may not be observable at room temperature, they are very sharp, with a FWHM of 0.30–0.38 nm and 0.28–0.37 nm, respectively.

All samples tested also had a moderately strong 737 nm emission line—actually, a doublet peak at 736.5 and 736.9 nm—due to the incorporation of trace amounts of silicon during growth. The FWHM of this peak varied from 0.91 to 1.04 nm. This peak could be very useful for identification of CVD-grown diamonds because it usually does not occur in natural diamonds or HPHT-grown synthetic diamonds (see, e.g., Zaitzev, 2001).

The He-Ne red laser at 632.8 nm is extremely efficient in exciting the silicon peak in diamond. For instance, in sample no. 58768, the concentration of Si is so low that no 737 nm emission could be

Figure 18. As was representative of the CVD synthetic diamonds examined, this UV-Vis-NIR absorption spectrum (from sample no. 57608) exhibited a broad band around 270 nm and two sharp absorption lines at 268 and 271 nm, all of which are related to trace isolated nitrogen. Weak but sharp lines at 625, 637, 653, and 737 nm were detected. Also evident were two relatively broad absorptions at 591 and 596 nm. The absorption at 737 nm is due to a trace amount of silicon. Note that a region of the sample without any HPHT synthetic diamond substrate was selected for spectroscopic analysis using a metal mask.

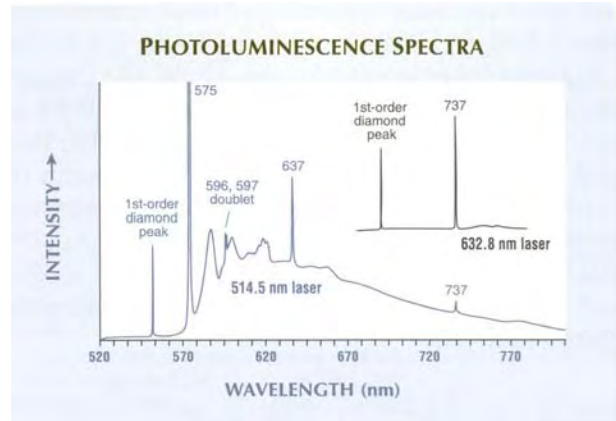
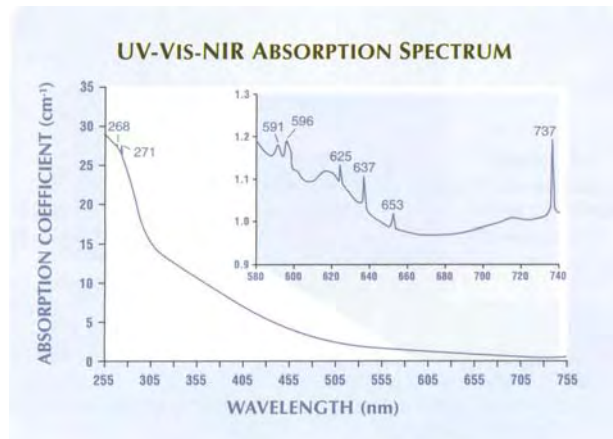


Figure 19. These representative photoluminescence spectra (here, from sample 48921a) display strong emissions from the N-V center at 575 and 637 nm, and also the sharp 596/597 nm doublet. The 737 nm emission is particularly sensitive to excitation by the 632.8 nm red laser.

detected when using the 514.5 nm laser. Weak but distinct 737 nm emission was confirmed in this sample by using the 632.8 nm laser. In addition to these strong emission lines, relatively weak lines at 543, 546, 559, 563, 588, 589, 591, 592, and 604 nm were also observed in some of the samples. In one case (no. 57597), the emission at 563 nm was as strong as the first-order diamond Raman peak. Assignment of these emission lines generally has not yet been determined.

## IDENTIFICATION

When they become available in the marketplace, CVD synthetic diamonds are likely to be difficult for a jeweler/gemologist to identify, since there are few diagnostic features that can be determined with standard gemological equipment. A brown coloration, the shallow depth of a cut stone, and the characteristic strain pattern of this CVD-grown material may provide clues in some cases. In the laboratory, the strong orange red luminescence seen with the DiamondView is generally the best visual clue to a CVD sample's identity. However, conclusive identification requires the use of advanced spectroscopic methods. All the Apollo samples examined are type IIa diamonds, although some showed an infrared absorption feature at 1344  $\text{cm}^{-1}$  due to trace amounts of isolated nitrogen. The two PL peaks related to the N-V center at 575 and

637 nm have been reported in HPHT-treated diamonds (see, e.g., Fisher and Spits, 2000), but in the CVD samples examined for this study, the intensities of both peaks were much stronger. A doublet at 596–597 nm, which has never been reported in natural diamond, was recorded in the PL spectra of almost all the samples tested. Finally, the infrared absorption due to hydrogen (mainly at 3123 cm<sup>-1</sup>) and the spectroscopic features due to silicon (at 737 nm) appear to be unique to these CVD-grown synthetic diamonds.

## CONCLUSION

Gem-quality synthetic diamonds grown by Apollo Diamond Inc. represent some of the first examples of single-crystal material produced by the CVD process that is intended for the jewelry trade. Although production is limited at present, plans call for larger-scale manufacturing of crystals weighing up to 3 ct in the near future. Faceted pieces of this material do not exhibit most of the characteristic features shown by HPHT-grown synthetic diamonds (such as pronounced color and fluorescence zoning, or metal inclusions), although they do have a distinctive strain pattern. Strong orangy red luminescence

as seen in the DiamondView provides another good indication. However, these CVD-grown synthetic diamonds can be positively identified only by spectroscopy, with instrumentation that typically is available only in advanced gemological laboratories.

Given the range of potential technological applications, further improvements in CVD growth processes are likely. Various additional kinds of CVD synthetic diamonds could become available in the future. These include high-purity colorless crystals and crystals that are blue due to the incorporation of boron. Also possible is the crystallization of CVD material on a natural gem diamond, either on a rough crystal that is then faceted, or perhaps as an overgrowth on portions of a faceted diamond, depending on its crystallographic orientation. These products may or may not exhibit the features described in this article. It is also important to note that the diagnostic absorption or emission features observed in the spectra of the CVD synthetic diamonds examined so far could be below the instrument detection limit with improved purity of this material. Gemological laboratories and others involved with gem identification must continue to develop techniques to recognize these new kinds of gem materials as they become available.

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Dr. Wang is a research scientist, Mr. Moses is vice president of Identification and Research, and Mr. Hall is supervisor of analytical equipment at the GIA Gem Laboratory, New York; Dr. Linares is chairman, Apollo Diamond Inc., Boston, Massachusetts; Dr. Shigley is director of GIA Research in Carlsbad, California; and Dr. Butler is head of the Gas/Surface Dynamics Section in the Naval Research Laboratory, Washington, D.C.

**ACKNOWLEDGMENTS:** Constructive reviews were provided by Prof. Alan Collins of Kings College, London, and Dr. Emmanuel Fritsch of the University of Nantes, France. HPHT annealing of the CVD synthetic diamonds was performed by Sundance Diamond in Orem, Utah, and Phoenix Crystal Corp. in Ann Arbor, Michigan. The authors are grateful to Mates Witriol of New York for repolishing two of the HPHT-annealed diamonds. Afkari & Sons Inc. of New York kindly mounted some of the CVD synthetic diamonds in jewelry.

## REFERENCES

- Angus J.C. (1994) Development of low-pressure diamond growth in the United States. In K.E. Spear and J.P. Dismukes, Eds., *Synthetic Diamond: Emerging CVD Science and Technology*, John Wiley & Sons, New York, pp. 21–39.
- Butler J.E., Woodin R.L. (1993) Thin film diamond growth mechanisms. *Philosophical Transactions of the Royal Society of London*, Vol. A342, pp. 209–224.
- Burns R.C., Davies G.J. (1992) Growth of synthetic diamond. In J.E. Field, Ed., *The Properties of Natural and Synthetic Diamond*, Academic Press, London, pp. 395–422.
- Crowningshield G.R. (1971) General Electric's cuttable synthetic diamonds. *Gems & Gemology*, Vol. 13, No. 10, pp. 302–314.
- Davies G. (1994) *Properties and Growth of Diamond*. Electronic Materials Information Service (EMIS) Dataviews Series No. 9, Institute of Electrical Engineers, London.
- Davis R.F. (1993) *Diamond Films and Coatings—Development, Properties, and Applications*. Noyes Publications, Park Ridge, NJ, 421 pp.
- De Beers Industrial Diamonds, Spits R.A., Burns R., Fisher D. (2001) *High Temperature/Pressure Color Change of Diamond*. International (PCT) patent application WO 01/72404A1, filed April 2.



- Deljanin B., Hainschwang T., Fritsch E. (2003) Update on study of CVD diamonds. *Jewellery News Asia*, No. 231, November 2003, pp. 134–139.
- Field J.E. (1992) *The Properties of Natural and Synthetic Diamond*. Academic Press, London.
- Fisher D., Spits R.A. (2000) Spectroscopic evidence of GE POL HPHT-treated natural type IIa diamonds. *Gems & Gemology*, Vol. 36, No. 1, pp. 42–49.
- Fritsch E., Conner L., Koivula J.I. (1989) A preliminary gemological study of synthetic diamond thin films. *Gems & Gemology*, Vol. 25, No. 2, pp. 84–90.
- Fritsch E. (1998) The color of diamond. In G. E. Harlow, Ed., *The Nature of Diamonds*, Cambridge University Press, pp. 23–47.
- Fuchs F., Wild C., Schwarz K., Muller-Sebert W., Koidl P. (1995a) Hydrogen induced vibrational and electronic transitions in chemical vapor-deposited diamond, identified by isotopic substitution. *Applied Physics Letters*, Vol. 66, No. 2, pp. 177–179.
- Fuchs F., Wild C., Schwarz K., Koidl P. (1995b) Hydrogen-related IR absorption in chemical vapor deposited diamond. *Diamond and Related Materials*, Vol. 4, Nos. 5/6, pp. 652–656.
- Goodwin D.G., Butler J.E. (1997) Theory of diamond chemical vapor deposition. In M.A. Prelas, G. Popovici, and L.K. Bigelow, Eds., *Handbook of Industrial Diamonds and Diamond Films*, Marcel Dekker, New York, pp. 527–581.
- Hunter G., Paparella A. (2003) New diamond age? Lab-made diamonds are dead ringers for natural ones. ABCNews.com, [http://abcnews.go.com/sections/GMA/SciTech/GMA030909Diamond\\_synthetics\\_hunter.html](http://abcnews.go.com/sections/GMA/SciTech/GMA030909Diamond_synthetics_hunter.html), posted Sept. 9, 2003.
- Lawson S.C., Fisher D., Hunt D.C., Newton M. (1998) On the existence of positively-charged single-substitutional nitrogen in diamond. *Journal of Physics C: Condensed Matter*, Vol. 10, No. 27, pp. 6171–6180.
- Linares R.C., Doering P. (1999) Properties of large single crystal diamond. *Diamond and Related Materials*, Vol. 8, Nos. 2/5, pp. 909–915.
- Linares R.C., Doering P.J. (2003) *System and Method for Producing Synthetic Diamond*. U.S. Patent 6,582,513, filed May 14, 1999.
- Ravi K.V. (1994) Technological applications of CVD diamond. In K.E. Spear and J.P. Dismukes, Eds., *Synthetic Diamond: Emerging CVD Science and Technology*, John Wiley & Sons, New York, pp. 533–580.
- Shigley J.E., Fritsch E., Reinitz I., Moses T.E. (1995) A chart for the separation of natural and synthetic diamonds. *Gems & Gemology*, Vol. 31, No. 4, pp. 256–264.
- Spear K.E., Dismukes J.P. (1994) *Synthetic Diamond: Emerging CVD Science and Technology*. John Wiley & Sons, New York, 663 pp.
- Wang W., Hall M., Moses T.M., Shigley J.E. (2003) Gem News International: Chemical vapor deposition (CVD)—A new source of gem-quality laboratory-created diamond. *Gems & Gemology*, Vol. 34, No. 3, pp. 237–239.
- Welbourn C.M., Cooper M., Spear P.M. (1996) De Beers natural versus synthetic diamond verification instruments. *Gems & Gemology*, Vol. 32, No. 3, pp. 156–169.
- Wilks E., Wilks J. (1994) *Properties and Applications of Diamond*. Butterworth-Heinemann, Oxford, 525 pp.
- Zaitsev A.M. (2001) *Optical Properties of Diamond*. Springer-Verlag, Berlin, 502 pp.

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