STRONGLY COLORED PINK CVD LAB-GROWN DIAMONDS

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This study characterizes CVD laboratory-grown diamonds from Apollo Diamond Inc. that have strong pink colors produced by high concentrations of NV centers. The samples examined weighed ~0.3–0.7 ct, and their color and clarity grades were comparable to top natural pink diamonds. A combination of optical centers were detected using photoluminescence and absorption spectroscopy. These centers are similar to those seen in previously studied pink-to-red diamonds that have been exposed to HPHT annealing, followed by irradiation and annealing at relatively low temperatures. These pink CVD products can be separated from natural and treated-color natural pink diamonds by a combination of gemological and spectroscopic properties, such as fluorescence color, growth zoning, and absorption features in the infrared and UV-Vis regions.

I n the past decade, significant progress has been made with synthetic diamonds produced by the chemical vapor deposition (CVD) method. Not only are larger sizes and better qualities being reported in the as-grown material, but multiple treatments have been applied to some CVD synthetic diamonds to improve their color after initial growth (e.g., Linares and Doering, 1999, 2010; Martineau et al., 2004; Yan et al., 2004; Meng et al., 2008; Wang and Johnson, 2010). Faceted CVD-grown diamonds are being traded in the jewelry market, with a few having been identified in gem laboratories during routine testing (e.g., Chadwick, 2008a,b; Wang, 2009; Kitawaki et al., 2010).

As grown, gem-quality CVD synthetic diamonds are typically colorless, near-colorless, or various tones of brown. Other colors can be introduced by modifying the occurrence or arrangements of particular lattice defects, either during growth or with post-growth treatments. In this study, we describe a group of strongly colored pink CVD lab-grown diamonds (e.g., figure 1) provided for examination by Apollo Diamond Inc. Standard gemological properties and spectroscopic data are presented, as well as key identification features that help separate these new products from natural, treated-natural, and HPHT-grown synthetic pink diamonds.

MATERIALS AND METHODS

Apollo Diamond provided 19 faceted CVD lab-grown diamonds to the GIA Laboratory for examination (table 1). They ranged from 0.27 to 0.72 ct, and showed remarkably saturated pink coloration. These CVD lab-grown diamonds are representative of the current pink-colored production process used at Apollo Diamond.

Experienced diamond grading staff determined

color and clarity grades using GIA's grading systems (see, e.g., King et al., 1994). Internal features were examined with both a standard gemological binocular microscope and a research-grade microscope, using a variety of lighting techniques. Reactions to ultraviolet (UV) radiation were checked in a darkened room with a conventional four-watt combination long-wave (365 nm) and short-wave (254 nm) UV lamp. We also examined all samples for fluorescence, phosphorescence, and growth characteristics using the Diamond Trading Company (DTC) DiamondView instrument (e.g., Welbourn et al., 1996). Phosphorescence images were collected with a 0.1 second delay and 5 seconds of exposure duration.

All spectroscopic analyses were conducted on all samples. We performed infrared absorption spectroscopy for the mid-IR (6000–400 cm^{-1}, at 1 cm^{-1} resolution) and near-IR (up to 11000 cm^{-1}, at 4 cm^{-1} resolution) ranges at room temperature with a Thermo-Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer equipped with KBr and quartz beam splitters. A beam condenser (6×) was employed to focus the incident beam on the sample, and we collected as many as 256 scans per spectrum to improve the signal-to-noise ratio. Dry N_2 gas was used to purge the sample chamber to reduce interference from CO_2 and water vapor in air. The spectra in the mid-IR region were normalized based on the two-phonon absorptions of diamond, and in the near-IR region based on its three-phonon absorptions. This allowed us to calculate absorption coefficients, as well as peak intensities and impurity concentrations.

Absorption spectra in the ultraviolet through visible to near-infrared range (UV-Vis-NIR, 250–1000 nm) were recorded with a custom-built instrument using multiple Avantes spectrometers, broad-band light sources, and CCD detectors. This high-resolution instrumentation enabled the detection of very weak and sharp absorptions in the UV-Vis-NIR region at liquid nitrogen temperature. The sampling interval in this four-channel device was 0.04–0.07 nm depending on specific wavelength ranges, with an entrance slit width in each spectrometer of 10 µm. A better than 0.2 nm spectral resolution was achieved. A very good signal-to-noise ratio was produced with 200 scans per spectrum. Samples were immersed in a specially designed liquid nitrogen bath which contains multiple layers of liquid nitrogen (patent pending), ensuring consistent temperature as well as a stable envi-

Figure 1. These CVD lab-grown diamonds (0.27–0.62 ct; sample nos. top–APD-8097, APD-9747, and bottom–APD-17, APD-21), produced recently by Apollo Diamond Inc., show strong pink colors that are comparable to top natural pink diamonds. They were color graded Fancy Intense to Fancy Vivid pink to purplish pink. Composite photo by Jian Xin (Jae) Liao.

ronment free of nitrogen gas bubbles.

The same cooling device was also used for photoluminescence (PL) spectral analysis with a Renishaw InVia Raman confocal microspectrometer. Four lasers with five excitation wavelengths were employed to activate various types of defects. An argon-ion laser was operated at two excitation wavelengths: 488.0 nm (for the range 490–850 nm) and 514.5 nm (for the range 517–850 nm). PL spectra were collected in the 640–850 nm range using a He-Ne laser (632.8 nm), and in the 835–1000 nm range using a diode laser (830.0 nm). In addition, a He-Cd metal-vapor laser (325.0 nm) was used for the 370–800 nm range. Up to three scans were accumulated for all PL analyses to achieve a better signal-to-noise ratio.

RESULTS

Color. All the samples had a strongly saturated pink hue, with color grades ranging from Fancy Intense

Sample no.	Weight (ct)	Cut	Color	Clarity	Fluorescence to long-wave UV	Fluorescence to short-wave UV
APD-11	0.63	Round brilliant	Fancy Vivid purple pink	VS$_1$	Strong orange	Moderate orange
APD-12	0.63	Rectangular brilliant	Fancy Vivid purplish pink	VS$_1$	Strong orange	Strong orange
APD-13	0.61	Round brilliant	Fancy Vivid purple pink	VS$_1$	Strong orange	Moderate orange
APD-14	0.65	Round brilliant	Fancy Vivid purplish pink	VS$_2$	Strong orange	Moderate orange
APD-15	0.72	Rectangular brilliant	Fancy Deep purplish pink	VS$_2$	Strong orange	Strong orange
APD-16	0.64	Round brilliant	Fancy Intense purplish pink	VS$_2$	Strong orange	Strong orange
APD-17	0.62	Rectangular brilliant	Fancy Deep pink	VS$_1$	Strong orange	Moderate orange
APD-18	0.45	Round brilliant	Fancy Intense pink	VS$_1$	Strong orange	Moderate orange
APD-19	0.53	Square brilliant	Fancy Intense pink	VS$_1$	Moderate orange	Moderate orange
APD-20	0.61	Round brilliant	Fancy Intense pink	VS$_1$	Moderate orange	Moderate orange
APD-21	0.27	Square brilliant	Fancy Vivid pink	VS$_2$	Strong orange	Moderate orange
APD-22	0.38	Rectangular brilliant	Fancy Deep pink	SI$_1$	Moderate orange	Moderate orange
APD-8094	0.48	Round brilliant	Fancy Vivid purplish pink	VS$_1$	Strong orange	Strong orange
APD-8095	0.67	Round brilliant	Fancy Vivid purple pink	VS$_1$	Strong orange	Strong orange
APD-8096	0.28	Round brilliant	Fancy Intense purplish pink	VVS$_2$	Moderate orange	Strong orange
APD-8097	0.36	Round brilliant	Fancy Intense purplish pink	VS$_1$	Strong orange	Strong orange
APD-9747	0.60	Rectangular brilliant	Fancy Vivid purple pink	VS$_1$	Moderate orange	Moderate orange
APD-9748	0.64	Round brilliant	Fancy Intense pink	VS$_2$	Moderate orange	Moderate orange
APD-9749	0.47	Round brilliant	Fancy Deep purplish pink	SI$_2$	Moderate orange	Moderate orange

to Fancy Deep (again, see figure 1 and table 1). Seven samples were pure pink; the remaining 12 also had a purple component. In general, all the CVD-grown diamonds showed even color distribution with no visible color concentrations.

Clarity. The samples had relatively high clarity. As shown in table 1, most (16) were given VS clarity grades, one was VVS, and only two received SI grades. Clarity grades were usually impacted by pinpoints and small black inclusions with irregular shapes (probably non-diamond carbon; figure 2). Small radial fractures were observed surrounding some of the relatively large inclusions. Typically, the small inclusions and pinpoints were randomly distributed. In two samples, they occurred together in cloud-like groups.

Reaction to UV Radiation. All the samples consistently showed moderate-to-strong orange fluorescence to both long- and short-wave UV radiation. Obvious turbidity (i.e., "chalkiness") was also observed. No phosphorescence to conventional long- or short-wave UV radiation was seen.
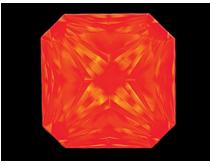
When exposed to the high-intensity ultra-short UV wavelength of the DTC DiamondView (~225 nm), all samples showed strong orange or orangy red fluorescence (figure 3). The fluorescence was evenly distributed in only three of the samples; all others had bands of weaker orange color. In general, the fluorescence bands were uniform in thickness—though thickness varied in portions of some samples—with sharp, well-defined boundaries that were oriented nearly parallel to the table facet (figure 3, center and right). Narrow growth striations, a common feature in CVD-grown diamond, were
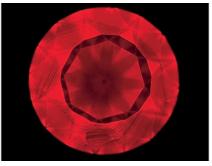

Figure 2. Most of the samples had VS clarity grades. The internal features that most affected clarity were small black inclusions (left, image width 1.4 mm) with irregular morphology and occasionally with small radial fractures, and pinpoints (right, image width 1.7 mm). Photomicrographs by W. Wang.
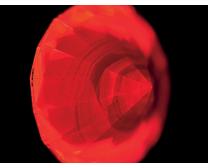
Figure 3. These pink CVD-grown diamonds display strong orange to orangy red fluorescence in the DiamondView. The fluorescence is typically chalky, as shown on the left (0.63 ct). Most samples showed bands of weaker orange fluorescence oriented nearly parallel to the table face (center and right; 0.28 and 0.47 ct, respectively). Characteristic striated growth features also are readily seen in the center sample. Photos by W. Wang.

NEED TO KNOW

- CVD laboratory-grown diamonds from Apollo Diamond Inc. have strongly saturated pink colors produced by high concentrations of NV centers.

- The samples show distinctive moderate-to-strong orange UV fluorescence (typically banded) to both long- and short-wave UV radiation.

- Internal graining, high strain, and zoned orange fluorescence, along with spectral features, distinguish these from similar-appearing natural, treated, and other synthetic diamonds.

observed in the DiamondView fluorescence of many of the samples. In addition, all samples had a weak-to-moderate orange-red phosphorescence reaction in the DiamondView (see images in the *G&G* Data Depository at www.gia.edu/gandg).

Graining and Birefringence. Graining was a common feature in all the Apollo CVD lab-grown diamonds studied. However, in contrast to that observed in natural diamonds, the internal graining in most of the CVD samples had indistinct boundaries. A few samples, however, had graining with relatively well-defined linear outlines (figure 4).

Varying intensity of anomalous double refraction was another important feature. When we viewed these synthetic diamonds with magnification and crossed polarizers, we saw low- to very high-order interference colors including red, blue, green, and even white (figure 5), with irregular, linear, or occasionally cross-hatched "tatami" type patterns. Extremely high-order interference colors with characteristic symmetrical patterns were com-

monly seen surrounding small black inclusions—a good indication of high localized internal strain.

Wang et al. (2007) reported the presence of distinct laser grooves on some of the cylindrical CVD samples they documented. The grooves remained on the girdles after the samples were faceted. In this study, similar laser grooves were observed on two of the samples that had unpolished girdles. In both samples, however, they were far less apparent than on the faceted samples examined for the earlier report, with the edges being more rounded (figure 6).

Infrared Absorption Spectroscopy. Defect-related absorptions were observed in three IR regions (1500–1100, 3300–2700, and 7000–5800 cm^{-1}). The main features in the 1500–1100 cm^{-1} region (figure 7) included a sharp peak at 1344 cm^{-1} and a broad band at ~1130 cm^{-1} attributed to isolated nitrogen, a

Figure 4. Internal graining was difficult to see in this group of CVD lab-grown diamonds. In a few samples, the graining formed straight lines. Photomicrograph by W. Wang; image width 2.1 mm.

Figure 5. Anomalous double refraction commonly was seen as low- to high-order interference colors in the samples (left, image width 2.2 mm). Very high-order interference colors also surround this black inclusion (right, image width 1.8 mm). Photomicrographs by W. Wang.

sharp and relatively strong peak at 1332 cm^{-1} possibly from positively charged nitrogen (N$^+$; Lawson et al., 1998), a sharp H-related peak at 1405 cm^{-1}, and absorption from the H1a defect at 1450 cm^{-1}. The H1a center is commonly observed in nitrogen-containing diamonds that have been irradiated and subsequently annealed at relatively low temperatures (~300°C; Clark et al., 1956). A few other sharp peaks at 1502, 1379, 1375, 1363, and 1341 cm^{-1} were also observed, but their assignments are not clear—except for the 1502 cm^{-1} peak, which is ascribed to interstitial nitrogen and may arise from a different charge state of the H1a center (Collins et al., 1988). In addition, we saw a broad band at ~1295 cm^{-1}, which was positioned significantly higher than the A form of aggregated nitrogen (1280 cm^{-1}). These absorption features were detected in all samples, but with some obvious variations in intensity. For example, the peak at 1341 cm^{-1} ranged from being as strong as the 1344 cm^{-1} peak to as weak as a minor shoulder. In general, though, these absorptions were very weak in intensity.

Since nitrogen impurities were detectable in all samples with IR spectroscopy, they were considered type I diamonds, despite being very close to type IIa. The intensity of the N-related 1344 cm^{-1} peak varied from 0.07 to 0.17 cm^{-1}, corresponding to 1.2–2.9

ppma of isolated nitrogen. Pink CVD lab-grown diamonds from Apollo examined by Wang et al. (2007) contained comparable amounts of isolated nitrogen, but those stones showed no IR features at 1502, 1450 (H1a), 1405, or 1295 cm^{-1} (again, see figure 7).

In the 3300–2700 cm^{-1} region (figure 8), the dominant absorption feature is the H-related band at 3107 cm^{-1} (0.23–0.82 cm^{-1} in intensity). The CVD-specific H-related peak at 3123 cm^{-1} is comparatively much weaker (0.01–0.03 cm^{-1}). Other absorptions in this region include weak peaks at 3310, 3030, 2990, 2975, 2949, and 2786 cm^{-1}, and broad bands at 2917, 2879, and 2835 cm^{-1}. Assignments of these absorptions in general are unclear. Note that the H-related peak at 3107 cm^{-1} was not detected in the pink Apollo CVD lab-grown diamonds examined previously (figure 8, bottom spectrum; Wang et al., 2007) or in other CVD samples from the same source (Wang et al., 2003).

Two extremely weak absorption peaks were detected in the near-IR region, at 6902 and 5892 cm^{-1} (figure 9). These peaks have not been reported previously in CVD synthetic diamonds. Their intensities varied from 0.004 to 0.025 cm^{-1}, with a good positive correlation (see *G&G* Data Depository) that suggested they may originate from the same defect. The absorption at 7353 cm^{-1} and numerous other peaks

Figure 6. Two of the samples showed laser grooves on their girdles. Compared to the laser grooves seen on other CVD synthetic diamonds in a previous study (left; Wang et al., 2007), the grooves are not as sharp (right). Photomicrographs by W. Wang; image widths 1.1 mm (left) and 1.9 mm (right).
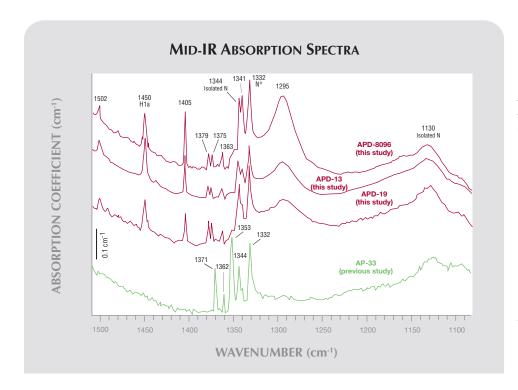
Mid-IR Absorption Spectra

Figure 7. In the 1500–1100 cm⁻¹ region of the IR spectrum, three representative pink CVD samples from the present study mainly show features due to isolated nitrogen, H-related defects, H1a, and possibly N⁺, as well as several smaller unassigned absorptions. The band at ~1295 cm⁻¹ is significantly higher in wavenumber than that due to the A-form of aggregated nitrogen in diamond (1280 cm⁻¹). A representative spectrum (AP-33) from pink CVD synthetic diamonds previously reported by Wang et al. (2007) is shown for comparison. Spectra are shifted vertically for clarity.

reported in the previously examined pink CVD synthetic diamonds (Wang et al., 2007; not shown here) were not detected in the current samples.

UV-Vis-NIR Absorption Spectroscopy. Consistent and strong absorption features in our high-resolution spectra included 574.9 (NV⁰), 594.3, and 637.0 (NV⁻) nm, and their sidebands (figure 10). The peak at 594.3 nm is usually referred to as the "595 nm" feature in gemological publications, and is typical of high-energy-beam irradiation and annealing (e.g., Collins, 1982). A weak absorption from the H3
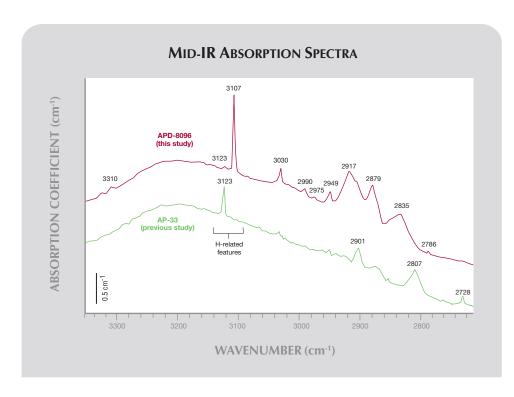
Mid-IR Absorption Spectra

Figure 8. In contrast to typical CVD synthetic diamonds, the 3123 cm⁻¹ optical center in these newer pink CVD products was very weak relative to the 3107 cm⁻¹ H-related peak. The latter peak is usually absent from CVD synthetic diamonds, as shown by the representative spectrum of sample AP-33. Spectra are shifted vertically for clarity.
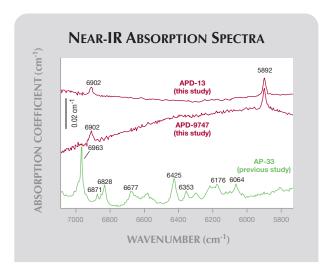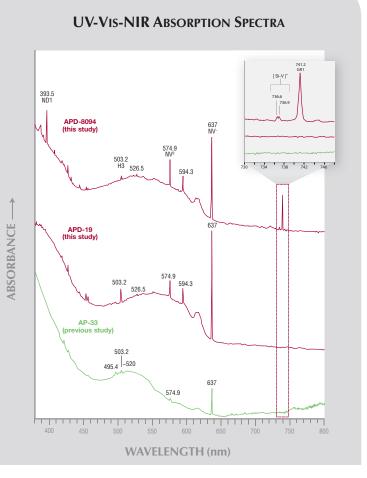
NEAR-IR ABSORPTION SPECTRA

Figure 9. In the near-IR region, weak optical centers with correlative intensity were detected at 6902 and 5892 cm⁻¹. These peaks have not been reported in CVD-grown diamonds, while several other near-IR features typical of such products (e.g., spectrum of earlier sample AP-33) were not detected in this new group of samples. Spectra are shifted vertically for clarity.

UV-VIS-NIR ABSORPTION SPECTRA

defect (503.2 nm) and a strong, broad band from isolated nitrogen centered at ~270 nm (not shown in the figures; Dyer et al., 1965) were also observed in all samples. It is important to note that the isolated-nitrogen concentration was high enough to be detected with both IR and UV-Vis absorption spectroscopy.

A sharp GR1 line with a zero phonon line (ZPL) at 741.2 nm and its related sidebands were recorded at varying intensities in all but two of the pink CVD samples. In those with a relatively strong GR1 line, additional absorptions from the ND1 defect (negatively charged vacancy) with ZPL at 393.5 nm and the [Si-V]⁻ defect (doublet at 736.6/736.9 nm) were also observed (figure 10, inset). Only four samples did not show these Si-related absorptions in the UV-Vis-NIR spectra. In addition, several weak, sharp absorptions—including at 404.8, 424.7, 429.5, 430.4, 441.9, 451.6, 454.3, and 454.7 nm—were consistently observed but not attributed (figure 11).

Photoluminescence and Raman Spectroscopy. Many PL emission lines were recorded using five laser excitations in the UV-to-IR region. Some emission systems were observed with multiple excitation wavelengths. The major PL features are summarized below on the basis of individual laser excitation in each defect's most sensitive region.

With UV laser excitation (325.0 nm; figure 12), the major and consistent emissions in all samples included two weak but clear lines at 388.9 and 415.2 (N3) nm, with clear side bands at ~430 and ~440 nm that were associated with the N3 ZPL. (Note that PL side bands are located on the opposite side of the ZPL than they are in absorption spectroscopy.) The sharp line at 388.9 nm and the related broad bands at ~400 and 410 nm are attributed to the 389 nm center, which previously has been associated with radiation damage in all types of diamonds and is particularly strong in those containing isolated nitrogen (Zaitsev, 2001).

Figure 10. Strong absorptions due to the NV centers with ZPLs at ~637 and 574.9 nm effectively absorb light in the yellow, green, and orange regions of the visible spectrum, and create transmission windows above 637 nm (red) and at ~450 nm (blue component). In addition, defects such as GR1, 594.3 nm, and ND1 with varying intensities were detected. A representative spectrum of an earlier pink CVD synthetic diamond (AP-33) is shown for comparison. The inset shows the GR1 and [Si-V]⁻ centers. Spectra are shifted vertically for clarity.
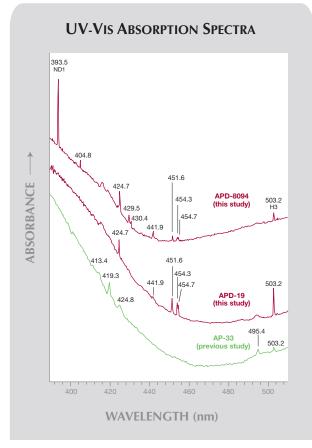
UV-VIS ABSORPTION SPECTRA

Figure 11. Several weak and sharp optical centers, such as those at 404.8, 424.7, 429.5, 430.4, 441.9, 451.6, 454.3, and 454.7 nm, were consistently observed in the absorption spectra of the present samples in the blue light region. These peaks have not been reported in previous CVD synthetic diamonds (e.g., AP-33). Spectra are shifted vertically for clarity.

PL spectra collected using blue laser (488.0 nm) excitation revealed relatively strong and consistent emissions in the 490–510 nm region (figure 13). Assignable emissions included the H4 (495.9 nm), H3 (503.2 nm), and 3H (503.5 nm) defects. Intensity of 3H emission varied significantly between samples, and did not show a clear correlation with other absorption or emission features. The 3H peak was clearly separated from H3 in four samples, occurred as a weak shoulder in six, and was not detected in the other nine. In addition, emissions at 498.2 and 505.0 nm were observed. All the emission centers described here were also present in the UV-Vis-NIR absorption spectra, but were weak due to a lower signal-to-noise ratio.

Green laser (514.5 nm) excitation revealed strong
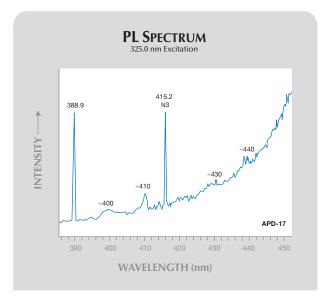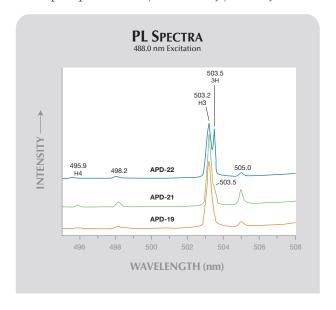

PL SPECTRUM
325.0 nm Excitation

Figure 12. The PL spectra of all samples with 325.0 nm UV laser excitation revealed a line at 388.9 nm and a portion of the N3 system with ZPL at 415.2 nm.

NV center emission systems in all samples, with ZPLs at 574.9 and 637.0 nm (figure 14). The 574.9 nm line was generally stronger. The 637.0/574.9 intensity ratio ranged from 0.10 to 0.90, with an

Figure 13. Relatively strong and consistent PL emissions in the 490–510 nm region were observed with 488.0 nm laser excitation, including H4, H3, and 3H. The intensity of the 3H emission varied significantly from sample to sample. Spectra are shifted vertically for clarity.

PL SPECTRA
488.0 nm Excitation

PL Spectra
514.5 nm Excitation

574.9
NV⁰ → NV^0

594.3

637.0
NV⁻ → NV^-
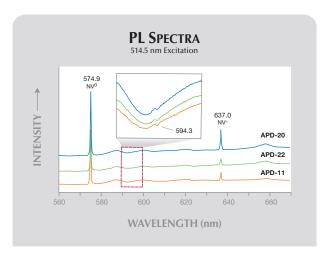
APD-20
APD-22
APD-11

WAVELENGTH (nm)
INTENSITY

Figure 14. Green laser (514.5 nm) excitation revealed strong PL emission systems of NV centers in all the pink CVD-grown diamonds, with ZPLs at 574.9 and 637.0 nm. A doublet at 596.5 and 597.0 nm is common in CVD synthetic diamonds, but is absent here. Instead, a negative peak at 594.3 nm, also detected in the UV-Vis absorption spectra, is observed. Spectra are shifted vertically for clarity.

average of 0.34. The full width at half maximum (FWHM) of the 574.9 nm peak showed limited variation of 0.32–0.47 nm, with an average of 0.38 nm. In contrast, the FWHM of the 637.0 nm line varied from 0.35 to 0.74 nm, with an average of 0.50 nm. There was a positive correlation between the FWHMs of these two peaks, as seen in natural-color and HPHT-treated natural type IIa diamonds (see *G&G* Data Depository).

Doublet emission at 596.5 and 597.0 nm has been documented as a common feature of colorless, near-colorless, and brown CVD synthetic diamonds (Wang et al., 2003, 2007), but it was not detected in this group of pink CVD lab-grown stones. Instead, a negative peak at 594.3 nm, which was easily detected with UV-Vis absorption spectroscopy, was observed in the PL spectra. A similar negative GR1 peak (ZPL at 741.2 nm) was seen in all samples in which UV-Vis detected a GR1. (These negative peaks are actually caused by absorption features present when a luminescence spectrum is collected.) Due to the strong fluorescence from NV centers, Si-related defects could not be detected with 514.5 nm laser excitation.

When excited by a red laser (632.8 nm), the doublet emissions caused by the [Si-V]⁻ defect at 736.6 and 736.9 nm (generally referred to as the 737 nm
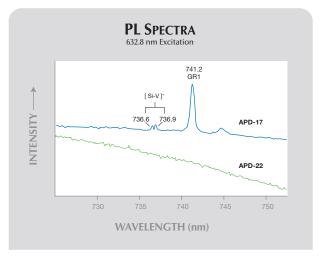
defect: Vavilov et al., 1980; Clark et al., 1995; Iakoubovskii et al., 2001) were confirmed in all but four samples (figure 15). In addition, emission from GR1 (741.2 nm) was observed in all but five samples. Of those that did not show GR1, three also had no detectable Si-related features, suggesting a possible correlation between these defects. Also, weak but consistent emissions at 796.9 and 806.4 nm (not shown) were observed in all samples. These features have not been reported in other CVD synthetic diamonds, and their assignments are unknown.

Analysis with the 830.0 nm laser revealed a weak but sharp emission at 945.5 nm in all samples from another Si-related defect, [Si-V]⁰ (Evans et al., 2006). An emission at 949.0 nm, assignment of which is not available, also occurred. Many other weak lines were detected in the 840–910 nm region, including those at 866.7, 867.8, 876.7, and 878.3 nm, which are not attributable.

DISCUSSION

The pink Apollo CVD lab-grown diamonds examined here are notably different from previous gem-quality CVD products, which were colorless, near-colorless, or some shade of brown. Although pink CVD synthetic diamonds were reported by Wang et al. (2007), the strong pink hue and even color distri-

Figure 15. The 736.6 and 736.9 nm doublet due to [Si-V]⁻ was recorded with varying intensity in the PL spectra of most of the present samples. The 632.8 nm laser was the most sensitive excitation for detecting this center, which was not resolved with the 514.5 nm laser. A weak correlation between this center and the GR1 was observed. Spectra are shifted vertically for clarity.

PL Spectra
632.8 nm Excitation

741.2
GR1

[Si-V]⁻

736.6   736.9

APD-17

APD-22

WAVELENGTH (nm)
INTENSITY

bution of the present samples are distinctive, and unlike those normally seen in natural or treated pink diamonds (e.g., Wang, 2009). In contrast to most previously examined CVD synthetics (Wang et al., 2003, 2007), these new samples did not contain surface-reaching fractures. The moderate-to-strong orange UV fluorescence to both long- and short-wave UV radiation was notably different from that previously reported for pink CVD lab-grown diamonds from Apollo (Wang et al., 2007), which displayed only very weak to weak orange to orangy yellow fluorescence to short-wave UV. The banded nature of the fluorescence in most of the new products is typical of CVD-grown diamonds. The high-order interference colors seen between crossed polarizers were in sharp contrast to the gray colors that are typical of natural type IIa diamonds, but comparable to other single-crystal CVD-grown diamonds.

The strong pink coloration of these new CVD samples is caused by NV centers, which efficiently absorb most yellow, green, and orange wavelengths. As a result, two transmission "windows" are created in the visible-light spectrum: one at a slightly higher wavelength than 637 nm, introducing a pink-to-red hue component to the bodycolor; and the other centered at ~450 nm, passing blue light and thus producing a blue component. Depending on the intensity of the blue transparency, many of the samples exhibited a strong pink color with varying amounts of a purple modifier. For example, the wavelength of maximum transmission in the blue region for sample APD-8094 was ~430 nm, toward the violet end of the visible spectrum, so the stone had a purplish hue. Sample APD-18, which had no purplish overtone, had maximum transmission at ~475 nm, toward the greenish end of the blue region. Sample AP-33 (from the previous study) was brownish pinkish orange; although it transmitted in the blue region at about the same position as APD-19, it lacked the NV^0 absorption (ZPL at 574.9 nm) needed to absorb the orange wavelengths.

Specific spectral features—such as a 3123 cm^{-1} absorption in the mid-IR region (Fuchs et al., 1995a,b); the 7353, 6855, 6425, and 5562 cm^{-1} absorptions in the near-IR region; and the doublet emissions at 596.5 and 597.0 nm—were common in previously studied CVD synthetic diamonds and were also important for their identification. However, the pink CVD lab-grown diamonds in this study had a distinctly different combination of lattice defects. In particular, H-related absorptions occurred dominantly at 3107 and 1405 cm^{-1}, while
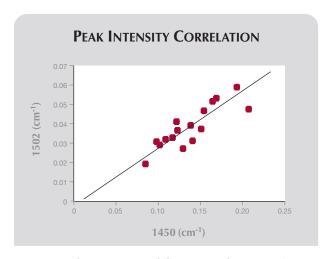

Figure 16. The intensities of the 1450 and 1502 cm^{-1} absorption peaks show good correlation, with a trend that can be extrapolated through the graph's origin.

the 3123 cm^{-1} peak was extremely weak or nearly absent (again, see figures 7 and/or 8). The 3107 and 1405 cm^{-1} bands have not been previously reported in CVD synthetic diamonds, but they are common features of natural type Ia diamonds; they show correlated intensities and are attributed to the same H-related defect. A similar relationship in intensity between these two peaks was observed in this group of CVD lab-grown diamonds, indicating that they originate from the same defect as found in natural diamonds.

The presence of some optical centers seen in previous studies of irradiated diamonds is another notable feature of these pink CVD synthetic diamonds. Absorption caused by H1a at 1450 cm^{-1} (again, see figure 7), which has been attributed to an interstitial defect seen in irradiated diamonds in a previous study (Collins et al., 1988), was observed in all samples. The positive correlation in intensity between the 1450 and 1502 cm^{-1} bands (figure 16) suggests that the 1502 cm^{-1} center is also related to this defect center. Other well-known defects—including GR1, ND1, 594.3 nm, and 388.9 nm—were observed in the UV-Vis and/or PL spectra (again, see figures 10 and 12). Furthermore, there were no doublet emissions at 596.5 and 597.0 nm in the PL spectra, and the previously documented (Wang et al., 2007) absorptions at 7353, 6855, 6425, and 5562 cm^{-1} in the near-IR region were also absent from this group of pink CVD lab-grown diamonds (figure 9).

Lattice Defect Configurations. Intense brown coloration is common in CVD synthetic diamonds produced at a high growth rate. As in natural type IIa diamonds, brown in CVD synthetics can be reduced by high-temperature annealing (Wang et al., 2003; Charles et al., 2004; Yan et al., 2004; Meng et al., 2008), although the causes of the brown hue in this material are not fully understood (Jones, 2009). Occasionally, HPHT-annealed CVD synthetic diamonds have been submitted to gem laboratories for identification (e.g., Chadwick, 2008a,b; Wang and Johnson, 2010; Kitawaki et al., 2010).

The characteristics of the H-related features in the present samples are particularly noteworthy: the near-absence of the 3123 cm^{-1} line and the presence of the 3107 cm^{-1} absorption. Cruddace et al. (2007) proposed that the 3123 cm^{-1} absorption in CVD synthetic diamond corresponded to the NVH$^-$ center, and Cruddace (2007) found that in most cases this line annealed out above 1500°C. Meng et al. (2008) also found that the 3123 cm^{-1} line (reported as 3124 cm^{-1}) disappeared after annealing at 1600°C for 10 minutes. (However, Khan et al. [2009] observed that heating below 600°C caused NVH^0 to be converted to NVH$^-$, resulting in the disappearance of the 3123 cm^{-1} line. It was therefore proposed that this line is in fact related to NVH^0 rather than NVH$^-$.) The 3107 cm^{-1} absorption was not reported in any of these annealing experiments, but Charles et al. (2004) found that it was not generated until the temperature reached 2200°C.

Adding low concentrations of nitrogen to the CVD growth environment can have an important impact on the growth rate, as well as on the nature and concentrations of the defects that are incorporated as the material grows (Teraji and Ito, 2004; Tallaire et al., 2006). In most studies of CVD-grown diamond, most incorporated nitrogen is detected in the single substitutional (i.e., isolated) form, with smaller amounts detected in the NV^0 and NV$^-$ states.

The H3 defect [(NVN)^0, 503.2 nm] forms in nitrogen-bearing diamonds through combination of the nitrogen A aggregate and a vacancy. This defect is often found in diamonds that have been irradiated and annealed at relatively high temperatures (e.g., Collins, 1982, 2001) or is associated with distinct plastic deformation features. While common in irradiated/annealed type Ia diamonds, varying concentrations of the H3 defect also occur in some natural-color type Ia diamonds. The presence of H3 centers was confirmed in both PL and absorption spectroscopy (again, see figures 10, 11, and 13).

With low-temperature PL spectroscopy, NV centers are almost always detected in as-grown CVD synthetic diamonds, except for rare high-purity samples (Martineau et al., 2004; Wang et al., 2005b). While NV emissions may be dominant in PL spectra, typically they are virtually undetectable or very weak in UV-Vis absorption spectra and have little, if any, effect on bodycolor. In the CVD samples in this study, however, high concentrations of NV centers were evident in our spectroscopic studies and also were the main cause of the pink color and distinctive orange fluorescence.

Si-related Optical Centers in Diamond. The pink CVD lab-grown diamonds in this study displayed relatively high concentrations of Si-related defects compared to those in other reports (Wang et al., 2003; 2005b; 2007; Martineau et al., 2004). Among the 19 samples analyzed, 15 showed detectable 737 nm lines (attributed to the negatively charged silicon split-vacancy [Si-V]$^-$) with the use of UV-Vis absorption spectroscopy, which was not sensitive enough to detect Si-related optical centers in previous CVD synthetic diamonds. A weak, but clear, 945.5 nm line (attributed to the neutral silicon split-vacancy [Si-V]^0) occurred in the PL spectra of all samples. This is the first report of a 945.5 nm center in CVD lab-grown diamonds from Apollo Diamond Inc. The 737 nm line was not observed in the PL spectra of four samples, probably due to the high spectral background from the luminescence of NV centers. The presence of Si-related defects is an important, but not unique, feature of CVD synthetic diamonds. Si-related defects also have been observed in a few natural diamonds (Breeding and Wang, 2008; GIA unpublished data).

Pink Diamond: Natural, Treated, and Synthetic. Two features are associated with pink color in natural untreated diamonds: NV centers and the 550 nm band (e.g., Collins, 1982). Natural pink diamonds colored by NV centers are type IIa and usually have very low color saturation, based on GIA's experience testing many samples of this type in the laboratory. In contrast, those that are colored by the 550 nm band, which include type IIa diamonds as well as type Ia diamonds from the Argyle mine, typically are more highly saturated. Purple modifiers are also common in those stones.

Several treatment techniques have been devel-

Figure 17. Some of Apollo Diamond's gems have been set into attractive jewelry. The 14K white gold pendant contains a 0.45 ct pink CVD lab-grown diamond surrounded by colorless CVD gems with a total weight of 1.03 ct. The CVD-grown diamonds in the platinum ring have a total weight of 1.08 ct. Courtesy of Bostonian Jewelers, Boston; photo by Robert Weldon.

oped to introduce a pink-to-red hue into both natural and synthetic diamonds. HPHT annealing has been used to enhance the pre-existing 550 nm band and thus intensify the pink color of a diamond, but the method depends on the properties of the starting material and is suitable primarily for type IIa diamonds (Hall and Moses, 2000; Fisher et al., 2009). (In addition, no laboratory process to create the 550 nm absorption band has been reported; Collins, 1982, 2001.) Consequently, enhancement of the 550 nm band can produce only very limited quantities of pink diamonds.

The other widely used technique involves conversion of trace amounts of isolated nitrogen into NV centers through a combination of irradiation and annealing processes. The trace amounts of isolated nitrogen needed for such a treatment (1) can occur naturally in the starting materials (i.e., as in type Ib diamonds), (2) can be generated at high temperatures by disaggregation of other nitrogen-bearing defects in natural diamonds through HPHT treatment, or (3) can be incorporated during synthetic growth. Treated orange, pink, or red diamonds from natural starting

materials (Wang et al., 2005c; Wang, 2009) and from HPHT-grown synthetic starting materials (Shigley et al., 2004) have been well documented. The samples described in this study, however, are the first group of CVD synthetic diamonds GIA has examined with pink color caused by NV centers, and this also was documented in treated-color red natural diamonds in which the NV centers were produced by HPHT annealing and subsequent irradiation and annealing at relatively low temperatures (Wang et al., 2005a).

Compared to the intense pink or purplish pink coloration of the CVD-grown diamonds in this study (again see, e.g., figure 1; also figure 17), the previous generation of pink CVD products from Apollo Diamond (Wang et al., 2007) displayed obvious brown and orange modifiers, as well as much weaker saturation. Despite some absorption from NV centers, those earlier samples were mainly colored by a broad absorption band centered at ~520 nm, and they showed significant differences in their IR and UV-Vis absorption features. Twitchen et al. (2007) successfully developed orange-to-pink colorations when they annealed brown CVD synthetic diamonds, but their

samples showed no typical radiation-related optical centers.

In brief, the strongly colored pink CVD-grown diamonds examined for this study show many similarities in gemological and spectroscopic features with treated orange-pink-red diamonds that were exposed to HPHT annealing followed by irradiation and annealing at relatively low temperatures (Wang et al., 2005a,c).

Identification Features. Separation of these treated pink CVD lab-grown diamonds from other pink diamonds can be readily achieved using various gemological and spectroscopic features. Outstanding gemological features of this group of pink CVD synthetic diamonds include a strong and even color saturation, internal graining with indistinct boundaries or well-defined linear outlines, a high degree of internal strain, black inclusions with irregular morphologies and/or pinpoint inclusions, and moderate-to-strong orange fluorescence to both long- and short-wave UV radiation. The DiamondView fluorescence images displayed a banded structure and characteristic striated growth pattern. This is a key feature in separating these CVD-grown diamonds from other pink-to-red diamonds, either natural-color or treated-color from natural or HPHT-grown synthetic starting materials.

Useful spectroscopic properties include absorptions at 3123 (very weak), 1502, 1450 (H1a), 1405, 1344, and 1295 cm^{-1} in the mid-IR region, and 6902 and 5892 cm^{-1} in the near-IR region. Strong absorptions from GR1, NV centers, 594.3 nm, and ND1 in the UV-Vis-NIR region are also useful. The occurrence of Si-related features in PL and absorption spectra continues to be one of the most useful characteristics for identifying CVD synthetic diamonds, including the strong pink samples examined in this study.

CONCLUSIONS

Highly saturated natural pink diamonds are rare. Consequently, several techniques have been developed to introduce pink color into natural and HPHT-grown synthetic diamonds. The CVD-grown diamonds examined in this study have pink hues that are comparable to those of their natural counterparts and offer a potential new source of attractive gems in the marketplace (again, see figure 17). Proper identification of this gem material can be achieved through a combination of standard gemological properties (e.g., unusual internal graining, high strain, and distinctive zoned orange fluorescence) and several characteristic spectroscopic features. There is no doubt that the growth technique will continue to improve, and CVD synthetic diamonds of better and better quality will be produced.

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