Color Alterations in CVD Synthetic Diamond with Heat and UV Exposure: Implications for Color Grading and Identification

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In response to heat and UV exposure, some synthetic diamond gemstones grown by chemical vapor deposition exhibit large, reversible changes in color. A significant reduction in color was achieved by heating several CVD synthetic gemstones to >450°C. Conversely, a darker color was observed in samples following exposure to UV radiation (such as that used in gem testing). Both the heated and UV-exposed samples returned to their initial (stable) color when they were illuminated for >30 minutes with a standard daylight-equivalent lamp used for grading. However, these color states did not change with time when the samples were kept in the dark. Heating and UV exposure also influenced the strengths of various IR absorption features that might be used to identify such a sample as a CVD synthetic. These nonpermanent changes might affect the apparent color grade of a CVD synthetic diamond, and care must be employed in the interpretation of spectroscopic features used to determine a stone's natural or synthetic origin.

I n recent years, chemical vapor deposition (CVD) techniques to grow synthetic diamond have evolved to the point that high-quality single crystals of moderate size can be produced (see, e.g., Achard et al., 2007). Gemological laboratory equipment (e.g., the infrared spectrometer and Diamond Trading Company's (DTC) DiamondView verification instrument) can be used to identify CVD-grown diamond gems as synthetic (Wang et al., 2003, 2007; Martineau et al., 2004), based on a number of properties detectable under special test conditions. These synthetic gemstones are now being marketed by, for example, Apollo Diamond Inc. of Boston, and the numbers being submitted to gemological laboratories are increasing (see, e.g., Chad-

wick and Breeding, 2008; Wang and Moses, 2008; Wang and Johnson, 2010).

Under some circumstances, adding a small concentration of nitrogen to the growth environment increases the growth rate (Teraji and Ito, 2004; Tallaire et al., 2006) while also resulting in the uptake of different types of point defects within the diamond lattice. Some of these defects are known: for example, single substitutional nitrogen (N_S) and nitrogen-vacancy (NV) centers. Other defects formed by the addition of nitrogen manifest themselves in a gradual rise in absorption toward shorter wavelengths (which results in brown coloration) and broad bands at ~360 and 515 nm (Martineau et al., 2004). However, those other defects have not been convincingly identified, and little has been reported about the properties of these absorption bands.

In certain rare natural diamonds, the color and absorption spectra can vary with either heating or extended storage in the dark; that is, such stones display thermochromic and/or photochromic effects. These are commonly called chameleon diamonds

Figure 1. The 11 CVD synthetic diamond samples examined for this study are shown here in their initial "stable" state (i.e., before exposure to heat or a UV lamp). The numbers on the nine round brilliants (0.40–0.92 ct) and two tabular plates (0.22 and 0.35 ct) correspond to the sample numbers used in table 1 and throughout the article. Composite photo by R. Khan.

(see, e.g., Hainschwang et al., 2005; Fritsch et al., 2007). "Classic" chameleon diamonds generally change from a stable "olive" green color to an unstable yellow, and "Reverse" stones change from a stable light yellow to an unstable greenish yellow or yellowish green. The unstable colors are induced by heating to ~150°C or prolonged storage in the dark, whereas the stable colors are achieved by exposure to normal (incandescent or fluorescent) lighting conditions. The chameleon effect is due to variations in the strength of two broad optical absorption features centered at ~480 and ~800 nm.

Pink natural diamonds also often exhibit a color alteration from pink to brown on UV exposure (de Weerdt and Van Royen, 2001). The pink color is a result of a broad optical absorption feature at 550 nm, and it may be reversibly bleached by exposure to the radiation from a UV lamp.

Temporary changes in color are usually caused by the transfer of electrons between defects, which alters the charges of the defects and therefore their influence on the absorption spectrum. These effects sometimes also lead to phosphorescence, where some of the electronic charge becomes trapped and then de-traps over a matter of seconds. Chameleon diamonds often exhibit phosphorescence.

The purpose of this article is to investigate temporary changes in color (and spectra) that may occur in CVD synthetic diamond in response to standard jewelry-manufacturing procedures (e.g., exposure to heat) or gemological testing (e.g., exposure to UV radiation). This is important, as any temporary change in color might potentially affect the grades given on laboratory reports. A previous study (Khan et al., 2009) had already established that charge-transfer processes were occurring in CVD synthetic diamond with UV exposure and heating. This article explores how these two processes affect the color of a number of standard gem-quality CVD synthetic diamond samples (figure 1), and categorizes any changes they produce in spectroscopic features that gemologists might use to identify a diamond as a CVD synthetic.

MATERIALS AND METHODS

The CVD synthetic diamond samples used for this study were grown by Element Six Ltd. within the DTC's Consumer Confidence Technical Research program, a fundamental aim of which has been to develop knowledge and instruments that will aid the identification of synthetics and treated diamonds. The samples investigated, which were grown for research purposes only, were all standard CVD synthetics similar to those discussed in a previous publication (Martineau et al., 2004). For all the samples, CVD layers were deposited on substrates of type Ib synthetic diamond that had been grown by a high-pressure, high-temperature (HPHT) process; after

deposition, the substrate was removed. Generally, greater degrees of brown coloration correlated with increased amounts of nitrogen added during deposition. A total of 11 samples were studied, all of which were from different deposition runs. The nine faceted CVD synthetics (0.40–0.92 ct) and two tabular plates (0.22 and 0.35 ct) were prepared using laser cutting and standard polishing techniques. We used the tabular plates for spectroscopic characterization, because their parallel geometry made it easier to obtain quantitative measurements (e.g., the strength of IR features).

The CVD synthetic diamond samples studied are shown in figure 1 and described in table 1. They exhibited a wide range of color, with two (nos. 4 and 6) being colorless or near-colorless, one (no. 5) being Fancy brown, two being pale pink (nos. 8 and 10), and the remainder falling somewhere between near-colorless and brown (see table). All the samples except numbers 4 and 6 were grown with a small concentration of nitrogen in the growth environment. Samples 4 and 6 were nominally undoped. Samples 8 and 9 were HPHT treated: sample 8 at a moderate temperature (~1600°C), and sample 9 at a higher temperature (2200°C); both samples were brown before HPHT treatment.

Each sample was examined in its initial (i.e., sta-ble) state. Then we exposed each of the samples to UV radiation and studied them, after which we heated each of the samples and re-examined them. For UV exposure, we employed either a mercury-xenon arc lamp (Thermo-Oriel 66902 with 6292 HgXe bulb, emitting a broad spectrum with several sharp peaks between 250 and 400 nm and extending into the near-infrared), or the ultra-short-wave xenon strobe lamp of a DiamondView luminescence imaging instrument (wavelength range between 120 and 227 nm; a low pass filter removed higher wavelengths). We obtained comparable results in either case; only short exposures (<5 minutes) were required for the full color alteration to be induced. For heating, we used a standard laboratory hot stage (Linkam TH1500) to heat the sample in the dark to 550°C over 15 minutes before cooling it back to room temperature. We attempted other heating conditions as well and generally found that exposure to >450°C for typically a few—that is, less than five—minutes had the same effect. Note that in both cases these are lower than the temperatures expected for, say, the retipping of gold prongs in a ring (i.e., ~700–800°C to melt gold solder; Knuth, 1994).

Color grading was performed at the Forevermark laboratory, which uses diamond color master sets that are based on standards universally accepted by

TABLE 1. The CVD synthetic diamond samples studied, with color grades as assigned in their initial state, after UV exposure, and after heating.

Sample no.	Weight and shape[a]	N_S^0 (ppm)[b]	HPHT treatment	Color (initial, stable)	Color after UV exposure (for 5 mins.)	Color after heating (to 550°C for 15 mins.)	Magnitude of color difference[c]
1	0.56 ct RB	0.13	None	L (brown)	M (brown)	H (brown)	Large
2	0.42 ct RB	0.11	None	K (brown)	K (brown)	H (brown)	Moderate
3	0.92 ct RB	0.20	None	P-T (brown)	W-X (brown)	M (brown)	Large
4	0.51 ct RB	0.02	None	E	E	D	Small
5	0.40 ct RB	1.7	None	Fancy brown	Fancy Deep brown	W-X (brown)	Large
6	0.80 ct RB	0.02	None	G (brown)	G (brown)	E	Moderate
7	0.45 ct RB	Unknown	None	J (brown)	J (brown)	E	Large
8	0.55 ct RB	Unknown	1600°C	L (pink)	N (pink)	J (pink)	Large
9	0.67 ct RB	Unknown	2200°C	H (brown)	H (brown)	G (brown)	Small
10	0.35 ct plate (2.1 mm thick)	0.5	None	Pale pink	Pink	Near-colorless	Moderate
11	0.22 ct plate (1.1 mm thick)	2.4	None	Brown	Deep reddish brown	Pale brown	Large

[a] RB = round brilliant. The colors of the tabular plates (samples 10 and 11) are qualitative assessments only.
[b] The initial N_S^0 concentrations. These values are observed to vary considerably with exposure to UV radiation or heating; ppm = parts per million atomic.
[c] The magnitude of the color difference is defined as follows: large represents >4 grades between heating and UV exposure; moderate, >2 grades; and small, <2 grades.

leading international diamond grading laboratories. All the samples were graded in a dark room, using a standard overhead desk-mounted light with two 15-watt General Electric F15T18-D Daylight tubes. Samples were graded with the tray holder ~8 in. (20 cm) from the light source and the grader ~12 in. (30 cm) from the synthetic gemstone (similar to conditions discussed in King et al., 2008). All samples were color graded three times: (1) in their initial state (i.e., the stable color), (2) after UV exposure, and (3) after heating. Grading was for research purposes only, as the Forevermark laboratory does not issue reports for synthetic diamond gemstones.

To record the bodycolor of the samples, optical micrographs were taken of each one with a computer-controlled Leica DC300F CCD camera attached to a Wild M420 optical microscope using a Volpi Intralux 150 H fiber-optic lamp for illumination. All samples were photographed in their initial state, after UV exposure, and after heating.

To quantify any spectroscopic changes and further investigate the defect centers involved, we recorded the optical absorption spectra of the two tabular plates (nos. 10 and 11) using an ultraviolet-visible–near infrared (UV-Vis-NIR) spectrometer (Perkin-Elmer Lambda 9), with the sample at room temperature. For sample 11, we also recorded the spectrum with the sample cooled to liquid-nitrogen temperature ($-196°C/77°K$) by means of an Oxford Instruments DN cryostat. We calculated absorption coefficients by dividing the measured absorbance by the sample thickness. To ascertain any changes in the strength of the IR features known to be present in the spectra of CVD synthetic diamond, we also recorded Fourier-transform infrared (FTIR) absorption spectra on these plates using a Nicolet Magna IR 750 FTIR spectrometer at a resolution of 0.5 cm^{-1}. All spectroscopic analyses were conducted on the samples in their initial state, after UV exposure, and after heating.

We investigated the temporal stability of the three states by placing two synthetic diamond gemstones (nos. 3 and 5) in the dark (i.e., in stone papers in a closed box) and re-grading them periodically over a total of three weeks. This was performed on the samples in their initial state, after UV exposure, and after heating.

We also illuminated three of the samples (nos. 1, 3, and 5) with daylight-equivalent grading lamps at a distance similar to that typically employed for grading (~8 in. from the light source; see, e.g., King et al., 2008) for >30 minutes and re-graded them in

NEED TO KNOW

• As-grown nitrogen-containing CVD synthetic diamond will commonly show less color with heating to >450°C and more color after exposure to UV radiation.

• Both types of color alteration are reversible—no permanent structural change is imparted via these heating and UV exposure procedures.

• The three color states (stable, UV-exposed, and heated) do not change with time when the synthetic gemstones are kept in the dark, but the stable color can be induced by prolonged exposure to a standard daylight-equivalent lamp.

• Heat and UV exposure can also modify the strength of certain IR absorption features that have been used to help identify CVD synthetic diamond.

an attempt to simulate the effect of cumulative lighting. In addition, we investigated whether it was necessary to illuminate the samples after UV exposure but before heating. Returning the samples to their "stable" state in this manner was found to have no effect on the outcome of the measurements performed after heating; that is, the order of UV/heat exposure did not play a significant role.

RESULTS AND DISCUSSION

Appearance of the Samples. Very marked changes in color were observed in the majority of the CVD synthetics investigated (again, see table 1). Figure 2 illustrates two of the samples studied (nos. 3 and 5) in each of their three states. As compared to their initial state (figure 2, left), they darkened slightly after UV exposure (figure 2, center) and, conversely, lost most of their color saturation after heating (figure 2, right). In their altered states, even prolonged exposure to light from the fiber-optic illuminator during photography changed their color (so the authors were careful to acquire images promptly). This effect was most noticeable in the samples after heating.

Color Grading. Compared to the initial state, all the samples had less color after heating, whereas UV exposure produced a darker color in some cases (with no difference in five samples). By repeating the measurements several times with successive UV exposure and heating steps, we established that these color alterations were reversible.

As was the case with photography, we noted that illumination from grading lamps affected the

Figure 2. These images illustrate samples 3 (top; 0.92 ct) and 5 (bottom; 0.40 ct) in their initial (stable) states (left), after UV exposure (center), and after heating (right). Composite photo by R. Khan.

color of the UV/heat-exposed samples. This was most clearly seen after heating, when we observed a darkening of the samples during grading that was due to exposure to light from the fluorescent tubes (grading typically takes up to a couple of minutes per gemstone).

Neither of the two samples we color graded in each of the three states (stable, UV-exposed, heated) showed any change in color grade over several weeks while kept in the dark. From this experiment, we concluded that the samples would not return to their initial (stable) state if kept in the dark indefinitely subsequent to UV exposure or heating. Note that this is different from what is observed in chameleon diamonds, where prolonged storage in the dark may cause a change in color.

Next, the three samples we illuminated under grading lamps for relatively long periods (at least 30 minutes) while they were in each of the three states revealed no change in color for samples in their stable state (as expected), and a return to the initial stable color grade for the UV/heat-exposed samples. We therefore suspect that if CVD synthetics were left lying on a table under normal ambient lighting for more than 30 minutes, they would return to their stable color.

Last, we note that the "initial" state in which a synthetic gemstone is received could be ill-defined, in that it might be affected by the lighting conditions the synthetic gem was exposed to before grading. To obtain a reliable, stable color state prior to grading, we recommend that CVD synthetic gems should be illuminated for a reasonable period of

time (we employed >30 minutes but shorter durations might be sufficient) under consistent lighting conditions (e.g., daylight-equivalent lamps at a distance of about 8 in.).

Spectroscopic Analysis. The initial (stable), post-heating, and post-UV-exposure UV-Vis absorption spectra for tabular sample 11 are shown in figure 3. The overall results for sample 10 were similar, but the peaks were weaker. In the spectra of the initial and after-UV states, we observed strong optical absorption features at ~270, 360, and 515 nm.

The feature at ~270 nm has been attributed to neutral single substitutional nitrogen defects (N_S^0), otherwise known as the C form (Chrenko et al., 1971). Although the eye is not sensitive in this area, an increase in the strength of this feature correlates with increased broad absorption over the blue region of the absorption spectrum. A sample possessing strong 270 nm absorption will appear yellow—as do, for example, most type Ib HPHT-grown synthetic diamonds. The features centered at ~360 and 515 nm also have a significant bearing on the color of a CVD synthetic diamond. The 360 nm band is broad and extends into the visible region of the spectrum. The 515 nm feature is particularly important, as the eye is at its most sensitive in this

Figure 3. These UV-Vis-NIR absorption spectra were recorded from a tabular plate of CVD synthetic diamond (sample 11) in its initial (stable) state, after UV exposure, and after heating. The features at 270, 360, and 515 nm increase in strength after UV exposure, while heating reduces their intensity, resulting in the color alterations seen.
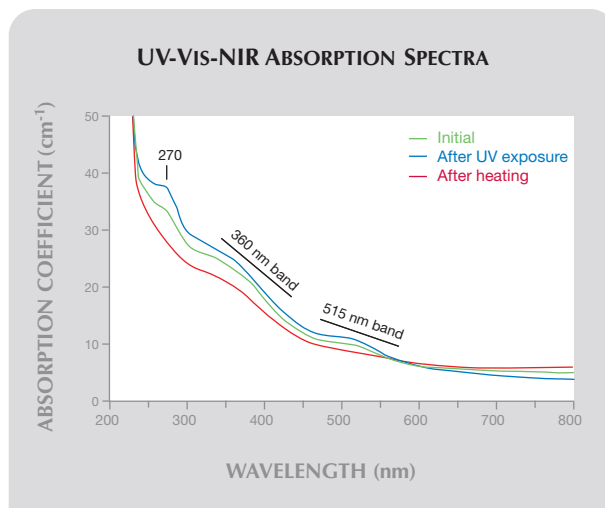

UV-VIS-NIR ABSORPTION SPECTRA

— Initial
— After UV exposure
— After heating

270

360 nm band

515 nm band

ABSORPTION COEFFICIENT (cm⁻¹)

WAVELENGTH (nm)

TABLE 2. Changes in the concentration of single-substitutional-nitrogen defects measured with IR spectroscopy in the initial state, after UV exposure, and after heating.

Sample no.	Defect	Spectroscopic feature (cm⁻¹)	Concentration (ppm)		
			Initial	After UV exposure	After heating to 550°C
10	N_S^+	1332	0.2 ± 0.2	0.2 ± 0.2	0.5 ± 0.2
	N_S^0	1344	0.5 ± 0.2	0.6 ± 0.2	0.2 ± 0.2
11	N_S^+	1332	2.5 ± 0.4	1.8 ± 0.4	4.7 ± 0.4
	N_S^0	1344	2.4 ± 0.4	3.5 ± 0.4	0.8 ± 0.4

region. Depending on the strength of other absorption features, strong 360 nm absorption will make samples appear more yellow and samples with a strong 515 nm band often appear pinkish.

Comparing the spectra in figure 3, we observe that the 270, 360, and 515 nm bands are much weaker after heating. The 270 and 360 nm features appear to be slightly stronger after UV exposure than when the diamond is in its initial state. Overall, we can conclude that the heating procedure weakened the three main absorption features, and thus reduced the color, which is consistent with our grading results. UV exposure strengthened the three main features, which is consistent with the stronger color recorded in the color grading. Again, via repeating the heating and UV-exposure episodes and re-measuring the samples, we established that these effects were reversible. This suggests that charge transfer between various defects might be responsible (Khan et al., 2009).

The reduction in the strength of the feature at 270 nm provides a clue to the reason for the color alterations. As it corresponds to neutral single substitutional nitrogen (N_S^0) defects, these must have been temporarily converted to another form when the sample was heated. One such form is positively charged single substitutional nitrogen (N_S^+); that is, N_S^0 that has lost an electron. Infrared spectroscopy enables us to investigate both forms of these single nitrogen defects.

Figure 4 shows the FTIR spectra for sample 11 in its initial (stable) state, after UV exposure, and after heating (again, the overall results were similar for sample 10). Both N_S^0 and N_S^+ possess IR-active modes in the region between 1500 and 1200 cm⁻¹. A component of the vibration associated with the N_S^+ defect occurs at 1332 cm⁻¹; likewise, a peak at 1344 cm⁻¹ corresponds to N_S^0 defects (Lawson et al., 1998). From figure 4, it is clear that on heating, the intensity of the 1344 cm⁻¹ peak decreased and that of the peak at 1332 cm⁻¹ increased. This suggests the conversion of single substitutional nitrogen from its neutral to its positively charged state; this

charge transfer is consistent with the measurements obtained via UV-Vis spectroscopy. We also note that the stable state lies between the UV-exposed and heated states.

For both tabular plates, we present the changes in concentrations for N_S^0 and N_S^+ derived from the strengths of the 1344 and 1322 cm⁻¹ features, respectively, in table 2. We estimate that, between the UV-exposed and heated states, there is a change of ~0.3 parts per million atomic (ppm; sample 10) and ~3 ppm (sample 11) in the single-nitrogen-defect concentration from the neutral to the positively charged state. From table 1, it is also apparent that the magnitude of the color alteration is loosely correlated to the concentration of N_S^0 centers. The synthetic diamond samples that had negligible N_S^0 showed less color alteration. Also note that the

Figure 4. The IR spectra in the region between 1500 and 1200 cm⁻¹ recorded from CVD synthetic diamond sample 11 reveal changes in the strengths of the 1344 (N_S^0) and 1332 (N_S^+) cm⁻¹ peaks, and variations in the strengths of the peaks at 1371, 1362, and 1353 cm⁻¹. Spectra are shown for the sample in its initial (stable) state, after UV exposure, and after heating.
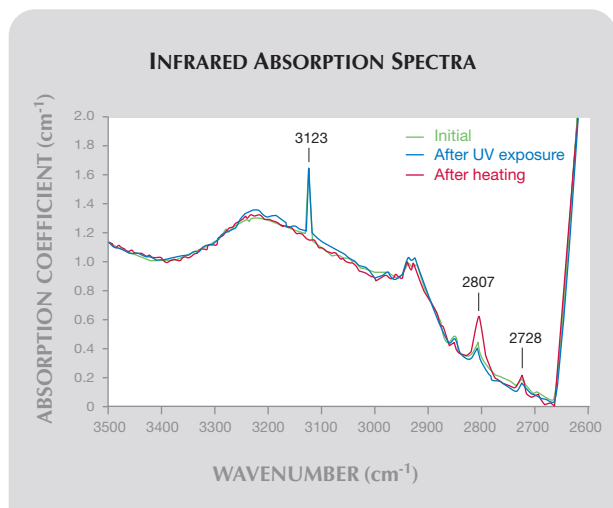

INFRARED ABSORPTION SPECTRA

INFRARED ABSORPTION SPECTRA
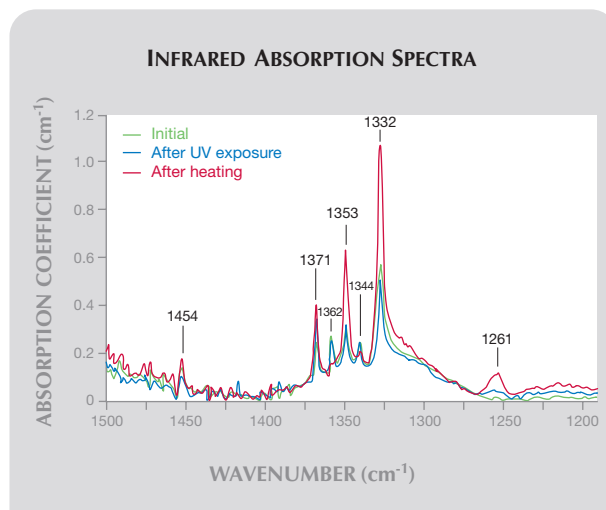
Figure 5. The IR spectra recorded from sample 11 in the 3500–2600 cm⁻¹ region illustrate the changes in the strengths of a number of peaks, including the one at 3123 cm⁻¹, which is believed to correspond to the neutral nitrogen-vacancy-hydrogen (NVH⁰) defect.

direction of the color alteration was the same in all of the samples, and in no case was the CVD synthetic rendered more colorless by UV exposure.

Similarly, figure 5 shows for sample 11 the region of the IR spectrum between 3500 and 2600 cm⁻¹, which contains various stretch modes of defects in diamond. Here we observe large changes in the strength of an absorption feature at 3123 cm⁻¹: After heating, it is not visible; but after UV exposure and in the initial state, it is clearly observed. This is one of several IR features that reportedly might help identify a diamond as an as-grown CVD synthetic (Wang et al., 2003), and our experiments show that it could be temporarily eliminated via heating. This line is thought to be a vibrational mode of the neutral nitrogen-vacancy-hydrogen center (NVH⁰: Glover et al., 2003; Khan et al., 2009). As the CVD process employs a large fraction of hydrogen in the gas feedstock, and because the carbon-containing source gas (methane) also contains hydrogen, it is not at all surprising that hydrogen-containing defects are present in CVD synthetic diamond.

The UV-Vis absorption measurements on sample 11 at liquid-nitrogen temperature allowed us to study the influence of UV exposure and heating on the concentrations of other known defect centers. The results of this experiment are not described in detail here, but we observed relative changes in the strength of the NV⁰ and NV⁻ peaks (at 575 and 637 nm, respectively): The NV⁻ concentration, calculated by fitting the area and using a known conversion

factor (Davies, 1999), decreased from 98 parts per billion atomic (ppb) after heating to 53 ppb following UV exposure, with a concomitant increase in the strength of the NV⁰ peak. This suggests that heating also converted NV defects into their negatively charged form, presumably via gain of electrons from the N_S centers, which would be consistent with the reduction in the strength of the 270 nm peak as mentioned above. However, this change in NV concentration is likely to be too small to have a profound effect on color, whereas changes in the strengths of the aforementioned bands (which are not associated with either the 575 or 637 nm features) have produced the observed color alterations.

Several other IR features are also altered with heating and UV exposure. We compared the spectra for sample 11 in its UV-exposed and heated states, and the results are shown in table 3. The spectra for the samples in their stable state consistently fell between those of the two altered states, but they are generally closer to those of the UV-exposed state. Therefore it is not always possible to observe changes in the strengths of lines between the stable and UV-exposed states. Various photoluminescence identification features (e.g., at 467.6 and 532.8 nm) also exist in these samples and have been discussed in a previous publication (Martineau et al., 2004).

Color Alteration Mechanisms. Based on our data and previous work, we propose that the color alterations are due to electron transfer from single substitutional nitrogen centers to electron acceptor defects (Khan et al., 2009). After UV exposure, these defects are neutral and contribute to the color, but after heating they are charged and do not. Some of these defects are of known origin (NVH) and some are of unknown origin. The NVH acceptors are likely to be present in most CVD synthetics doped with nitrogen (Glover et al., 2003). For a large alteration in color, significant concentrations of both N_S and acceptors are required, in which case the initial color of the CVD synthetic would be expected to be darker brown. Note, though, that these various defects are present in practically all types of as-grown CVD synthetic diamond. Even in unintentionally doped material, they can be present in trace concentrations. This means that even nominally pure, near-colorless as-grown CVD synthetic gemstones can show some small changes in color.

Table 1 shows an apparent trend between the single-nitrogen concentration and the strength of the effect, but we have not observed similar color

TABLE 3. Changes in strength of IR spectroscopic features of sample 11 between UV-exposed and heated states.

Position (cm^{-1})	Variation with UV exposure	Variation with heating (550°C)
1332	Decreases	Increases
1344	Increases	Decreases
1353	Decreases[a]	Increases
1362	Increases[a]	Decreases
1371	Decreases[a]	Increases
2728	Decreases	Increases
2807	Decreases[a]	Increases
2900–2950	No change	No change
3123	Increases	Decreases
6451 (1550 nm)[b]	Decreases	Increases
6857 (1458 nm)[b]	Decreases	Increases
7354 (1360 nm)[b]	Decreases	Increases

[a] No apparent change between stable and UV-exposed state.
[b] Not shown in figures 3, 4, or 5.

alterations in HPHT-grown synthetic diamond samples (which contain appreciable single nitrogen but not these acceptors; Khan et al., 2009).

Last, though large changes in color were observed in the sample that was HPHT-treated to a moderate temperature (no. 8, 1600°C), the sample annealed at the higher temperature (no. 9, 2200°C) showed little color alteration between subsequent heating and UV exposure. In sample 8, HPHT treatment had the effect of removing most of the brown color but leaving the broad absorption feature centered around 515 nm, resulting in a slightly pink hue (for details of this process, see Twitchen et al., 2007). For sample 9, the 515 nm feature was also annealed out, resulting in the removal of much of the visible absorption seen in the as-grown sample. The results for samples 8 and 9 suggest that once the defect responsible for absorption centered at ~515 nm is annealed out, CVD synthetic diamond does not show significant changes in color with subsequent heat or UV exposure. As the 3123 cm^{-1} IR feature anneals out at the same temperature as the 515 nm absorption band, and both display similar charge-transfer dependence, we speculate that the latter may correspond to an optical transition of the NVH^0 defect, though further investigations are required.

CONCLUSIONS

Gemologists should be aware that the color of as-grown CVD synthetic diamond gemstones may not be stable. Some color-causing defects in CVD synthetics doped with nitrogen trap electrons in a way that causes their charge state to change on exposure to UV radiation and heat. UV exposure causes a conversion of these defects to a neutral charge state so they absorb light over the visible range, increasing the apparent color. Conversely, heating to >450°C converts these defects to a charged state where they absorb less light over visible wavelengths, thus reducing the observed color.

These photochromic and thermochromic effects are reversible, and no permanent change occurs. A stable color—which is intermediate between the colors produced by UV exposure and heat—may be induced by illumination with grading lamps (we employed at least 30 minutes' illumination, but shorter durations may be sufficient). However, all three of the states (stable, UV-exposed, and heated) do not change with time if the gemstones are not disturbed by incident light (or heat), such as when they are stored in stone papers in a box at room temperature. The effect is analogous to the Reverse chameleon effect in natural diamond, except that the unstable color in Reverse chameleons can be induced by prolonged storage in the dark (Hainschwang et al., 2005), and it is the opposite of the photochromic and thermochromic changes that occur in some pink natural diamonds (where the more saturated pink coloration is induced by heating and removed by UV exposure).

Although these measurements were only performed on samples grown by Element Six, we suspect that CVD synthetic diamond gemstones from other producers would show similar effects if they were also nitrogen doped and not annealed at high temperature. Note that even the colorless CVD synthetics (which were grown without nitrogen deliberately added), showed some small changes, presumably due to low concentrations of intrinsic defects.

Gemologists should also be aware that a near-colorless CVD synthetic diamond could be heated prior to grading to improve its apparent color. If immediately after heating the synthetic gem was wrapped in thick paper and kept in the dark at room temperature until grading, it might obtain a better grade than merited by its stable color. The color alterations may be significant, in some cases the equivalent of several GIA color grades.

Conversely, a fancy-color CVD synthetic diamond may achieve a more intense color after UV exposure; in this case, too, the color grade might not be a true representation of its stable state. Note, though, that the UV-induced color can be removed by heating, for example, using a suitable furnace or torch to elevate the gemstone to >450°C. A gemolo-

gist can ensure that a synthetic diamond has reverted to a stable intermediate color by illuminating it with a standard daylight-equivalent lamp for a period of time, such as at least 30 minutes as in our study.

Although our experiments involved UV/heat exposures that would not typically occur in a standard diamond-grading environment, some color alteration is possible, and indeed likely, under normal grading conditions. Standard tests applied to diamonds (such as examination in a DiamondView, or using a UV lamp to check for fluorescence) involve exposure to UV radiation, which we have shown may profoundly affect the color. It is also possible that the temperature of gemstones may on occasion—for example, during acid cleaning, polishing, or use of a torch in the repair of jewelry—be raised high enough to cause a temporary color alteration.

Last, some CVD-specific spectroscopic identification features (e.g., a peak at 3123 cm^{-1} in the mid-IR spectrum) may diminish or even disappear on heating or UV exposure, so the absence of such features should not be the sole criterion by which a gemstone is identified as a natural diamond rather than a CVD synthetic.

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