

Enhanced optical properties of chemical vapor deposited single crystal diamond by low-pressure/high-temperature annealing

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Single crystal diamond produced by chemical vapor deposition (CVD) at very high growth rates (up to 150 $\mu\text{m}/\text{h}$) has been successfully annealed without graphitization at temperatures up to 2200 °C and pressures <300 torr. Crystals were annealed in a hydrogen environment by using microwave plasma techniques for periods of time ranging from a fraction of minute to a few hours. This low-pressure/high-temperature (LPHT) annealing enhances the optical properties of this high-growth rate CVD single crystal diamond. Significant decreases are observed in UV, visible, and infrared absorption and photoluminescence spectra. The decrease in optical absorption after the LPHT annealing arises from the changes in defect structure associated with hydrogen incorporation during CVD growth. There is a decrease in sharp line spectral features indicating a reduction in nitrogen-vacancy-hydrogen (NVH⁻) defects. These measurements indicate an increase in relative concentration of nitrogen-vacancy (NV) centers in nitrogen-containing LPHT-annealed diamond as compared with as-grown CVD material. The large overall changes in optical properties and the specific types of alterations in defect structure induced by this facile LPHT processing of high-growth rate single-crystal CVD diamond will be useful in the creation of diamond for a variety of scientific and technological applications.

microwave plasma | hydrogen | vacancy | nitrogen

Despite the large intrinsic band gap of diamond (5.5 eV), most natural diamond absorbs light in the UV, visible, and infrared spectral regions as a result of the presence of defects, impurities, and/or strain (1). High-pressure/high-temperature (HPHT) annealing has been shown to significantly alter the optical properties of diamond, specifically by lowering the UV-visible absorption, thereby increasing the potential use of the material in a variety of applications. Single-crystal diamond can be synthesized by chemical vapor deposition (CVD) techniques. Diamond produced in this fashion can exhibit a broad range of optical properties, from transparency to the intrinsic band gap to strong absorption throughout the visible spectrum. Single crystal chemical vapor deposited (SC-CVD) diamond can be produced at high growth rates (i.e., up to 150 $\mu\text{m}/\text{h}$) by microwave plasma assisted techniques (2, 3). Diamond produced at such high growth rates can exhibit strong and broad UV-visible absorption, in part by the intentional addition of nitrogen (1–5% N_2/CH_4) to the synthesis process gas. Nevertheless, the nitrogen content can be low (<10 ppm), and the material is classified as type IIa diamond. This contrasts with the brown natural type Ia diamond, which has a N content >100 ppm, and the brown natural type IIa diamond, which is considered to have experienced extensive plastic deformation (4, 5). SC-CVD diamond can have much narrower X-ray rocking curves than natural brown diamond while also exhibiting extremely high fracture toughness (6). This SC-CVD diamond is found to have a lower density of dislocations and is regarded as optically homogeneous brown diamond (7). High-growth rate SC-CVD diamond can be HPHT-annealed

to remove features in the optical spectrum (6–10) and to tune its mechanical properties (i.e., hardness and toughness) (6).

High-pressure/high-temperature annealing has become a commercial process for altering the optical properties of natural diamond (11, 12). This process requires temperatures in the range of 1800–2500 °C (13), and pressures >5 GPa are typically used to prevent the diamond from graphitizing. However, the origins of the changes in optical properties and the annealing mechanism in both natural and CVD diamond remain unclear. The reduction in visible absorption for HPHT-annealed type IIa natural diamond with low nitrogen concentration has been attributed to the removal of strain associated with plastic deformation (4, 12). In HPHT-annealed type Ia natural diamond with high nitrogen concentration, it is believed that during annealing nitrogen aggregates are dissociated and vacancies released from dislocations. The vacancies are then trapped to form N-V-N centers (11, 12). High-temperature treatment (>700 °C) at atmospheric pressure can decrease the visible absorption of brown natural diamond presumed to have experienced natural irradiation (14, 15), these processes are thought to produce damage in the form of isolated lattice vacancies and self-interstitials that can begin to migrate at temperatures \approx 600 °C and 425 °C, respectively (16–18). Thus, the response of diamond to high-temperature annealing varies depending on the origin of its UV-visible absorption features, growth history, and subsequent processing (19).

Optically homogeneous brown SC-CVD diamond exhibits fewer but characteristic defects as compared to brown natural diamond. This type of diamond contains a much lower density of dislocations than the brown natural type IIa diamond that has presumably experienced plastic deformation (4, 17). Because of the nitrogen-containing growth environment with high concentrations of hydrogen, the as-grown brown CVD diamond incorporates nitrogen as substitutional nitrogen species N_s^0 and N_s^+ (8) and contains nitrogen-vacancy (NV⁻ and NV⁰), nitrogen-vacancy-hydrogen (NVH⁻) (20), vacancy-hydrogen (21), and hydrogenated amorphous carbon (a-C:H) (9) complexes. Recent first-principles calculations suggest that the broad visible absorption of this diamond arises from vacancy disks in the {111} planes and that the optical activity of these disks can be passivated by hydrogen (4). With the presence of hydrogen impurities and vacancies, color centers contributing to the visible absorption of the CVD diamond may be less stable during annealing than the centers in the brown natural diamond.

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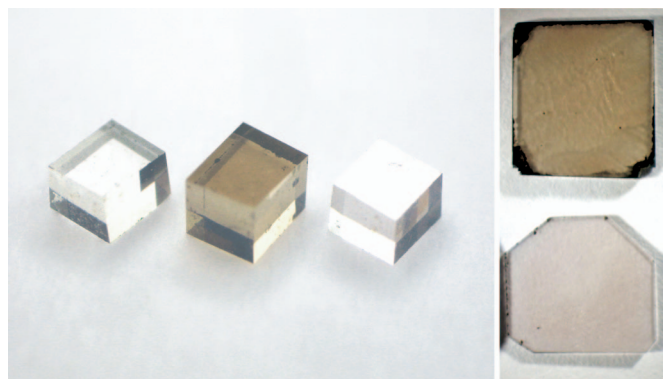


Fig. 1. Examples of LPHT annealing of SC-CVD diamond. (Left) Three segments of the same diamond produced at a high growth rate. The middle piece is an as-grown segment; left and right are annealed segments (at 1900 °C for 2 min and at 1800 °C for 3 min respectively). (Right) SC-CVD diamond crystals. (Upper) as-grown (brown, 10 × 9 × 0.9 mm (3)); (Lower) annealed at 1700–1800 °C for 15 min (brownish pink, 10 × 9 × 0.6 mm (3)).

Diamond is an unstable form of carbon at atmospheric pressure and all temperatures (22). High-temperature treatment of single crystal diamond at ambient pressure is usually performed at 700 °C–1600 °C (11); annealing at ≈800 °C is often used as a treatment subsequent to the irradiation of diamond (14, 23). To prevent graphitization, for high temperatures (e.g., >1600 °C), high pressure annealing is usually used. In the case of the SC-CVD diamond, as-grown crystals with fewer bulk defects than natural diamond have a lower probability of graphitization because graphite formation usually starts at discrete nucleation centers such as inclusions, boundaries, and cracks (22). We report here the effects of exposure of the SC-CVD diamond produced at high growth rate to high temperatures and low (i.e., below atmospheric) pressure. We find significant changes in the optical properties of diamond without the occurrence of significant graphitization at temperatures up to 2200 °C. A variety of spectroscopic methods are used to quantify the observed changes in optical properties and to provide insight into the origin of the phenomena.

Results

Over forty SC-CVD diamond plates with nitrogen impurity <10 ppm and thicknesses of 0.2–6.0 mm were subjected to low pressure/high temperature (LPHT) processing at temperatures of 1400–2200 °C at pressures <300 torr (see Methods section below). The samples were subsequently characterized by the following methods.

UV-Visible Absorption. The LPHT treatment produced dramatic changes in optical properties of the high-growth rate CVD diamond (Fig. 1). The changes in optical properties of the bulk material are reflected in the large decrease in UV-visible absorption (Fig. 2). The dark as-grown CVD diamond typically exhibits three broad bands in the UV-visible absorption spectrum, specifically at 270 nm, which arises from substitutional nitrogen (8), 370 nm, and 550 nm (8). The absorption coefficients were lowered by the annealing process by factors of 2 to 6. Similar changes in optical absorption have been reported after HPHT annealing (8, 9). In terms of gemological color grades calibrated and quantified by SAS2000 spectrometer (Adamas Gemological Laboratory), the optical properties are improved in average by 3 grades (e.g., from J to G). No significant change in the UV-visible absorption of the CVD diamond was observed after annealing at temperatures <1600 °C. Fig. 3 shows the much

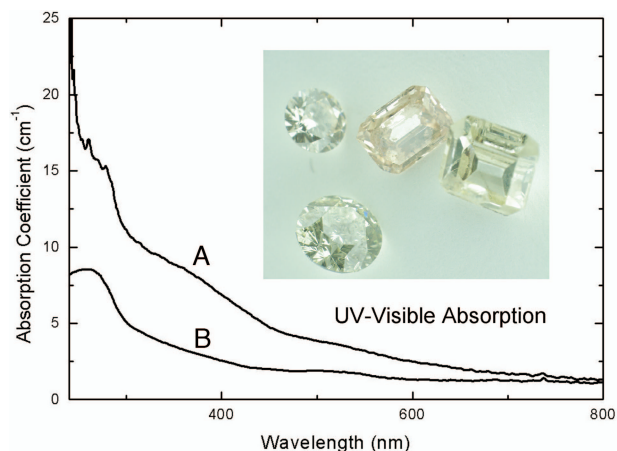


Fig. 2. UV-visible absorption spectra of SC-CVD diamond measured at 300 K (A) before LPHT annealing (B) after LPHT annealing at 1800 °C for 2 min. The Inset shows the annealed SC-CVD diamond produced at high growth rates.

more transparent LPHT-treated SC-CVD diamond plates produced at high growth rate.

Photoluminescence. Photoluminescence (PL) spectra were also measured. These spectra are characterized by PL systems with zero-phonon lines at 575 and 637 nm excited with a 488 nm argon-ion laser line (Fig. 4). By using band assignment for previously reported PL spectra of the diamond, these changes show that the original nitrogen-vacancy NV^0 and NV^- centers at 575 nm and 637 nm, respectively, still exist after LPHT annealing and that the H3 center (N-V-N) at 503 nm, which did not exist before annealing, emerges after annealing. We also note that in most of samples the PL intensity at 737 nm associated with the silicon-vacancy center greatly decreased or disappeared after LPHT annealing. This change is probably associated with the disappearance of the red fluorescence.

These measurements show that the NV centers react to the LPHT annealing in different ways depending on the annealing conditions (Fig. 5). At annealing temperatures <1700 °C or short annealing times >1700 °C, the PL intensities of NV^0 and NV^- centers increase by a factor of up to 5, and this may explain the strong orange fluorescence induced by 488 nm excitation. Before annealing, the as-grown brown diamond shows a dark red fluorescence. The orange hue of the LPHT

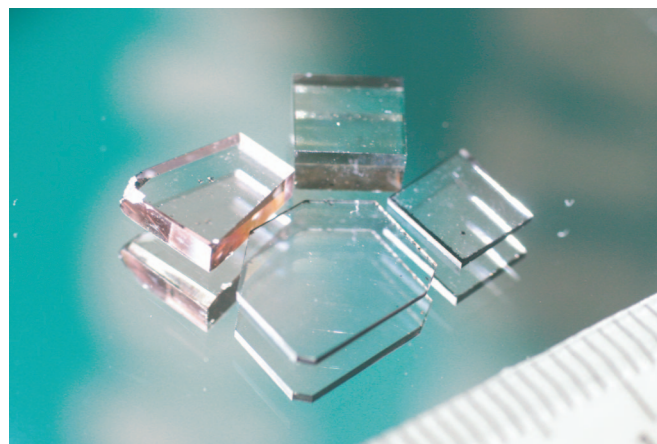


Fig. 3. Transparent LPHT-treated (up to 2000 °C) SC-CVD diamond plates produced at high growth rates.

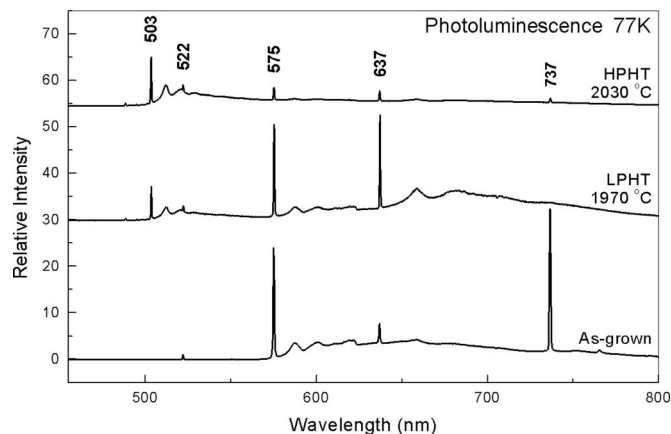


Fig. 4. Photoluminescence spectra of three segments of the same CVD diamond measured at 77 K with 488 nm laser excitation. The intensities are normalized to the T_{2g} Raman peak of the diamond at 522 nm. The spectra have been displaced vertically for clarity; (Bottom) an as-grown segment; (Middle) an LPHT annealed segment; (Top) an HPHT annealed segment.

annealed CVD diamond is thought to come from this orange fluorescence. At >1700 °C and longer annealing times, the PL from the NV^0 and NV^- centers decreases. Unlike LPHT treatment, after HPHT annealing the NV centers either decrease or disappear and PL spectra are dominated by strong H3 centers (Fig. 4). The behavior of NV centers may have important implications for quantum computing applications (24).

Infrared Absorption. Infrared absorption spectroscopy is extremely useful for identifying impurities and defect species in diamond (25). IR absorption spectra of our samples reveal major changes in hydrogen-related vibrational and electronic transitions caused by the LPHT annealing. The *Inset* of Fig. 6 shows the C-H stretching region at 2800 – 3200 cm^{-1} . The broad band at 2930 cm^{-1} attributed to hydrogenated amorphous carbon (a-C:H) (26) is observed in the high-growth rate CVD diamond and its intensity correlates with that of the brown color of the diamond. After annealing, the IR spectrum in this region exhibits bands at 2810 cm^{-1} [sp^3 -hybridized bonds on {111} (27, 28)], 2870 cm^{-1} [sp^3 -CH₃ (27)], 2900 cm^{-1} [sp^3 -hybridized bonds on {100}, ref. 26], 2925 cm^{-1} (sp^3 -CH₂-), 2937 cm^{-1} , 2948 cm^{-1} , 3032 cm^{-1} , and 3053 cm^{-1} [sp^2 -hybridized bonds (27, 29)]. The results indicate that the dangling bonds of the a-C:H on {100} in the as-grown brown CVD diamond are transformed by LPHT annealing to a locally denser structure (e.g., ref. 6) and a lower overall UV-visible absorption. Possible mechanisms for the production of the enhanced optical properties have been described in ref. 4 based on the changes in C-H stretching vibra-

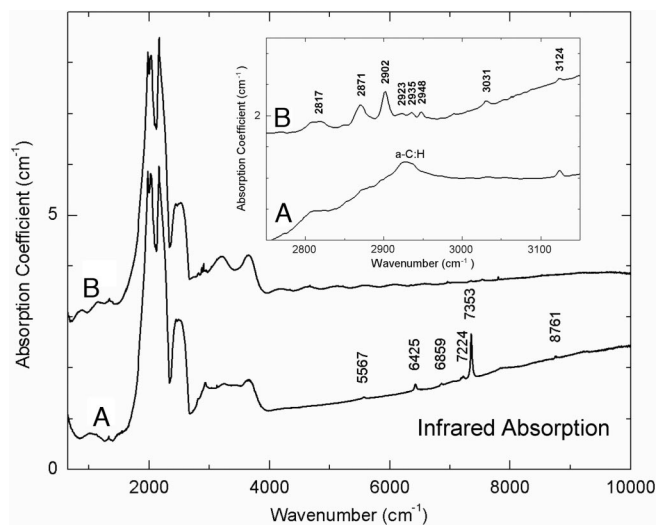


Fig. 6. Infrared absorption spectra of CVD diamond produced at high growth rate: (A) as-grown crystal (B) after LPHT annealing at 1600 °C for 10 min. The spectra are displaced vertically for clarity. The *Inset* shows the CH stretching vibration region.

tions of the HPHT annealed CVD diamond (6, 8). In the near IR region (Fig. 6), the main absorption bands at 7357 cm^{-1} , 7220 cm^{-1} , 6856 and 6429 cm^{-1} , and weaker features at 8761 and 5567 cm^{-1} greatly decreased or disappeared after LPHT annealing. Moreover, the absorption continuum increasing from 5000 to 10000 cm^{-1} also decreased.

The LPHT annealing effects described above are broadly similar to those of HPHT annealing (8) but with the following differences: The LPHT-annealed and as-grown CVD diamond both exhibit a peak at 3124 cm^{-1} [attributed to H involving one C (30)] and bands at 7357 cm^{-1} , 7220 cm^{-1} , 6856 cm^{-1} , and 6429 cm^{-1} that are not observed in the HPHT-treated CVD diamond. The LPHT-treated CVD diamond does not exhibit the 3107 cm^{-1} absorption feature [sp^2 -CH = CH- (31, 32), related to gray color and existing in the HPHT annealed samples (8)] and the bands at 2972 cm^{-1} [sp^2 -CH₂- (27)] and 2991 cm^{-1} . Finally, the high-pressure induced sp^3 C-H bond shift by 3 – 15 cm^{-1} to higher wave numbers at 2820 cm^{-1} , 2873 cm^{-1} and 2905 cm^{-1} , present in the HPHT-annealed samples is absent in the LPHT-treated crystals.

Discussion

Characterizations of the SC-CVD diamond produced by high growth rate techniques before and after the LPHT processing provides information on the annealing mechanism of these

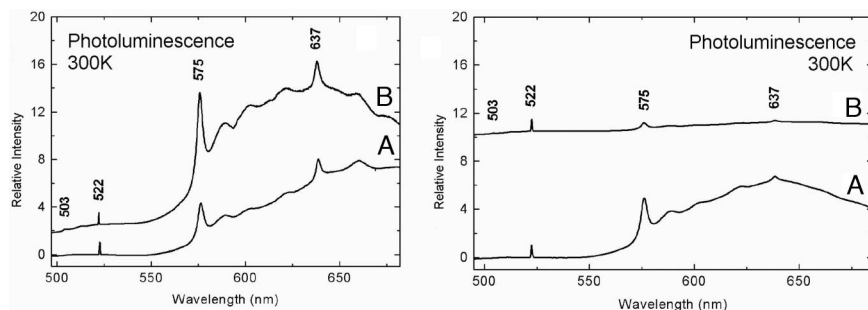


Fig. 5. Examples of photoluminescence spectra of CVD diamond measured at 300 K with 488 nm laser excitation. The intensities are normalized to the T_{2g} Raman peak of the diamond at 522 nm. The spectra have been displaced vertically for clarity; (Left): (Line A) before LPHT annealing; (Line B) after LPHT annealing at 1500 °C for 1 h; (Right): (A) before LPHT annealing; (B) after LPHT annealing at 1700 °C for 1 h.

materials. UV-visible, PL and IR measurements on SC-CVD diamond compared with data on diamond subjected to HPHT annealing reveal insights into the origin of the diverse spectroscopic features reported for diamond in general. The PL and IR spectra indicate the existence of three temperature regimes associated with changes in the properties of these diamond samples. When the temperature reaches 700 °C, vacancies become mobile (16–18). Some of these vacancies are subsequently trapped by substitutional N_s centers and cause an increase in the number of NV centers. This is the reason why PL intensities associated with NV^0 and NV^- centers increase after annealing at lower temperatures or for shorter times.

The broad visible absorption giving rise to the brown color remains unchanged until the diamond is annealed to >1400 °C, at which the diamond begins to become more transparent. The intensities of the 270 nm and 370 nm absorption bands decrease, whereas the intensity of the absorption band near 550 nm increases or remains unchanged. We suggest that hydrogen migrates above this temperature. Hydrogen is usually the most abundant impurity in the diamond grown under the conditions described here. The formation of brown diamond could be due to the enhancement of growth rate by nitrogen present in the gas used for the CVD growth; diamond produced at this high growth rate has more extended defects (i.e., under-bonded carbon or vacancy clusters). Nitrogen could decorate these defects, and hydrogen is incorporated with those defects as unstable centers: a-C:H (and other hydrogen-related infrared absorption bands) and NVH^- (21). Both HPHT and LPHT annealing mobilize the incorporated hydrogen. There is evidence that the annealing of a polycrystalline CVD diamond at ≈ 1400 °C (33) causes hydrogen located on internal grain boundaries or in the inter-granular material to become mobile. IR absorption spectra, after annealing, reveal that the concentration of a-C:H decreases and hydrogen forms stable C-H bonds on {100} and {111}. First principles calculations suggest that the largely featureless absorption spectra of the brown diamond is attributed to vacancy disks lying on {111} planes and that hydrogen can passivate the optical activity of the disks resulting in reduced absorption (4).

The 370 nm absorption feature may be associated with hydrogen-related defects (35). CVD diamond annealed above 1400 °C but below 1700 °C usually attains a brownish pink color, indicating that the pink hue of the annealed CVD diamond is associated with the 550 nm band, and very likely originates from the NV centers. We propose that the 550 nm absorption band corresponds to emission associated with NV centers at 575 nm and 637 nm. However, the 550 nm absorption feature is very broad and does not coincide with the electron-phonon bands at 575 nm or 638 nm and cannot be directly correlated with NV centers. It is possible that these spectral features are associated with NV centers, and the 550 nm absorption band corresponds to the broad fluorescence superimposed by emission associated with NV centers, which may be due to the vacancy discs or clusters decorated by a low concentration of nitrogen. Detailed study, in particular at low temperatures, is needed to provide detailed band assignments and further information about the origin of these optical features.

The most significant changes are observed at temperatures >1700 °C, at which some nitrogen-related defects become mobile. It is possible that vacancies are more easily trapped by hydrogen than by nitrogen at temperatures at which hydrogen atoms are mobile. At the same time, at higher temperatures, the stable NV centers are annealed out because N also tends to form H3 aggregates. Another change that can happen at elevated temperatures is the breaking of the C-H bonds, which can also cause loss of hydrogen. Such an effect has been observed during annealing of the polycrystalline CVD diamond at 1600 °C (33).

In our experiments, the hydrogen content (27) calculated from the integrated intensities of the C-H band decreased from 4 ppm to 1.5 ppm (Fig. 6). We observed a decrease in intensity of the C-H stretching band after annealing at even higher temperatures (1800–2200 °C).

The results of the LPHT annealing process indicate that the intensity of the 370 nm absorption band correlates with the absorption continuum increasing toward shorter wavelengths although the persistence of the 550 nm band shows a correspondence with the residual absorption features. There are three main factors that are related to the broad visible absorption of the CVD diamond: nitrogen, vacancies, and hydrogen. The intensity of the absorption continuum in UV-visible range for the as-grown CVD diamond depends on the concentration of nitrogen in the gas used for the CVD process (2). The broad absorption increases with increasing PL intensity of the NV^0 (575 nm) and NV^- (637 nm) centers. The transparent as-grown CVD diamond has either no or very low content of NV centers. When the optical absorption of the diamond is annealed out, the number of NV centers is reduced. PL spectra in type IIa natural brown diamond reveals the presence of NV centers, whereas no NV luminescence is observed in type IIa natural diamond that is nearly transparent in the UV-visible range (34). The HPHT-treated type IIa natural brown diamond exhibits a small number of NV centers, but the greater the crystal absorption, the stronger the NV^- fluorescence band (34). However, whereas LPHT annealing decreases the broad absorption, instead of decreasing the number of the NV centers, the intensity of the corresponding band increases, which shows that the NV centers are not the only cause of the absorption. CVD diamond grown at high rates can be very different from natural diamond. The major characteristic impurity in our standard high-growth rate CVD diamond is hydrogen and that impurity is associated with under-bonded carbon (e.g., π -bonds in extended defects) or vacancy clusters, which may be decorated by nitrogen. The a-C:H peak in brown CVD diamond is replaced on annealing by various well-resolved C-H stretching bands, while the intensities of hydrogen-induced electronic absorption bands decrease. The 3124 cm^{-1} and the a-C:H vibrational bands, and electronic transitions associated with hydrogen-related centers in the near-IR region, are absent in the transparent CVD diamond grown without the addition of nitrogen (3). This observation suggests that hydrogen-related defects correlate with nitrogen impurities. Nitrogen doping promotes {100} faceted growth. Orange to orange red luminescence and striations are typically observed for N-doped CVD diamond. These striations are a result of a different uptake of impurity-related defects on the risers and terraces of surface growth steps (9).

The a-C:H peak at 2930 cm^{-1} occurs in the region that corresponds to absorption of C-H groups on {100}. In hydrogen-rich natural diamond, hydrogen is incorporated mostly in cuboid sectors (35). The 370 nm band is present in brown cuboid sectors while absent in gray octahedral sectors in the same diamond (35). Hydrogen may be incorporated into NV^- complexes on {100} in CVD diamond during its growth. NVH^- is a common defect in nitrogen doped SC-CVD diamond and can be present in higher concentrations than the NV centers (21). It has been proposed that hydrogen atoms are bonded to the nitrogen, and the unpaired electrons located in the dangling bonds of the three equivalent nearest-neighbor carbon atoms, with very little localization on the nitrogen (20). EPR spectra show that the NVH^- centers exist in our as-grown nitrogen doped CVD diamond and that they are removed by both the LPHT and HPHT treatment. Concentrations of paramagnetic defects follow the sequence $N_s^0 > NVH^- > NV^-$ (unpublished data) (8). The intensities of the three

UV-visible absorption bands follow the order 270 nm (N_s) > 370 nm (unknown) > 550 nm (possibly NV related). The NVH^- centers may also be associated with the 3124 cm^{-1} feature and the near-IR hydrogen-induced electronic absorption. The 370 nm emission was observed in brown CVD diamond after irradiation and its intensity increased as the nitrogen intensity increased in local areas (7).

The susceptibility of the electron-phonon vacancy related color centers to LPHT processing makes it possible to reduce broad visible absorption of the CVD diamond produced at high growth rates. Movement of hydrogen atoms from the unstable hydrogen-incorporated centers (e.g., NVH^-) to more stable C-H bonds can explain the dramatic enhancement in optical transparency of this diamond. We also note that the SC-CVD diamond can endure longer annealing times than polycrystalline CVD diamond without graphitization.

Conclusions

Processing SC-CVD diamond at LPHT has been shown to be effective in enhancing the optical properties of these crystals, and this treatment provides important insight into the nature of defects and impurities associated with diamond. In contrast to HPHT annealing, this LPHT method is applicable in CVD reactors as a subsequent treatment after growth and not constrained by the size of the crystals. Spectroscopic characterization of LPHT annealed crystals has advanced understanding of the mechanism of annealing. The 370 nm absorption band and increasing absorption continuum toward shorter wavelengths of the as-grown SC-CVD diamond appear to originate from the presence of hydrogen incorporated extended defects (under-bonded carbon or vacancy clusters), which may be decorated with nitrogen forming defect centers (e.g., NVH^-). The optical enhancement may be attributed to the changes in defect structure associated with hydrogen incorporation during CVD growth. There is a decrease in sharp line spectral features indicating a reduction in NVH^- defects. We suggest that the residual absorption (≈ 550 nm) of the annealed CVD diamond is associated with the increased concentration of the NV centers as compared with the as-grown material. Because the spin associated with the NV^- complex may have a practical use, and the number of NV^- complexes could be controlled by the LPHT annealing process, the LPHT-annealed SC-CVD diamond could be a promising material for applications such as quantum computing which

Table 1. LPHT annealing conditions of brown SC-CVD diamond

Temperature, °C	Pressure, torr	Time, min
2100–2200	220–300	0.1–0.5
1700–2000	200–220	1–60
1400–1600	150–200	10–720

require detailed information on the concentration and distribution of these complexes.

Methods

SC-CVD diamond samples were produced by the MPCVD method described elsewhere (2, 3). Typically the diamond samples were grown under the following conditions: $N_2/CH_4 = 0.2$ –5.0%, $CH_4/H_2 = 12$ –20%, total pressures of 120–220 torr, and temperatures of 900–1500 °C. For the purpose of annealing, a 6 kW, 2.45 GHz microwave plasma CVD system with a redesigned cavity and molybdenum substrate stage was used to generate stable and energetic hydrogen plasmas (2). SC-CVD diamond plates were heated in the CVD chamber to temperatures in the range 1400 °C to 2200 °C, at pressures between 150 and 300 torr. Typically, samples were heated stepwise to the maximum annealing temperature, kept at the maximum temperature for a chosen time, and ramped down to room temperature. The processing conditions are summarized in Table 1. Temperatures were measured by an infrared two-color pyrometer. It should be noted that all diamond used in the experiments consisted of high quality single crystal material to prevent significant graphitization and cracking at temperatures >1600 °C at low pressures outside the diamond stability range, and energetic hydrogen plasma etch (6).

Samples were characterized before and after LPHT processing by micro-photoluminescence (PL), and micro-UV-visible and synchrotron IR absorption spectroscopy. Photoluminescence spectra were measured at 77 K and room temperature by using a custom-built micro Raman/PL system. PL spectra were typically excited by the 488 nm argon-ion laser. The laser power was ≈ 50 mW and the focal spot diameter was ≈ 5 μm . The UV-visible absorption spectra were measured at room temperature with a custom-built micro UV-visible absorption setup based on an Ocean Optics spectrometer. The spot diameter was ≈ 20 μm . Synchrotron IR absorption spectra were obtained at the U2A beamline of the VUV ring of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The spectra were measured in the range 400–10000 cm^{-1} .

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