Evolution of nitrogen structure in N-doped diamond crystal after high pressure and high temperature annealing treatment*

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In this paper, we have reported an investigation on the evolution of nitrogen structures in diamond crystals which contain nitrogen donor atoms in the range of 1500 ppm–1600 ppm following an annealing treatment at a high pressure of about 6.5 GPa and high temperatures of 1920 K–2120 K. The annealing treatment was found to completely transform nitrogen atoms originally arranged in a single substitutional form (C-center), into a pair form (A-center), indicated from infrared (IR) spectra. The photoluminescence (PL) spectra revealed that a small fraction of nitrogen atoms remained in C-center form, while some nitrogen atoms in A-center form were further transformed into N3 and H3 center structures. In addition, PL spectra have revealed the existence of two newly observed nitrogen-related structures with zero phonon lines at 611 nm and 711 nm. All these findings above are very helpful in understanding the formation mechanism of natural diamond stones of the Ia-type, which contains nitrogen atoms in an aggregated form.

Keywords: IaA-type diamond crystal, nitrogen aggregation, H3 center, N3 center

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1. Introduction

Natural diamonds, which display a wide range of colors, can absorb light in the ultraviolet (UV), visible, and infrared spectral regions due to the presence of defects, impurities, and strains.[1,2] Synthetic diamond crystals produced in a high pressure and high temperature (HPHT) process also exhibit a broad range of optical properties, from transparency to the intrinsic band gap to strong absorption across the visible spectrum. Colorless diamond crystals of the IIa type with undetectable nitrogen impurities can be prepared under HPHT conditions by adding nitrogen getters in the metal reaction bath to form stable nitrides.[3,4] Single diamond crystals produced at HPHT generally contain a significant amount of nitrogen donor atoms, resulting in a yellow color.[5,6] Deliberately N-doped diamond crystals can even exhibit a green or dark color.[7–10] Chemical vapour deposition (CVD) diamond crystals also readily absorb nitrogen impurities from the gas phase, which are then incorporated as single substitutional nitrogen and nitrogen-vacancy complexes.[11,12] Previous experimental results indicated that the color of diamond crystals is affected primarily by nitrogen structures. Nitrogen donor atoms usually exist in an aggregated form in natural diamond stones, while it always exists in a single substitutional form, namely the C-center, in synthetic diamond stones. However, when synthetic diamond samples are subjected to more aggressive HPHT conditions, nearly colorless specimens with the same nitrogen form as the natural diamond stones can be obtained.[13–16] This fact suggested that Ia-type diamond stones with nitrogen in an aggregated form might have been exposed to high temperatures after their initial formation.

There have been few reports regarding the evolution of nitrogen structures in diamond crystals containing high concentrations of nitrogen. Gem-quality diamond samples with high levels of nitrogen impurities have been previously proven to be difficult to produce by either HPHT or CVD process. Recently, we have successfully produced gem-quality diamond crystals containing nitrogen impurities at concentrations above 1000 ppm (1 ppm = 1.76×10^{17} atoms/cm^3) via a laboratory-scale HPHT process.[7–10] Accordingly, a HPHT annealing method was employed to treat nitrogen-rich diamond crystals in order to observe the evolution of nitrogen-related structures created under HPHT conditions. The main objective of the present work is to develop a deeper understanding of natural diamond genesis.

2. Experimental details

Experiments with annealing diamond crystals were carried out in a China-type cubic anvil HPHT apparatus (SPD-6×1400) equipped with special anvils designed with double bevel edges to improve the pressure limit of the high-pressure apparatus. A more detailed description concerning this technique has been presented previously.[17] Annealing temperatures were maintained between 1920 K and 2120 K. The temperature was extrapolated from a correlation between the ap-

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plied temperature and input power, which was calibrated using a Pt6%Rh–Pt30%Rh thermocouple. The operating pressure was maintained at about 6.5 GPa, which is the estimated pressure limit for this high-pressure apparatus based on a curve derived from the pressure-induced phase transitions of bismuth, thallium, and barium. The N-doped diamond samples were grown at a constant pressure of about 6.0 GPa and a temperature of 1550 ± 30 K. A temperature gradient between the carbon source and the seed crystal was estimated to be approximately 20 K–50 K.

Annealing samples consisted of Ib-type diamond crystals with an approximate C_N of 1600 ppm (2.82×10^{20} atoms/cm^3) were grown at HPHT with TGM employing the {111} facet as an epitaxial face. Diamond crystals with a size range of 2 mm–3 mm were pressed into the cylinder graphite samples and fixed in the assembly for annealing treatment, as shown in Fig. 1. Ampoules of 13 mm in diameter for annealing diamonds were made from ZrO_2 (80 wt%) and MgO (20 wt%), which were sintered at a temperature of 1470 K within 2 h. Each annealing run was maintained at HPHT for 1 h. After the power was switched off, the pressure of the apparatus was slowly released. The collected samples were then placed into a mixture of concentrated H_2SO_4 and HNO_3 (3/1, v/v) in order to separate the diamond crystals from graphite. The purified diamonds were viewed under an optical microscope, and nitrogen concentrations were measured by a Fourier transform infrared (FTIR) spectrometer. For the infrared absorption measurements, a Bomem M110 FTIR spectrometer equipped with a Spectra Tech IR-PLANTM microscope and a liquid-nitrogen-cooled detector were utilized. The IR beam size was rescaled to a 100-μm square aperture in order to transmit only the diamond samples. Crystals of KBr pressed into a flat slice served as a reference sample. A spectral resolution of 1 cm^{-1} and a summation of 100 scans were used throughout the FTIR measurement. A spectrometer (F4500) was used to measure the photoluminescent properties of the diamond samples, which were excited with a laser wavelength of 371 nm.

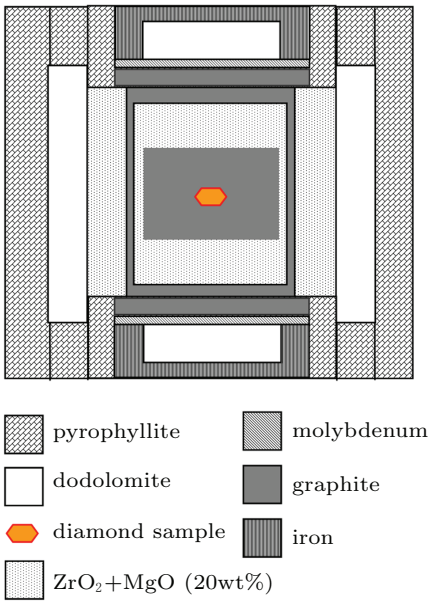


Fig. 1. (color online) Assembly for annealing N-doped as-grown diamond crystals at HPHT.

3. Results and discussion

As-grown Ib-type diamond crystals doped with nitrogen atom donors generally exhibit a green color due to high concentrations of dispersed nitrogen atoms corresponding to absorption peaks at 1130 cm^{-1} and 1344 cm^{-1} in the one-phonon region (500 cm^{-1}–1500 cm^{-1}) of the IR spectra.[5,7] As the diamond crystal with a nitrogen concentration (C_N) of 1550 ± 50 ppm was annealed at a pressure of 6.5 GPa and a holding temperature of 1920 ± 30 K, an obvious absorption peak at 1282 cm^{-1} could be observed in the IR spectra, suggesting that the isolated substitutional nitrogen atoms had aggregated together to form an A-center (nitrogen pairs). The absorption peaks at 1130 cm^{-1} and 1344 cm^{-1} became weaker simultaneously, as seen in Fig. 2.

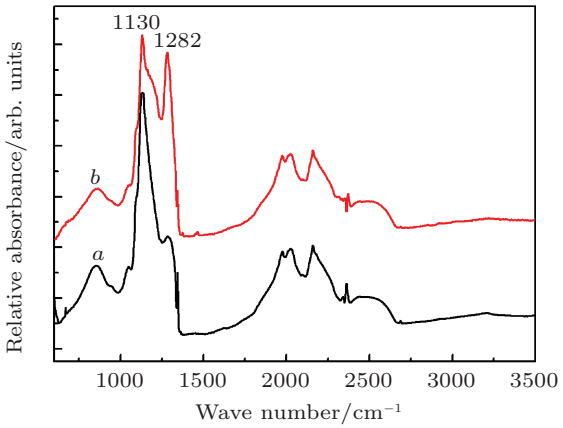


Fig. 2. (color online) FTIR spectra from diamond crystals with C_N of 1550 ± 50 ppm before (curve *a*) and after (curve *b*) annealing treatment at 1920 ± 30 K.

The FTIR spectra obtained from high-quality diamond specimens allowed for an accurate quantitative analysis of nitrogen concentration. C_N, in A-center form, is determined by an absorption coefficient of 1282 cm^{-1} which multiplies the absorption factor (16.5 atomic ppm per cm^{-1}) after the IR spectrum is decomposed into two individual components according to the procedure described in Refs. [18] and [19]. C_N, in C-center form, is obtained from an absorption coefficient of 1130 cm^{-1}, namely, 25.0 atomic ppm per cm^{-1}. The N-doped diamond crystal varied remarkably in color from a dark green (nearly opaque) to light green, as shown in Figs. 3(a) and 3(b). The color change was attributed to the N-aggregation process indicated from the FTIR spectra. The percentage of

nitrogen aggregation from C-center to A-center was estimated to be 38 ± 4%.

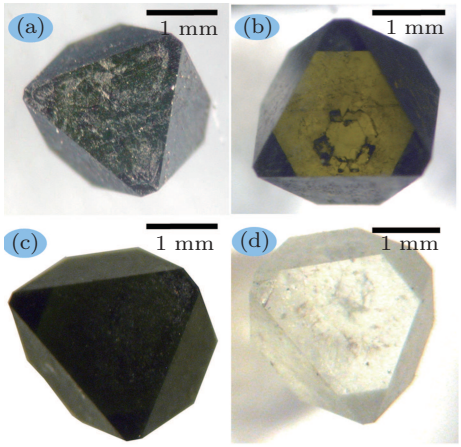


Fig. 3. (color online) Optical images of high-concentration N-doped diamond crystals. (a) As-grown, (b) after annealing treatment at 1920 ± 30 K, (c) as-grown, and (d) after annealing treatment at 2120 ± 30 K.

As the annealing temperature was increased, a higher temperature was applied and higher concentrations of aggregated nitrogen were present in the N-doped diamond crystals. As the holding temperature was increased to 2120 ± 30 K, an expected phenomenon occurred: the N-doped diamond crystal transformed from dark green to nearly colorless, as seen in Figs. 3(c) and 3(d). It can be seen in the FTIR spectra (Fig. 4): absorption peaks of 1130 cm^{-1} and 1344 cm^{-1}, characteristic of C-center nitrogen atoms, were no longer detectable after HPHT annealing treatment. Instead, a strong absorption peak at 1282 cm^{-1}, characteristic of an A-center formed of nitrogen atoms, was present. The variation in FTIR spectra described previously confirms that a fraction of nitrogen atoms have been transformed from C-center form to A-center form following a HPHT process.

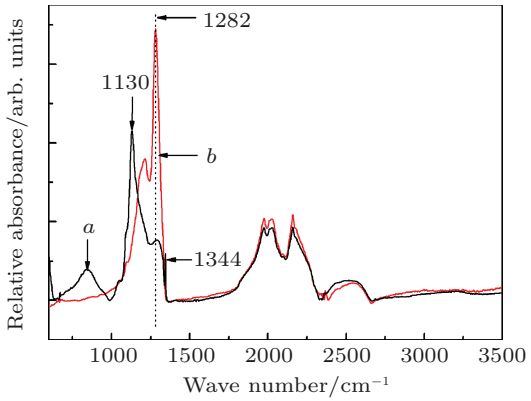


Fig. 4. (color online) FTIR spectra from the diamond crystal with dispersed nitrogen around 1550 ± 50 ppm before (curve *a*) and after (curve *b*) annealing treatment at 2120 ± 30 K.

Although IR spectra can provide detailed information about nitrogen defects in diamonds, this spectral method revealed a limitation of the technique for detecting some forms of nitrogen in diamonds. Luminescence is a phenomenon in which the electronic state of a substance is excited by an external energy and the excitation energy is emitted as light. If the excitation source is radiation, the emission is called photoluminescence (PL) spectra. In the PL process, the material may emit light regardless of its form, shape, size, or state. Accordingly, PL can provide additional information regarding the evolution of nitrogen structure in diamonds during the annealing process. As shown in Fig. 5, diamond samples with C_N of 1500 ppm–1600 ppm were analyzed with a fluorescence spectrophotometer before and after annealing treatment at temperatures of 1920 K–2120 K. As shown in curve *a* of Fig. 5, the as-grown diamond sample with high C_N emits strong fluorescence in the wavelength region of 300 nm–430 nm. When this diamond specimen was treated at 1920 ± 30 K, the fluorescence band of 260 nm–472 nm became more pronounced and a weak absorption peak at 325 nm was present, as shown in curve *b* of Fig. 5. After diamond samples were annealed at 2120 ± 30 K, the strong fluorescence band nearly disappeared, but a new weak absorption peak at 371 nm was produced, as shown in curve *c* of Fig. 5.

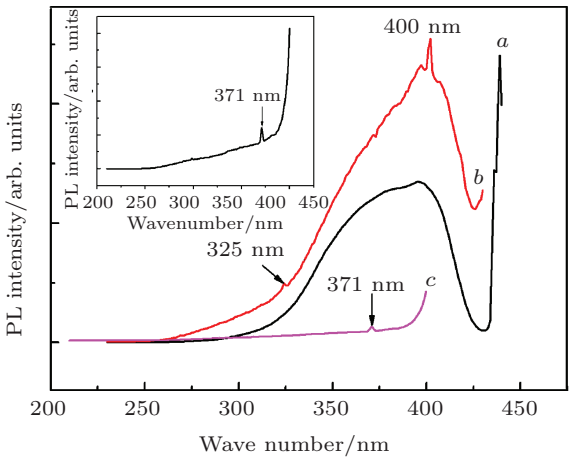


Fig. 5. (color online) PL excitation spectra from the diamond crystals with C_N of 1500 ppm–1600 ppm: untreated (curve *a*), treated at 1920 ± 30 K (curve *b*), and treated at 2120 ± 30 K (curve *c*). The inset from curve *c* has been displayed for clarity.

The emission spectra of PL for N-doped diamond crystals excited with a laser wavelength of 371 nm before and after HPHT annealing treatment provided valuable insight into nitrogen structures in diamond crystals. The emission spectra of PL from diamond samples are shown in Fig. 6. The PL spectrum from untreated diamond had an intense emission band at 442 nm accompanied by two weak peaks located at 611 nm and 711 nm, as displayed in curve *a* of Fig. 6. After the sample was annealed at a temperature of 1920 ± 30 K, the PL spectra showed a weaker emission band at 442 nm and stronger peaks at 611 nm and 711 nm. A new emission peak of 415 nm was also produced, as illustrated in curve *b* of Fig. 6. These results confirm that the emission band at 442 nm is associated with

the C-center form of nitrogen atoms. Analysis of changes in PL and FTIR spectra before and after the annealing treatment process indicated a decrease of C_N in the C-center form after the experience of annealing treatment. At a temperature of 2120 ± 30 K, a diamond sample containing 1600 ppm of nitrogen impurities exhibited an emission band of 442 nm in PL spectra with significantly lower intensity, as pictured in curve *c* of Fig. 6. This observation suggested that a small fraction of nitrogen atoms in C-center form structure still existed in the diamond crystal, even though there was no detectable peak regarding isolated C-center nitrogen in the FTIR spectra. Observation on spectral results in curve *c* of Fig. 6 also shows that the emission peaks of 415 nm, 503 nm, 611 nm, and 711 nm do not change considerably compared with these in curve *b* of Fig. 6. The emission peak at 415 nm is attributed to N3 center, with three neighboring nitrogen atoms surrounding a vacant side, and the peak at 503 nm is attributed to H3 center, the nitrogen–vacancy–nitrogen (N–V–N) structure, consisting of one vacancy surrounded by two adjacent substitutional nitrogen atoms.[16,20,21] The formation process of H3 center structure can be described as the combination of A-center with a vacancy, while N3 center structure can be considered as the collision of the H3 center with a C-center nitrogen atom, from the collision view. Accordingly, a reasonable formation process of nitrogen-related structure is given as follows: N + N $\rightarrow$ A; A + V $\rightarrow$ H3; H3 + N $\rightarrow$ N3, where N and A denote C-center and A-center formed nitrogen atoms, respectively, and V indicates a vacancy. The H3 and N3 center structures in diamond crystals absorb light in the visible region, whereas A-center absorbs no light, which can be used to explain why the emission peak associated with the A-center structure was not observed in the PL spectra. It is worth noting that the emission peaks at 611 nm and 711 nm were considerably higher in intensity. It is therefore reasonable to conclude that an emission peak at 611 nm may be correlated with a complicated structure consisting of nitrogen and a vacancy, in that the NV^0 structure (consisting of one nitrogen atom and one neutral vacancy) is associated with an emission peak at 575 nm and the NV^- structure (consisting of one nitrogen atom and one negative vacancy) corresponds to an emission peak at about 637 nm.[22–25] This newly observed nitrogen structure was originally present in a diamond lattice, induced by the entrapment of substantial nitrogen donor atoms during the growth process. This N–V related structure may play a significant role in enhancing the aggregation process of isolated nitrogen in the high-concentration N-doped diamond samples previously reported.[26,27] The observation that the emission peak at 711 nm originally present in as-grown N-doped diamond crystals was enhanced after annealing treatment suggests that this peak may be evidence of a nickel-nitrogen-related structure. Yelisseyev *et al.* in 2002 reported that a 732-nm emission peak was responsible for Ni–N complex structure,[28] while Wolfer *et al.* in 2009 reported that a peak at 788 nm was also associated with the Ni–N complex structure.[29] Based on these prior findings, assignment of the peak at 711 nm to Ni–N complexes seems reasonable. A more detailed investigation regarding emission peaks at 611 nm and 711 nm will be conducted in our future research.

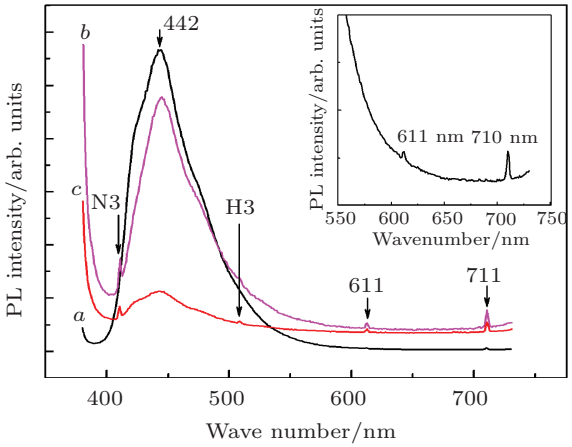


Fig. 6. (color online) PL emission spectra from the high-level N-doped diamond crystals: untreated (curve *a*), treated at 1920 ± 30 K (curve *b*), treated at 2120 ± 30 K (curve *c*). The insert from curve *a* has been displayed for clarity.

4. Conclusion

We explored the evolution of nitrogen-associated structures in diamond crystals containing high concentrations of nitrogen after the annealing treatment at high pressure and temperature conditions. Experimental results demonstrated that diamond crystals, with nitrogen concentration in the thousand ppm range, originally green in color are transformed into nearly colorless specimens after an annealing treatment process at a temperature of 2120 K and a pressure of about 6.5 GPa. FTIR spectra revealed that the dispersed nitrogen atoms, C-center form, were completely transformed into the paired form. PL spectra provided more detailed information about the evolution of the nitrogen structure, revealing that the evolution of the majority of nitrogen atoms under these conditions followed a sequence of C-to-A, while a small fraction of nitrogen further transformed from A-center into H3 center, N3 center, and other nitrogen-related structures.

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