Influence of annealing treatment on as-grown Ib-type diamond crystal at a high temperature and high pressure*

Huang Guo-Feng(黄国锋)[a], Yin Ji-Wen(尹辑文)[a], Bai Hong-Bo(白洪波)[a]†, HuYi-Ga(胡义嘎)[a], Kai Li(凯 丽)[a], Jing Jing(静 婧)[a], Ma Hong-An(马红安)[b], and Jia Xiao-Peng(贾晓鹏)[a][b]

[a] *Department of Physics and Electronic Engineering, Chifeng College, Chifeng* 024000, *China*
[b] *National Laboratory of Superhard Materials, Jilin University, Changchun* 130012, *China*

(Received 26 January 2012; revised manuscript received 6 May 2012)

In this paper, we report on the influence of annealing treatment on as-grown Ib-type diamond crystal under high pressure and high temperature in a china-type cubic anvil high-pressure apparatus. Experiments are carried out at a pressure of 7.0 GPa and temperatures ranging from 1700 °C to 1900 °C for 1 h. Annealing treatment of the diamond crystal shows that the aggregation rate constant of nitrogen atoms in the as-grown Ib-type diamond crystal strongly depends on diamond morphology and annealing temperature. The aggregation rate constant of nitrogen remarkably increases with the increase of annealing temperature and its value in octahedral diamond is much higher than that in cubic diamond annealed at the same temperature. The colour of octahedral diamond crystal is obviously reduced from yellow to nearly colorless after annealing treatment for 1 h at 1900 °C, which is induced by nitrogen aggregation in a diamond lattice. The extent of nitrogen aggregation in an annealed diamond could approach approximately 98% indicated from the infrared absorption spectra. The micro-Raman spectrum reveals that the annealing treatment can improve the crystalline quality of Ib-type diamond characterized by a half width at full maximum at first order Raman peak, and therefore the annealed diamond crystals exhibit nearly the same properties as the natural IaA-type diamond stones of high quality in the Raman measurements.

Keywords: high pressure and high temperature, diamond crystal, annealing, nitrogen aggregation

PACS: 81.10.Fq, 61.72.S–, 74.62.Dh, 07.57.Ty **DOI:** 10.1088/1674-1056/21/10/108102

1. Introduction

Most natural diamonds exhibit no colour but contain aggregated nitrogen impurities. These are termed Ia type diamonds. Some of them containing pairs of nearest-neighbouring substitutional nitrogen atoms (A-centers) are classified as IaA type and those containing complexes of four substitutional nitrogen atoms surrounding a lattice vacancy (B-centers) are classified as IaB type.[1,2] Diamond crystals grown with the temperature gradient growth method (TGM) at high pressure and high temperature (HPHT) always display a yellow colour caused by nitrogen impurities in a dispersed form (C-centre). In order to gain a colorless diamond, nitrogen getters were usually doped into the diamond-growing environment to eliminate nitrogen impurities.[3] However, it was reported that the annealing treatment of diamond could be used to change the state of nitrogen in diamond crystal under appropriate conditions.[4] The annealing treatment could also be used to change the optical properties of the single crystal diamond prepared by chemical vapour deposition.[5] It is, therefore, a potential method to gain colorless diamond crystals from as-grown Ib-type diamond crystals.

As is well known, natural diamonds are usually found in kimberlite, which contains many inorganic minerals, such as olivine, picrite, and phosphorite. Hence, in order to reveal the genesis of natural diamond stones, it is thought that the diamond crystals containing aggregated nitrogen can be synthesized by employing inorganic mineral catalyst/solvent. So far, substantial inorganic minerals have been chosen as catalysts to synthesize diamond, including carbonates, oxides, hydroxides, chlorides, phosphorus, and a large number of other compounds.[6–10] The experimental results demonstrated that perfect diamond crystals cannot be prepared with those catalysts. Neverthe-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50572032 and 50731006).
†Corresponding author. E-mail: hbbai@vip.sina.com
© 2012 Chinese Physical Society and IOP Publishing Ltd

less, there is another clue to revealing the genesis of a natural diamond crystal, that the majority of natural diamonds contain A-centre or B-centre nitrogen. It was suggested that the natural diamonds had undergone extremely high temperature after formation.[11] Thus, we first synthesize diamond crystals using a transition metal as a solvent with TGM at HPHT. The as-grown diamond crystals were then annealed under HPHT conditions. In this paper, we mainly investigate the influence of HPHT treatment on Ib-type diamond crystals, including nitrogen aggregation, diamond crystal color, and crystalline quality. This study is helpful for changing the properties of the synthetic diamonds and conducive to revealing the formation mechanism of a natural diamond.

2. Experimental detail

Experiments on annealing diamond crystals were carried out in a china-type cubic anvil HPHT apparatus (SPD-6×1200). Annealing temperatures were operated in a range of 1700 °C–1900 °C. The temperature was extrapolated from a correlation between the temperature and input power, calibrated with a Pt6%Rh–Pt30%Rh thermocouple.[12] The operating pressure was loaded to about 7.0 GPa estimated by the curve that was established based on the pressure-induced phase transitions of bismuth, thallium, and barium.

The annealed samples are Ib-type diamond crystals grown at HPHT with TGM, with {100} surface and {111} surface of seed crystals used as epitaxial facets, respectively. The shapes of the annealed diamond crystals are cubic and octahedral, respectively. Diamond crystals with sizes in a range of 3 mm–4 mm were pressed into holes which had been drilled in cylindrical graphite samples. These were then loaded into the capsule. The capsule for annealing the diamonds was 10 mm in diameter and was made from MgO and ZrO_2. The schematic diagram of assembly used to anneal the diamond sample is shown in Fig. 1. Each annealing run was kept at HPHT for 1 h. After the power was switched off, the pressure of apparatus was slowly released. The collected samples were put into a mixed concentrated acid consisting of H_2SO_4 and HNO_3 (3/1) to isolate the diamond crystals from graphite. After the annealed diamonds were purified, they were observed by the optical microscope, and the nitrogen concentrations in diamond were determined using a Fourier transform infrared (FTIR) spectrometer. For the infrared absorption measurements, a Bomem M110 FTIR spectrometer equipped with a Spectra Tech IR-PLANTM microscope was utilized. The IR beam size was rescaled to a 100-μm square aperture in order to only pass through the diamond samples. Moreover, micro-Raman spectroscopy was applied to the analysis of diamond crystals before and after the HPHT annealing treatment. A high-quality natural diamond (IaA type) was also selected to compare with the annealed diamond crystals in the Raman properties.

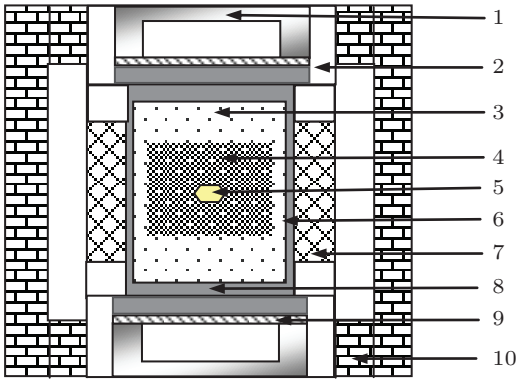


Fig. 1. Assembly for annealing as-grown diamond crystals at HPHT. 1: steel ring; 2: dolomite; 3: MgO+ZrO_2; 4: graphite medium; 5: diamond sample; 6: heater tube; 7: NaCl sleeve; 8: graphite sheet; 9: titanium plate; and 10: pyrophyllite.

3. Result and discussion

3.1. Dependence of nitrogen aggregation on temperature and morphology

As is well known, the as-grown Ib-type diamond crystals without any intentional doping always display a yellow colour caused by C-centres corresponding to 1130 cm^{-1} and 1344 cm^{-1} in one-phonon region of the IR spectrum[13,14] as displayed in Fig. 2. However, as diamond crystals were annealed at a pressure of 7.0 GPa, with the increase of annealing temperature in a range of 1700 °C–1900 °C, nitrogen atoms would aggregate together in the form of an A-centre with an obvious absorption peak at 1282 cm^{-1} in the IR spectrum as indicated in Fig. 3. It can be seen that the strength of the absorption peak at 1282 cm^{-1} in one-phonon region is much stronger from octahedral diamond than that from cubic diamond. There is a weak change in the IR spectrum recorded from the cubic diamond, whereas it is shown in the spectrum recorded from octahedral diamond that the intensities

of 1130 cm^{-1} and 1344 cm^{-1} correlated with C-centres become weaker remarkably with the increase of the annealing temperature. Nitrogen concentrations in an isolated form and aggregated form in annealed diamonds are calculated with the absorption coefficients at 1130 cm^{-1} and 1282 cm^{-1}, multiplied by 25 atom ppm/cm^{-1} and 16.5 atom ppm/cm^{-1}, respectively, after the IR spectra were decomposed into two individual components utilizing the procedure described in Refs. [15] and [16]. The results concerning nitrogen concentrations are displayed in Table 1 with an uncertainty of around 5%. It is shown that with the increasing annealing temperature, the content of aggregated nitrogen increases and the dispersed nitrogen declines in both cubic diamonds and octahedral diamonds after HPHT annealing treatment. It is worth noting that the change of nitrogen concentration is more obvious in octahedral diamond crystals. The extent of nitrogen aggregation can approach approximately 98% and the isolated nitrogen nearly disappears, after annealing the octahedral diamond crystal at 1900 °C for 1 h, as displayed in Fig. 3 (curve *f*). This transformation suggests that nitrogen atoms may be deposited in natural diamond in a dispersed state during growth. The annealing treatment may change the state of nitrogen from the dispersed state to the aggregated state during long residence in the high-temperature environment deep within the earth.

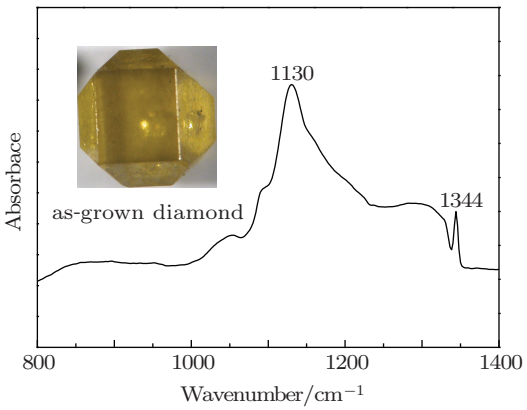


Fig. 2. (colour online) The FTIR spectrum of an as-grown Ib-type diamond crystal in one-phonon region.

The process of nitrogen aggregation follows the second order kinetic.[17,18] The kinetic of this reaction is described as $Kt = 1/C_{\rm f} - 1/C_0$, where K (atomic $ppm^{-1}{\cdot}s^{-1}$) is an aggregation rate constant of nitrogen; t is the annealing duration expressed in second; C_0 and $C_{\rm f}$ are the concentrations of C-centres before and after HPHT treatment, respectively, which can be determined by the IR spectra recorded from the diamond crystal. It is found that K is influenced by the diamond morphology, and the dispersed nitrogen in octahedral diamonds migrated to form an A-centre with a much faster rate, indicated in Table 1. We suggest that the difference in nitrogen aggregation between the two types of morphologies may relate to the growth process of the diamond samples by using the distinct surfaces of seed crystal as epitaxial facets. For the octahedral diamonds prepared at a higher temperature, with the {111} surface used as an epitaxial facet, the point defects in diamond crystal such as vacancies and nickel defects are easily formed during growth, in that the higher temperature can induce the high activity of the metal solvent and a high growth rate of the diamond crystal. On the contrary, for the cubic diamonds grown at a lower temperature, with the {100} surface used as an epitaxial facet, lattice imperfections are generally fewer than that in the octahedral diamond. The fact that the crystal perfection in cubic diamond is higher than that in the octahedral diamond has been confirmed by researchers. Consequently, the high degree of lattice imperfection in octahedral diamonds leads to the higher diffusion rate of nitrogen atoms and so results in a higher aggregation rate. Previously, in the case of the mechanism concerning nitrogen aggregation, the vacancy-assisted mechanism was brought forward by some researchers.[19,20] We argue that the vacancy-assisted mechanism may be present. However, the essence of transformation about nitrogen states in diamond is a phase transition of nitrogen impurities just like the phase transition of carbon from graphite to diamond induced by temperature and pressure. This suggestion is based on the fact that the various states of nitrogen can be transformed, and this transformation can be described with the followed equation: $\mathrm{N} + \mathrm{N} \rightleftharpoons \mathrm{A}$, where N represents an isolated nitrogen atom; A denotes the A-centre. As for our experiments, the aggregation reaction is observed. It is, however, observed that the reverse reaction takes place at a low pressure of 5 GPa–6 GPa for natural diamond.[21] The completely colorless diamonds are difficult to prepare due to this reverse reaction. To sum up, the most significant thing is that the aggregation process of nitrogen is easily realized in octahedral diamond, which provides good information about changing the diamond properties or preparing the Ia-type diamonds.

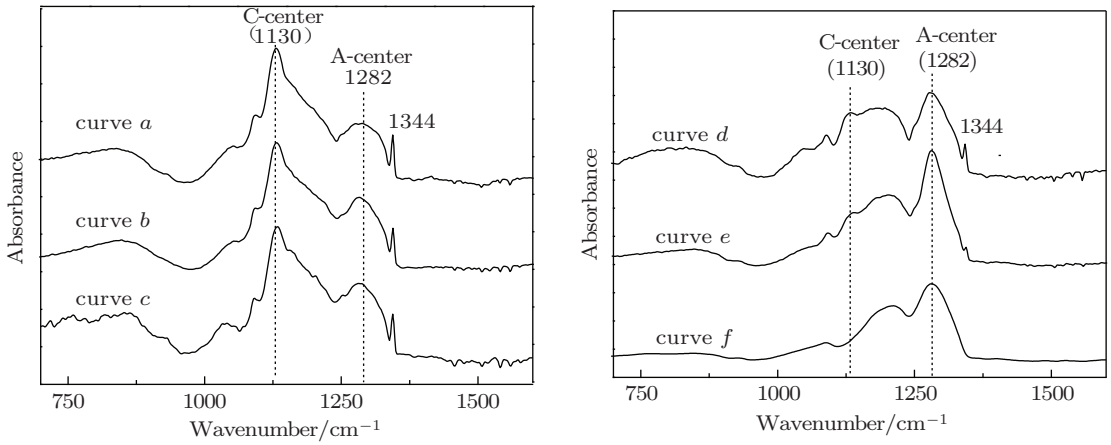


Fig. 3. The FTIR spectra in the one-phonon region from samples C_1 (curve a), C_2 (curve b), C_3 (curve c), C_4 (curve d), C_5 (curve e), and C_6 (curve f).

Table 1. Nitrogen concentrations and aggregation rate constants.

No.	T/°C	Morphology	C_0/ppm	C_f/ppm	Percent/%	$k/10^{-7}$ ppm^{-1}·s^{-1}
C_1	1700	cube	224	210	6	0.8
C_2	1800	cube	306	264	14	1.4
C_3	1900	cube	121	101	17	4.5
C_4	1700	octahedron	201	112	44	11.4
C_5	1800	octahedron	161	49	70	39.4
C_6	1900	octahedron	312	6	98	454.1

3.2. Influence of annealing treatment on diamond colour

There is no obvious change in colour for the cubic diamond crystal synthesized with TGM, with the {100} surface used as an epitaxial facet, after annealing treatment in a temperature range of 1700 °C–1800 °C as described in Figs. 4(a) and 4(b). The diamond crystals all exhibit an intense yellow colour before annealing treatment, whereas it displays a light yellow colour after HPHT annealing treatment for 1 h at 1900° as displayed in Fig. 4(c). However, the octahedral diamond crystals grown with the crystal surface {111} used as a growth surface change more obviously in colour with increasing annealing temperature, and the diamond sample annealed at 1900 °C is nearly colorless and transparent as shown in Figs. 4(d)–4(f). The colour change of the annealed diamond crystal is in excellent agreement with the calculation result of nitrogen aggregation according to the FTIR spectrum. When the annealing temperature is beyond 1900 °C, the graphitized diamond samples will be prepared, in that the annealing temperature is not located in the diamond-stable range and below the diamond-graphite equilibrium line in carbon phase diagram.

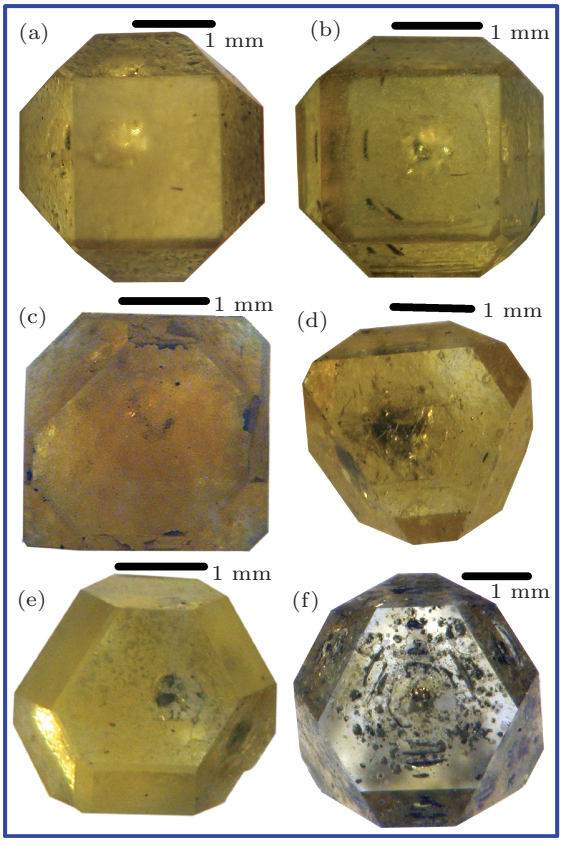


Fig. 4. (colour online) Optical microscopy images of cubic diamond samples ((a)–(c)) and octahedral diamond samples ((d)–(f)) after annealing treatment.

3.3. Influence of annealing treatment on micro-Raman spectrum of the diamond crystals

The diamond crystal is characterized with micro-Raman spectra before and after HPHT (7.0 GPa, 1900 °C) annealing treatment as shown in Figs. 5(a) and 5(b). The measured results demonstrate that the first order Raman peak shifts from 1333.0 cm^{-1} to 1330.3 cm^{-1}, and the half width at full maximum (HWFM) at a Raman peak associated with a sp3-bonded carbon atom varying from 9.0 cm^{-1} to 7.0 cm^{-1}. It is indicated that the crystalline quality of diamond crystal turns better as a result of nitrogen aggregation and recrystallization of diamond crystals. Furthermore, a natural diamond (IaA-type) containing nitrogen impurities at the same level is also measured with micro-Raman spectroscopy as seen in Fig. 5(c). It is shown that the first order Raman peak is at 1329.7 cm^{-1} and HWFM is about 7.2 cm^{-1}, which is almost the same as that of the annealed diamond crystal. Accordingly, diamond crystals annealed with the HPHT method exhibit nearly the same properties as the IaA-type natural diamond in the micro-Raman spectrum.

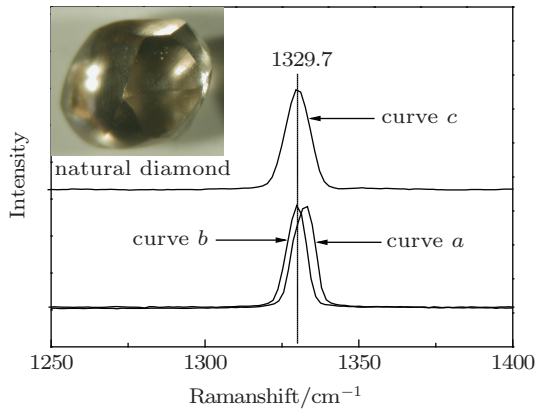


Fig. 5. (colour online) Micro-Raman spectra from the as-grown diamond crystal before curve *a* annealing and after curve *b* annealing, and from the IaA-type natural diamond curve *c*.

4. Conclusions

The gem-quality diamond crystal grown by TGM, with the {111} surface used as an epitaxial facet, is annealed into a nearly colorless diamond at an extremely high pressure (7.0 GPa) and a high temperature (1900 °C). Annealing experiments reveal that with the annealing temperatures increasing, the nitrogen aggregation rate constant increases, especially for octahedral diamonds. We suggest the transformation of nitrogen states in diamond is a phase transition of nitrogen impurities. The micro-Raman spectrum indicates that the crystalline quality of diamond crystal turns better and displays nearly all the same properties as those of the IaA-type natural diamond stones which have a high quality. This variation is caused by the nitrogen aggregation and recrystallization of diamond crystal at HPHT.

References

[1] Liang Z Z, Jia X P and Liang J Q 2007 *Chin. Phys. Lett.* **24** 3551
[2] Huang G F, Jia X P, Li Y, Hu M H, Li Z C, Yan B M and Ma H A 2011 *Chin. Phys.* B **20** 078103
[3] Sumiya H and Toda N 2005 *New Materials* **60** 15
[4] Kiflawi I and Bruley J 2000 *Diamond Relat. Mater.* **9** 87
[5] Meng Y F, Yan C S, Lai J, Krasnicki S, Shu H Y, Yu T, Liang Q, Mao H K and Hemley R J 2008 *Appl. Phys. Sci.* **105** 17620
[6] Akaishi M, Kanda H and Yamaoka S 1990 *J. Cryst. Growth* **104** 578
[7] Akaishi M, Kanda H and Yamaoka S, 1990 *J. Appl. Phys.* **29** 1172
[8] Wang Y and Kanda H 1998 *Diamond Relat. Mater.* **7** 57
[9] Akaishi M, Kanda H and Yamaoka S 1993 *Science* **259** 1592
[10] Taniguchi T, Dobson D, Jones A P, Rabe R and Milledges H J 1996 *J. Mater. Res.* **11** 2622
[11] Collins A T, Kanda H and Kitawaki H 2000 *Diamond Relat. Mater.* **9** 113
[12] Ma H A, Jia X P, Chen L X, Zhu P W, Guo W L, Guo X B, Wang Y D, Li S Q, Zou G T, Zhang G and Bex P 2002 *J. Phys.: Condens. Matter* **14** 11269
[13] Zhang Z F, Jia X P, Liu X B, Hu M H, Li Y, Yan B M and Ma H A 2012 *Chin. Phys.* B **21** 038103
[14] Li Y, Jia X P, Hu M H, Liu X B, Yan B M, Zhou Z X, Zhang Z F and Ma H A 2012 *Chin. Phys.* B **21** 058101
[15] Huang G F, Jia X P, Li S S, Hu M H, Li Y, Zhao M, Yan B M and Ma H A 2010 *Sci. Chin.* Ser. G **53** 1831
[16] Kanda H and Yamaoka S 1993 *Diam. Relat. Mater.* **2** 1420
[17] Yelisseyev A P, Vins V G, Lobanov S S, Afonin D V, Blinkov A E and Maximov A Y 2010 *J. Cryst. Growth* **318** 539
[18] Chrenko R M, Tuft R E and Strong H M 1977 *Nature* **270** 141
[19] Collins A T 1980 *J. Phys.* C: *Solid State Phys.* **13** 2641
[20] Nadolinny V A, Yelisseyev A P, Baker J M , Twitchen D J, Newton M E, Feigelson B N and Yuryeva O P 2000 *Diamond Relat. Mater.* **9** 883
[21] Weerdt F D and Collins A T 2003 *Diamond Relat. Mater.* **12** 507