Growth of gem-grade nitrogen-doped diamond crystals heavily doped with the addition of $Ba(N_3)_2$*

Huang Guo-Feng(黄国锋), Jia Xiao-Peng(贾晓鹏), Li Yong(李 勇), Hu Mei-Hua(胡美华), Li Zhan-Chang(李战厂), Yan Bing-Min(颜丙敏), and Ma Hong-An(马红安)†

National Laboratory of Superhard Materials, Jilin University, Changchun 130012, *China*

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Additive $Ba(N_3)_2$ as a source of nitrogen is heavily doped into the graphite–Fe-based alloy system to grow nitrogen-doped diamond crystals under a relatively high pressure (about 6.0 GPa) by employing the temperature gradient method. Gem-grade diamond crystal with a size of around 5 mm and a nitrogen concentration of about 1173 ppm is successfully synthesised for the first time under high pressure and high temperature in a China-type cubic anvil high-pressure apparatus. The growth habit of diamond crystal under the environment with high degree of nitrogen doping is investigated. It is found that the morphologies of heavily nitrogen-doped diamond crystals are all of octahedral shape dominated by {111} facets. The effects of temperature and duration on nitrogen concentration and form are explored by infrared absorption spectra. The results indicate that nitrogen impurity is present in diamond predominantly in the dispersed form accompanied by aggregated form, and the aggregated nitrogen concentration in diamond increases with temperature and duration. In addition, it is indicated that nitrogen donors are more easily incorporated into growing crystals at higher temperature. Strains in nitrogen-doped diamond crystal are characterized by micro-Raman spectroscopy. Measurement results demonstrate that the undoped diamond crystals exhibit the compressive stress, whereas diamond crystals heavily doped with the addition of $Ba(N_3)_2$ display the tensile stress.

Keywords: temperature gradient method, gem-grade nitrogen-doped diamond crystals, high temperature and high pressure, additive $Ba(N_3)_2$

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1. Introduction

In diamond lattice, nitrogen can be present in the single substitutional form (C-centre) or in the aggregated form (A-centre and B-centre). An overwhelming majority of natural diamonds are of type-Ia containing aggregated nitrogen ranging from less than 1 ppm (1 ppm $=1\times10^{-6}$) to thousands ppm, whereas as-grown diamonds belong to type-Ib containing dispersed nitrogen (C-centres) about 100 ppm–400 ppm.[1−3] The form and the concentration of nitrogen in diamond lattice can significantly affect its optical property and thermal stability. Therefore, the investigation regarding the growth of diamond crystal with high nitrogen concentration can broaden its application field, such as micro-electronics and optics field. Additionally, the detection of nitrogen state and concentration in nitrogen-doped diamond crystal is conducible to the exploration of the formation mechanism of natural diamond.

It was reported that the powder $Ba(N_3)_2$ was an efficient dopant in the synthesis of diamond grit with a high nitrogen concentration.[4] It was, however, never applied to the growth of gem-grade nitrogen-doped diamond crystals. Recently, we have found that Fe-based solvent is more appropriate to grow diamond crystal containing nitrogen impurity with higher concentration.[5,6] Therefore, additive $Ba(N_3)_2$ is employed as a doping agent and KOV metal ($Fe_{59}Ni_{25}Co_{16}$) is selected as solvent to grow nitrogen-doped diamond by the temperature growth method (TGM). In order to investigate the growth habit of diamond crystal under the high-nitrogen-concentration environment, the diamond growth region is enlarged by applying a relatively high pressure (about 6.0 GPa). The nitrogen concentrations and the forms in diamonds grown at various temperatures are detected by Fourier transform infrared (FTIR) spectrometer and strain in diamond crystal is characterized by micro-Raman spectroscopy.

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†Corresponding author. E-mail: maha@jlu.edu.cn

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2. Experimental details

The experiments were carried out in a China-made cubic anvil high-pressure and high-temperature apparatus (SPD-6×1200) with the assembly described in Ref. [6]. The size of the synthesis bath made of ceramic material is around 13 mm in diameter. The synthetic pressure was approximately 6.0 GPa, which was estimated by the curve that had been established based on the pressure-induced phase transitions of bismuth, thallium and barium. The growth temperature in the reaction cell was about 1350–1450 °C estimated from a relation between the temperature and input power, which had been calibrated using a Pt6%Rh–Pt30%Rh thermocouple.[7] The heat generated in the carbon-tube resistance heater flowed out of the cell in such a way that the axial temperature gradient in the tube was useful for diamond crystallization. The temperature gradient between the carbon source and seed crystal was about 30–50 °C.

The {111} facet with a size of 0.5 mm was selected as epitaxial face. High-purity graphite used as carbon source Kovar alloy ($Fe_{59}Ni_{25}Co_{16}$) was employed as a catalyst/solvent, and additive $Ba(N_3)_2$ (99.99%) mixed with graphite powder pressed into cylindrical sample was placed into the growth bath. The added amount of $Ba(N_3)_2$ was about 0.6% in mass compared with the quantity of graphite. After synthesis operating under high temperature and high pressure, the collected samples were first placed into the dilute nitric acid to isolate the diamond crystal from metal. Then, the diamond crystals were boiled in strong acid to eliminate the impurities left on the crystal surface. Then, the as-grown diamond crystals were observed by the optical microscope and the nitrogen concentration and the nitrogen state in diamond were detected by using FTIR spectrometer. For the infrared (IR) absorption measurements, a Bomem M110 FTIR spectrometer fitted with a Spectra Tech IR-PLANTM microscope was employed. Circular aperture was used to define a 150-μm diameter region on the sample. The IR absorption spectra over the range of 800–3500 cm^{-1} were recorded at room temperature. Finally diamond crystals were measured by micro-Raman spectroscope to analyse the stress in diamond lattice.

3. Result and discussion

3.1. Morphologies of diamond crystals heavily doped with nitrogen donor

Diamond crystals without intentional doping can change in morphology from cubes to cube-octahedron to octahedron with temperature increasing in a growth region.[8,9] However, the diamond crystals have distinctive growth habit under the environment with high nitrogen concentration. Diamond crystals heavily doped with $Ba(N_3)_2$ (0.6%) show no variation in morphology with temperature increasing in the growth region. The crystals are always of octahedral shape dominated by {111} facets even grown at relatively low temperature ranging from 1350 °C to 1400 °C as illustrated in Fig. 1. When the operating temperature is lower than 1350 °C, no perfect diamond can be gained except twinned crystals, multicrystals and skeleton crystals. This result is in good agreement with the experimental results given by Palyanov *et al.*[10] The octahedral growth habit indicates that the incorporation of nitrogen greatly changes the correlation between the growth rates in ⟨100⟩ and ⟨111⟩ directions, and renders the growth rate in the ⟨100⟩ directions faster than that in the ⟨111⟩ directions. The reason for this phenomenon can be explained by using specific surface energy described in Ref. [6]. As facets corresponding to vertical directions with higher growth rate vanish and those with lower growth rate survive at the end of crystal growth process, diamond crystals heavily doped with nitrogen impurity always show to be of octahedral shape.

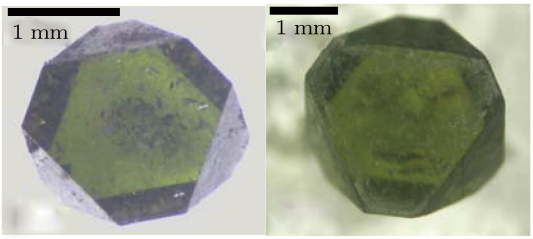


Fig. 1. (colour online) Optical microscopy of gem-grade nitrogen-doped diamond crystals heavily doped with $Ba(N_3)_2$, grown at (a) 1350 °C (sample C_1) and (b) 1400 °C (sample C_2).

3.2. Growth of gem-grade diamonds heavily doped with $Ba(N_3)_2$

As is known, with the content of nitrogen increasing in growth environment, the temperature window of high-quality diamond crystal becomes narrower.[5,6] In order to maintain diamond crystal unceasingly

growing in growth region, the synthesis pressure was loaded up to approximately 6.0 GPa. Moreover, optimization of growth temperature was chosen and the growth duration was prolonged up to 33 h. A nitrogen-doped diamond crystal with a perfect shape size of 5.0 mm and a weight of about 0.5 carat is successfully grown as shown in Fig. 2. It was the largest nitrogen-doped diamond crystal containing nitrogen concentration beyond 1000 ppm with high quality reported so far.

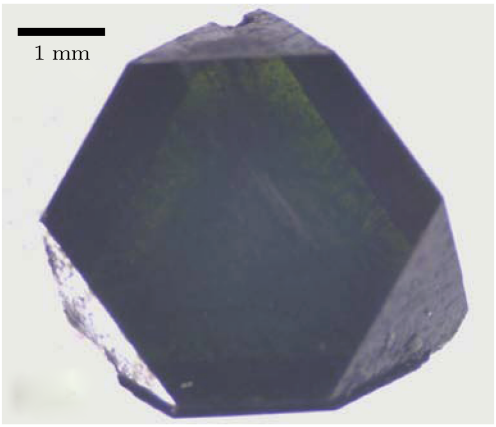


Fig. 2. (colour online) Optical microscopic image of gem-grade nitrogen-doped diamond crystal with a size of 5 mm, which is heavily doped with $Ba(N_3)_2$ and grown at 1400 °C for 33 h (sample C_3).

3.3. Form and concentration of nitrogen in diamond crystal

The diamond crystals heavily doped by nitrogen impurity were characterized by FTIR spectroscope as displayed in Fig. 3. The forms of nitrogen existing in diamonds are determined by intrinsic absorption peaks of IR spectra in one-phonon region (800–1400 cm^{-1}). It can be seen that strong absorption peaks occur at 1130 cm^{-1} and weak absorption peaks appear at 1282 cm^{-1}, simultaneously, in the IR spectra for the samples grown under high-nitrogen-concentration environment. It is indicated that the nitrogen exists in diamond lattice predominantly in the form of C-centre accompanied by a small quantity of A-centre form.

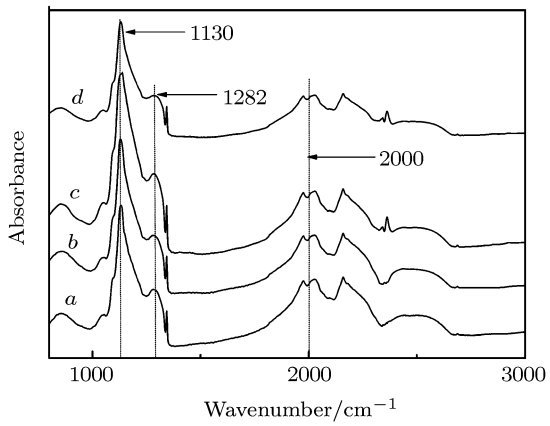


Fig. 3. FTIR spectra of diamond synthesized by TGM heavily doped with $Ba(N_3)_2$, grown at *a*, 1350 °C for 12 h (sample C_1); *b*, at 1400 °C for 12 h (sample C_2); *c*, at 1400 °C for 33 h (sample C_3); and *d*, at 1450 °C for 12 h (sample C_4).

The concentration of nitrogen only in the C-centre form (N_C) in diamond can be calculated from the absorption coefficient α_C/cm^{-1} of the peak at 1130 cm^{-1}[11] to be

$$N_C/10^{-6} = 25\alpha_C. \quad (1)$$

The concentration of aggregated nitrogen only in the A-centre form (N_A) is determined by measuring the absorption coefficient α_A/cm^{-1} of the peak at 1282 cm^{-1}[12] to be

$$N_A/10^{-6} = 16.5\alpha_A. \quad (2)$$

On the assumption that spectra are linearly overlapped, the concentration of A-centres and C-centres in mixed type of diamond IaA+Ib is still determined by the absorption coefficients α_C and α_A which are expressed in the terms of α_{1130} and α_{1282}[13] to be

$$\alpha_C = 1.1\alpha_{1130} - 0.2\alpha_{1282}, \quad (3)$$
$$\alpha_A = 1.1\alpha_{1282} - 0.2\alpha_{1130}, \quad (4)$$

where α_{1130} and α_{1282} are absorption coefficients of the peaks at 1130 cm^{-1} and 1282 cm^{-1}, respectively. The absorption coefficient of the peak at 2000 cm^{-1} is well known to be 12.3 cm^{-1}, so α_{1130} and α_{1282} can be obtained by comparing their absorption intensity (μ) with that of the peak at 2000 cm^{-1} as follows:

$$\alpha_{1130} = \mu(1130\ cm^{-1})/\mu(2000\ cm^{-1}) \times 12.3, \quad (5)$$
$$\alpha_{1282} = \mu(1282\ cm^{-1})/\mu(2000\ cm^{-1}) \times 12.3. \quad (6)$$

The values of absorption intensity are calculated according to the recorded value A in IR spectra to be

$$\mu(1130\ cm^{-1}) = A(1130\ cm^{-1}) - A(1370\ cm^{-1}), \quad (7)$$
$$\mu(2000\ cm^{-1}) = A(2000\ cm^{-1}) - A(1370\ cm^{-1}), \quad (8)$$
$$\mu(1282\ cm^{-1}) = A(1282\ cm^{-1}) - A(1370\ cm^{-1}). \quad (9)$$

Using equations motioned above, N_A and N_C can be calculated. The calculated results with an uncertainty less than 5% are shown in Table 1, where T is the growth temperature, and N_{Total} is the total nitrogen concentration.

Table 1. Nitrogen concentrations and growth parameters.

Sample	Time/h	Growth rate/mg·h^{-1}	T/°C	Nitrogen concentration/ppm		
				$N_{\rm A}$	$N_{\rm C}$	$N_{\rm Total}$
C_1	12	1.5	1350	79	958	1037
C_2	12	1.9	1400	115	970	1085
C_3	33	3.0	1400	185	988	1173
C_4	12	2.4	1450	228	1030	1258

Table 1 demonstrates that $N_{\rm A}$, $N_{\rm C}$ and $N_{\rm Total}$ ($N_{\rm C}$ + $N_{\rm A}$) increase with temperature increasing. With the consideration of errors in IR measurement, growth time has no obvious influence on $N_{\rm C}$ and $N_{\rm Total}$, whereas $N_{\rm A}$ apparently increases with duration prolonging from 12 h to 33 h. The increase of $N_{\rm Total}$ with temperature increasing reveals that the nitrogen donors are trapped more easily by growing diamond crystal at higher temperature. It may be attributed to the high diffusing rate of nitrogen donors in solvent at high temperature while the layer growth rate of diamond crystal changes little. The increase of $N_{\rm A}$ with temperature increasing implies that the crystallization temperature plays a very significant role in the formation of C–N bonds. With crystallization temperature increasing, the crystal growth rate increases and the solvent becomes active, so that the solvent is more easily incorporated into growing crystal. Accordingly, the content of solvent (Ni and Co) existing in diamond lattice can increase with temperature increasing. It has been well approved that the elements of Ni and Co can enhance the aggregation of nitrogen in diamond crystals.[14,15] Consequently, the increase of A-centre concentration with temperature increasing can be explained. Furthermore, increasing temperature itself might enhance the formation of A-centre. In addition, the dependence of aggregation of nitrogen on growth time suggests that most A-centres originate from C-centres annealed during crystal growth.

3.4. Stress in nitrogen-doped diamond crystals

The undoped diamond and heavily nitrogen-doped diamond were measured by a micro-Raman spectroscope in this study, and the results are displayed in Fig. 4. As is well known, the first order Raman peak of purity diamond crystal appears at 1332.0 cm^{-1} usually under the assumption of free strain.[16] According to Raman shift compared with pure diamond, it is found that stress in diamond is extremely complex. The compressive stress appears in undoped standard Ib-type diamond crystal with Raman peak at 1333.3 cm^{-1}, while tensile stress occurs in heavily nitrogen-doped diamond with Raman peaks varying from 1330.2 to 1331.7 cm^{-1}. As is known, various impurities can affect stress in diamond crystals, such as nitrogen, oxygen and solvent metal (Ni, Co), and their existing forms and distributions in diamond crystals can also influence stresses.[17] Hence, the changing state of stress in diamond crystal cannot be simply interpreted by the changing length of chemical bond. Nevertheless, we are convinced that substantial nitrogen donors doping into diamond lattice indeed give rise to the first order Raman peak shifting toward lower frequency, through measuring several diamonds with micro-Raman spectroscopy. This result is distinguished from the case of nitrogen-doped diamond film due to difference in growth mechanism. Generally, doping nitrogen into diamond film had no effect on Raman shift or induced first-order Raman peak shifting toward higher frequency.[18,19]

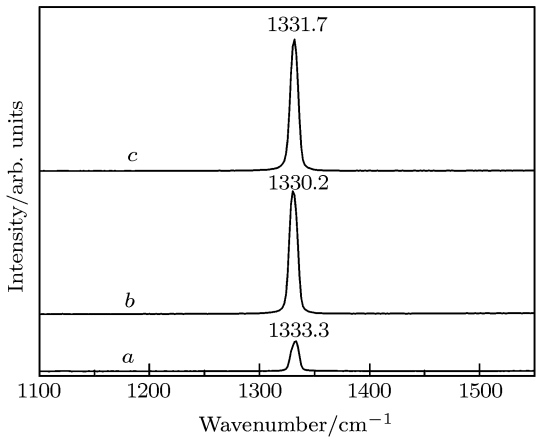


Fig. 4. Micro-Raman spectra from *a*, undoped diamond at a temperature of 1350 °C; *b*, heavily nitrogen-doped diamond grown at 1350 °C; and *c*, heavily nitrogen-doped diamond grown at 1450 °C.

4. Conclusion

The growth habit of diamond crystals heavily doped with the addition of $Ba(N_3)_2$ is investigated

in detail. The crystal morphology is always octahedral when the crystallization temperature varies from low to high in growth region. Based on these findings, growth temperature is optimized and the growth duration is prolonged up to 33 h. Hence, gem-grade diamond crystal with a size of 5 mm and a nitrogen concentration of about 1173 ppm is successfully synthesized for the first time by the temperature gradient method under high temperature and high pressure. The results of FTIR reveal that the nitrogen impurity is predominantly in the dispersed form, accompanied by the aggregated form. The total concentration of nitrogen in diamond crystal increases with temperature increasing. This result demonstrates that nitrogen donors are trapped more easily by growing crystals at higher temperatures. Moreover, the concentration of aggregated nitrogen in diamond increases with temperature and duration. According to micro-Raman spectra, the undoped diamond crystals exhibit compressive stress, whereas diamond crystals heavily doped with nitrogen impurities display tensile stress.

References

[1] Woods G S 1984 *Phil. Mag.* B **50** 673

[2] Sumiya H, Toda N, Nishibayashi Y and Satoh S 1997 *Journal of Crystal Growth* **178** 485

[3] Tian Y, Jia X P, Zang C Y, Li S S, Xiao H Y, Zhang Y F, Huang G F, Li R, Han Q G, Ma L Q, Li Y, Chen X Z, Zhang C and Ma H A 2009 *Chin. Sci. Bull.* **9** 1459

[4] Yu R Z, Ma H A, Liang Z Z, Liu W Q, Zheng Y J and Jia X 2008 *Diamond Relat. Mater.* **17** 180

[5] 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 **10** 1831

[6] Huang G F, Jia X P, Li S S, Zhang Y F, Li Y, Zhao M and Ma H A 2010 *Chin. Phys.* B **19** 118101

[7] 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

[8] Zang C Y, Jia X P, Ma H A, Li S S, Tian Y and Xiao H Y 2006 *Chin. Phys. Lett.* **1** 214

[9] Zhou L, Jia X P, Ma H A, Zheng Y J and Li Y T 2008 *Chin. Phys.* B **17** 4665

[10] Palyanov Y N, Borzdov Y M, Khokhryakov A F, Kupriyanov I N, and Sokol A G 2010 *Crystal Growth and Design* **10** 3169

[11] Kiflawi I, Mayer A E, Spear P M, van Wyk J A and Woods G S 1994 *Philos. Mag.* B **9** 1141

[12] Boyd S R, Kiflawi I and Woods G S 1994 *Phil. Mag.* B **69** 1149

[13] Chepurov A A, Dereppe J M, Fedorov I I and Chepurov A I 2000 *Diamond Relat. Mater.* **9** 1374

[14] Fisher D and Lawson S C 1998 *Diamond Ralat. Mater.* **7** 299

[15] Babicha Y V, Feigelson B N, Fisher D and Lawson S C 2000 *Diamond Ralat. Mater.* **9** 893

[16] Solin S A and Ramdas A K 1970 *Phys. Rev.* B **1** 1687

[17] Anthony T R 1995 *Diamond Ralat. Mater.* **4** 1346

[18] Cao G Z, Schermer J J, Van Enckevort W J P, Elst W A L M and Giling L J 1996 *J. Appl. Phys.* **3** 1357

[19] Baranauskas V, Li B B, Peterlevitz A, Tosin M C and Durrant S F 1999 *J. Appl. Phys.* **85** 7455