Synthesis and characterization of a single diamond crystal with a high nitrogen concentration*

Zhang Zhuang-Fei(张壮飞), Jia Xiao-Peng(贾晓鹏), Liu Xiao-Bing(刘晓兵), Hu Mei-Hua(胡美华), Li Yong(李 勇), Yan Bing-Min(颜丙敏), and Ma Hong-An(马红安)†

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

(Received 12 September 2011; revised manuscript received 28 October 2011)

In this paper, we explore diamond synthesis with a series of experiments using an Fe–Ni catalyst and a P_3N_5 additive in the temperature range of 1250–1550 °C and the pressure range of 5.0–6.3 GPa. We also investigate the influence of nitrogen on diamond crystallization. Our results show that the synthesis conditions (temperature and pressure) increase with the amount of P_3N_5 additive increasing. The nitrogen impurity can significantly influence the diamond morphology. The diamonds stably grow into strip and lamellar shapes in the nitrogen-rich environment. The Fourier-transform infrared spectrum shows that the nitrogen concentration increases rapidly with the content of P_3N_5 additive increasing. By spectrum analysis, we find that with the increase of the nitrogen concentration, the Ib-type nitrogen atoms can aggregate in the *A*-centre form. The highest *A*-centre nitrogen concentration is approximately 840 ppm.

Keywords: characterization, morphology, diamond, nitrogen concentration

PACS: 81.10.Fq, 61.72.S–, 64.70.dg, 07.57.Ty **DOI:** 10.1088/1674-1056/21/3/038103

1. Introduction

Nitrogen is the dominant impurity in an overwhelming majority of both natural and synthetic diamonds, which significantly influences both their physical and chemical properties.[1−7] Diamond crystals are classified into I-type with and II-type without nitrogen impurities. Nitrogen-containg diamonds are further classified into types IaA, IaB, and Ib, which contain nitrogen atoms in the manners of paired nearest neighbouring nitrogen atoms (*A* centre), four nitrogen atoms aggregating around a vacancy (*B* centre), and single substitutional atoms (*C* centre) in the crystal structure, respectively. Generally, most natural diamonds are of Ia type and contain nitrogen impurities with maximum concentrations up to 3000–5000 ppm. The synthetic diamond in a metal–carbon system typically contains 200–300 ppm in the *C*-centre form. Since nitrogen atoms are readily available during diamond crystallization, it is important to study the mechanism of nitrogen incorporation into a diamond crystal structure. To our knowledge, until recently investigations of the formation process are still lacking.

Recently, diamonds with high nitrogen concentrations ranging from 1000 ppm to 3300 ppm were synthesized with some nitrogen-containing compound additives in the catalyst materials, such as BN, NaN_3 and $Ba(N_3)_2$, $CaCN_2$, and FeN_3.[4−12] It is interesting to note that the diamond morphology and colour are significantly influenced by the incorporation of nitrogen during the diamond crystallization. However, the formation process and the growth mechanism are still unclear. Previously, we have synthesized some strip-shaped diamond crystals with nitrogen concentrations ranging from 1000 ppm to 2400 ppm using NaN_3 and $Ba(N_3)_2$ as the nitrogen sources in the metal catalyst.[7,8] Some diamonds containing 1200–2000 ppm of nitrogen were also synthesized with the BN additives.[1,9] However, we note that most of the nitrogen atoms are in the *C*-centre form. Up to now, the highest value of nitrogen concentration was approximately 3300 ppm, as reported by Borzdov *et al.*[11] with Fe_3N as the nitrogen source during the diamond crystallization, which is equal to that of natural diamond. Moreover, it is interesting to note that some nitrogen atoms aggregated in the *A* centres in the diamond growth process. Unfortunately, the obtained diamonds exhibited poor qualities, and all the diamonds

*Project supported by the National Natural Science Foundation of China (Grant No. 51172089) and the Program for New Century Excellent Talents in University, China.

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

© 2012 Chinese Physical Society and IOP Publishing Ltd

contained a lot of cyclic twins and frequently formed polysynthetic and aggregate structures, which is detrimental to the further study of the properties of the diamond. However, the previous investigations revealed that the nitrogen-containing compound in the catalyst plays a key role in determining the nitrogen concentration and the stable form of the diamond crystal structure. Thus, more attention should be paid to the study of the influence of the nitrogen source in the catalyst on the diamond crystallization under high pressure and high temperature (HPHT) conditions.

In this work, we investigate in detail the diamond crystallization in a catalyst–carbon system with a new nitrogen-containing compound, P_3N_5, as the nitrogen source in the temperature range from 1250 °C to 1550 °C and the pressure range of 5.0–6.3 GPa for 15 min. The spontaneous diamond nucleation and growth are obtained by the film growth (FG) process.[13,14] The morphology of the synthesized diamonds is characterized by using an optical microscope and a scanning electron microscope (SEM) after each experiment. The concentration and the stable states of the nitrogen in diamond are evidenced by a Perkin-Elmer 2000 Fourier-transform infrared (FTIR) spectrometer. Our work will be greatly conducive to the deep understanding of the mechanism for the incorporation of nitrogen atoms in diamond.

2. Experiment

Diamond crystals are synthesized in a cubic anvil high-pressure and high-temperature apparatus (SPD-6×1200) with a sample chamber of 13 mm edge length at temperatures of 1250–1550 °C and pressures of 5.0–6.3 GPa for 15 min. The sample assembly for diamond synthesis is shown in Fig. 1. The starting materials are high purity graphite (99% purity, as the carbon source) and $Fe_{70}Ni_{30}$ alloy powder (200 meshes, as the catalyst). We take the phosphorus nitride compounds, P_3N_5(99.99%), as the nitrogen source in the catalyst. The carbon source and the catalyst (1:1, weight ratio) are mixed with the nitrogen source for 4 h. Then the mixed power is pre-pressed into a small cylindrical sample of 13 mm in diameter and 12 mm in height for the diamond crystallization. We control the concentration of nitrogen in the catalyst by changing the content of P_3N_5 additive in the mixed powder from 0.1 wt.% to 0.4 wt.%. The temperature (T) is measured in each experiment using a Pt RH/Pt Rh6 thermocouple, whose junction is placed near the crystallization. The pressure (P) is calibrated at room temperature by the change in the resistance of the standard substance and at high temperature by the graphite–diamond equilibrium in the P–T diagram.

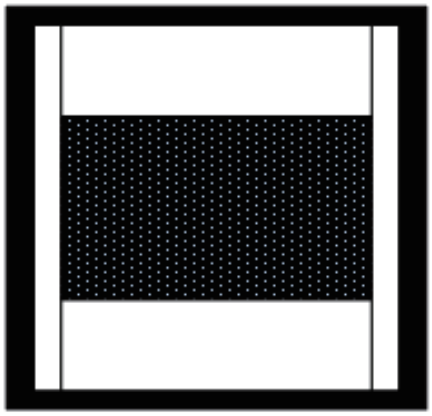


Fig. 1. Sample assembly for diamond synthesized by HPHT.

After the experiment, the collected samples are cracked and dissolved in hot nitric acid to remove the remaining graphite components and the metal catalysts. Then the characterizations of the diamond crystals are carried out by using an optical microscope and an SEM. The concentration of nitrogen in the diamond is measured by using an FTIR spectrometer. For the infrared (IR) absorption measurements, a Bomem M110 Fourier transform infrared spectrometer fitted with a Spectra Tech IR-PLANTM microscope is used. The IR beam size is limited to a 150 μm square by apertures so as to pass only the diamond particle.

3. Results and discussion

3.1. Diamond crystallization

The diamond crystallization experiments are carried out at temperatures of 1250–1550 °C and pressures of 5.0–6.3 GPa for 15 min. The experimental results are presented in Table 1. We implement the diamond nucleation and growth in the Fe–Ni–C system at 5.2 GPa (N-1). The synthesized diamonds are yellow in colour (Fig. 2(a)) and exhibit cubic, cuboctahedron, and octahedron shapes at 1250 °C, 1350 °C, and 1400 °C, respectively. The average size is about 200–300 μm. When P_3N_5 is added into the catalyst, we find that the minimum pressure and the minimum temperature for the diamond crystallization increase significantly. Neither the spontaneous nucleation nor the diamond growth on the seed crystal is

Table 1. Experimental results and characteristics of the obtained diamond.

Run	Time/min	P_3N_5/wt.%	P/GPa	T/°C	Morphology	Colour	Size/mm
N-1	15	0	5.2	1250–1400	cubic, cuboctahedron, octahedron	yellow	0.2–0.3
N-2	15	0.1	5.8	1350–1450	cuboctahedron	green	0.4–0.5
N-3	15	0.2	6.0	1400–1500	strip	deep green	0.6–0.7
N-4	15	0.4	6.3	1440–1550	strip and slice	deep green	0.6–0.8

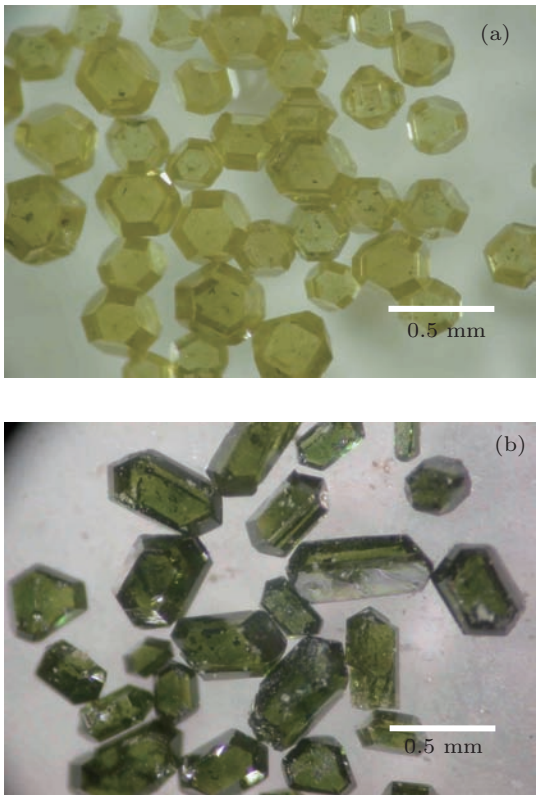


Fig. 2. (colour online) Images of diamond crystals synthesized from Fe–Ni–C system (a) without and (b) with P_3N_5 additive.

found in the system with 0.1 wt.% P_3N_5 additive until the pressure and the temperature increase up to 5.8 GPa and 1350 °C (N-2), respectively. We note that the reaction conditions become 6.0 GPa and 1400 °C in the system with 0.2 wt.% P_3N_5 additive (N-3), and 6.3 GPa and 1440 °C with 0.4 wt.% additive (N-4). The experimental results of crystallization of the carbon phases with and without the P_3N_5 additive are summarized in a P–T sketch diagram (Fig. 3). Furthermore, it is interesting to find that the morphologies of the synthesized diamond crystals are rather special, most of the samples exhibit strip and lamellar shapes, and are dark green in colour (Fig. 2(b)). Most of the synthesized strip-shaped diamond crystals look like stretched cuboctahedrons along the {100} or the {111} crystal surface. The maximum size of the synthesized diamond can reach approximately 600–800 μm in a 15 min run. On the basis of the above results, we suggest that the diamond growth habits are significantly influenced by the addition of P_3N_5 into the catalysts.

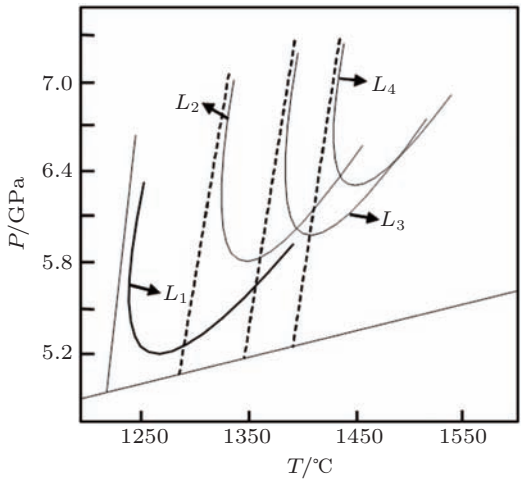


Fig. 3. Schematic P–T diagrams of diamond and graphite crystallization: L_1 represents the growth region for the diamond crystallization in the Fe–Ni–C system; L_2, L_3, and L_4 denote the growth regions for the diamond crystallization in the Fe–Ni–C system with 0.1 wt.%, 0.2 wt.%, and 0.4 wt.% P_3N_5 additives, respectively.

3.2. Morphology

To investigate the morphologies of the diamond crystals, we examine the samples by using an SEM. The morphologies of the diamond crystals obtained in the Fe–Ni–C system are quite different from those of the crystals obtained with the P_3N_5 additive, as shown in Fig. 4. In Fig. 4(a) for the diamond crystals synthesized in the Fe–Ni–C system, we note that the predominant crystal surfaces are {100} and {111}. The surfaces are flat, smooth, and without any melting pit. The latter is found in the diamond crystal synthesized in the P_3N_5 additive system. Figure 4(b) shows a strip crystal stretched along the {100} face. We find that the junction of two stretched {100} faces forms not one edge, but two edges. The {111} crystal faces along the two edges intersect inside the crystal

as indicated by the arrow. Figure 4(c) shows a strip crystal stretched along the {111} faces. From the images, we find that the stretched {111} face exhibits a distinct growth step at the arrow-pointed location. In the middle of the edge, we find a melting pit at the position of the circle. Figure 4(d) shows a diamond crystal with a plate-like shape. The crystal is 500 μm in size and approximately 60 μm in thickness. From the results, we find that the dislocations and the defects appear mainly in the stretched faces. In the previous work,[7,9,10,15,16] the strip-shaped diamond crystals were synthesized under nitrogen-rich conditions. Those diamond crystals seemed to form stretched cubes or stretched octahedrons along the {100} and the {111} crystal faces. Thus, we suggest that the formation of the special morphology can be attributed to the consequence of the incorporation of nitrogen impurity into the crystal structure during the diamond growth. In addition, the special shape and morphology may play an important role in diamond-coated tools.

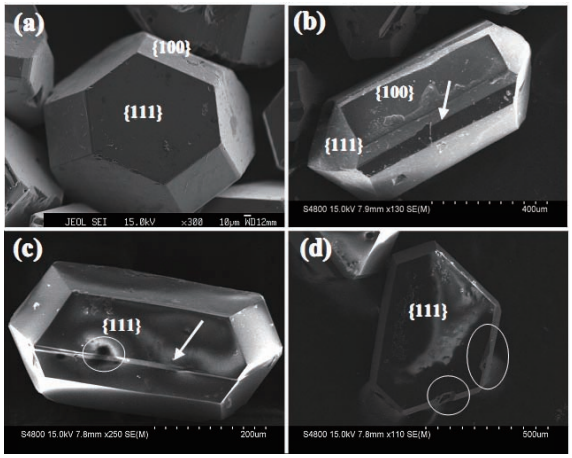


Fig. 4. SEM images of diamond crystals synthesized (a) without and ((b), (c), (d)) with P_3N_5 additive.

3.3. FTIR spectrum and nitrogen concentration of diamond crystal

For the infrared absorption measurements, a number of diamond crystals are selected with suitable sizes (700–800 μm) and quality. The typical FTIR spectra recorded for the synthesized diamonds in the systems with 0 wt.%, 0.1 wt.%, 0.2 wt.%, and 0.4 wt.% P_3N_5 additives are presented in Figs. 5 and 6. As is well known, the nitrogen concentration and the stable states can be determined by the absorption in the defect-induced one-phonon region (900 cm^{-1} and 1400 cm^{-1}). The spectra (curves s_2 and s_3) are similar to each other. The FTIR spectra reveal that the synthesized diamond crystals contain nitrogen impurities in the form of C centres with the absorption at 1130 cm^{-1} and 1344 cm^{-1} (related to the single substitutional nitrogen atoms). Generally, the concentration of the nitrogen impurities in the Ib diamond is proportional to the intensity of the absorption band at 1130 cm^{-1}, and the proportion is 25 in the ideal spectrum.[8,11,17,18] The concentration of C centres can be evaluated according to the absorption coefficient of the IR spectrum, which can be determined by the formula $N_{1130}(\text{ppm}) = (\mu_{1130}/\mu_{2120}) \times 5.5 \times 25$. These spectra show that the absorption intensities in the one phonon region of the diamond synthesized in the system with P_3N_5 additive are obviously increased. The concentrations of the nitrogen impurities in the synthesized diamonds are summarized in Table 2. The highest nitrogen concentration of the nitrogen impurities in the form of C centres is approximately 1500 ppm obtained in the system with 0.2 wt.% P_3N_5 additive.

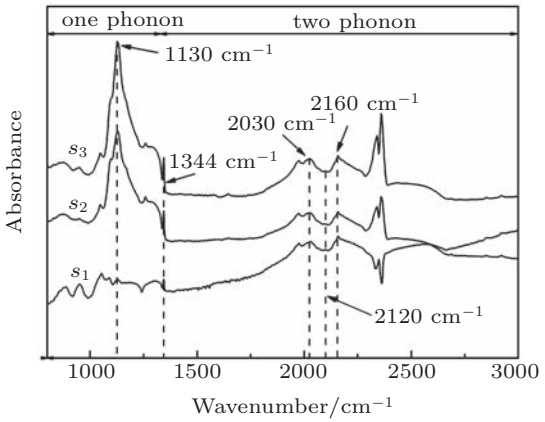


Fig. 5. FTIR spectra of diamond crystal synthesized in the Fe–Ni–C system with the contents of P_3N_5 additive being 0 wt.% (s_1), 0.1 wt.% (s_2), 0.2 wt.% (s_3).

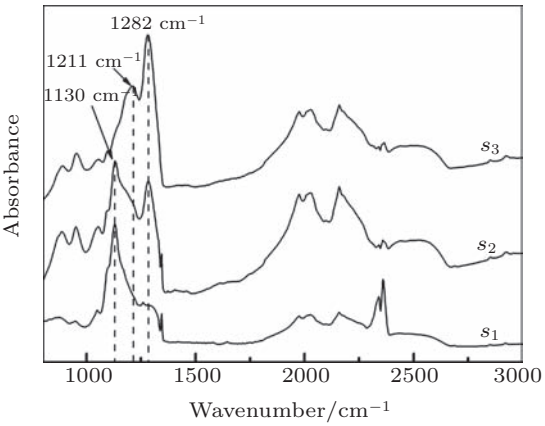


Fig. 6. FTIR spectra of three types of diamond crystals (s_1: Ib, s_2: IaA+Ib, s_3: IaA) synthesized in the Fe–Ni–C system with 0.4 wt.% P_3N_5 additive.

Table 2. Nitrogen concentrations in diamonds synthesized with different P_3N_5 content.

Sample	P_3N_5/wt.%	Type of diamond	Concentration of nitrogen/ppm
1	0	Ib	200–400
2	0.1	Ib	800–1000
3	0.2	Ib	1200–1500
4	0.4	Ib/IaA	1300–1600
		IaA	840

However, we note that the IR spectra show remarkable changes in the system with the P_3N_5 (0.4 wt.%) additive, including a strong decrease of the 1130 cm^{-1} and the 1344 cm^{-1} peaks (associated with the C centres) and the appearances of the 1211 cm^{-1} and the 1282 cm^{-1} peaks (associated with the A centres). The spectrum curve s_2 in Fig. 6 shows higher intensities of the absorption peaks at 1130 cm^{-1} and 1282 cm^{-1}. The shape of the absorption band indicates that the nitrogen atoms appear in both single and paired forms, i.e., a mixture of types Ib and IaA. In addition, the spectrum curve s_3 in Fig. 6 shows that the most prominent feature in some of the synthesized diamond crystals is the maximum peak near 1282 cm^{-1}, and no absorption peaks at 1130 cm^{-1} and 1344 cm^{-1} (C centres) are found, indicating that the nitrogen impurities in the synthesized diamond crystals exist only in the form of nitrogen pairs (A centres). The concentration of the nitrogen impurities in the form of the A centre can be determined by the strength of the absorption peak at 1282 cm^{-1}, and it is obtained to be (16.1±2) atomic ppm per cm^{-1} of absorption at 1282 cm^{-1}. The nitrogen content in the sample is found to be approximately 840 ppm. For the diamond sample with both type Ib and IaA characteristics, the spectrum is decomposed into two bands of C and A centres before making the calculation.[19−21] The A centre concentration can be evaluated according to the absorption coefficient of the IR spectrum through the formula $N_{1282}(\text{ppm}) = \mu_{1282}/\mu_{2120} \times 5.5 \times 16.1$. The total nitrogen concentrations of both A-form and C-form defects are approximately 1300–1600 ppm in the studied systems.

The most interesting result in this work is the synthesis of the diamond single crystals with the type IaA nitrogen in the system with the P_3N_5 additive (0.4 wt.%). In the previous paper,[20,22−28] we knew that the rate of nitrogen aggregation can be significantly enhanced by various factors, e.g., nickel or vacancy related defects. Herein, we suggest that the nitrogen aggregating into the A form structure could make contributions to high reaction temperatures during the diamond growth and the influence on some other impurities in the system (nickel, phosphorus). However, we have no detailed information about these impurities in the diamond crystal structure, analysis of the obtained cubic components should be performed in the future.

4. Conclusion

The purpose of this work is to investigate the influence of nitrogen impurity on the diamond crystallization in the Fe–Ni–C system with the P_3N_5 additive under the HPHT conditions. Diamond crystals with perfect a strip shape and high nitrogen concentration are successfully synthesized. The synthesized diamond crystals exhibit a green or a deep green colour. The FTIR spectra reveal that the diamond crystals contain nitrogen impurities in the forms of A and C centres. The concentration of the nitrogen content in the diamond crystal increases with the increase of the P_3N_5 additive, and it is approximately 1600 ppm in the substitutional form. The stable form of nitrogen is A centre formed in the nitrogen-rich diamond crystal. The maximum nitrogen concentration of type IaA diamond crystal approaches 840 ppm.

References

[1] Kanda H, Akaishi M and Yamaoka S 1999 *Diamond Relat. Mater.* **8** 1441

[2] Reinitz I M, Fritsch E and Shigley J E 1998 *Diamond Relat. Mater.* **7** 313

[3] Collins A T, Kanda H and Kitawaki H 2000 *Diamond Relat. Mater.* **9** 113

[4] Yuri N P, Yuri M B, Alexander F K, Igor N K and Alexander G S 2010 *Crystal Growth Design* **10** 3169

[5] Liang Z Z, Kanda H, Jia X, Ma H A, Zhu P W, Guan Q F and Zang C Y 2006 *Carbon* **44** 913

[6] Zhang Y F, Zang C Y, Ma H A, Liang Z Z, Zhou L, Li S S and Jia X 2008 *Diamond Relat. Mater.* **17** 209

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

[8] Liang Z Z, Jia X, Ma H A, Zang C Y, Zhu P W, Guan Q F and Kanda H 2005 *Diamond Relat. Mater.* **14** 1932

[9] Liu X, Jia X, Zhang Z, Zhao M, Guo W, Huang G and Ma H 2011 *Crystal Growth Design* **11** 1006

[10] Liu X, Jia X, Zhang Z, Li Y, Hu M H, Zhou Z X and Ma H 2011 *Crystal Growth Design* **11** 3844

[11] Borzdov Y, Pal'yanov Y, Kupriyanov I, Gusev V, Khokhryakov A, Sokol A and Efremov A 2002 *Diamond Relat. Mater.* **11** 1863

[12] 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** 118101

[13] Liu X, Jia X, Gou X K, Zhang Z and Ma H 2010 *Crystal Growth Design* **11** 1006

[14] Sung J 2000 *Journal of Materials Science* **35** 6041

[15] Hu M H, Ma H A, Liu W Q, Zhang Z F, Zhao M, Li Y, Guo W, Qin J M and Jia X P 2010 *Gryst. Growth.* **312** 2989

[16] Di G Q 2011 *Acta Phys. Sin.* **60** 753 (in Chinese)

[17] Boyd S R, Kiflawi I and Wood G S 1994 *Philos. Mag.* B **69** 1149

[18] Yu T Y, Qin Y, Liu D Q and Zhang F S 2010 *Acta Phys. Sin.* **59** 2546 (in Chinese)

[19] Kanda H and Yamaoka S 1993 *Diamond Relat. Mater.* **2** 1420

[20] Kiflawi I, Kanda H, Fisher D and Lawson S C 1997 *Diamond Relat. Mater.* **6** 1643

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

[22] Chrenko R M, Tuft R E and Strong H M 1977 *Nature* **270** 141

[23] Collins A T 1980 *J. Phys.* C **13** 2641

[24] Kiflawi L, Kanda H and Mainwood A 1998 *Diamond Relat. Mater.* **7** 327

[25] Fisher D and Lawson S C 1998 *Diamond Relat. Mater.* **7** 299

[26] Kiflawi I, Kanda H, Lawson S C 2002 *Diamond Relat. Mater.* **11** 204

[27] Babich Y V, Feigelson B N and Yelisseyev A P 2004 *Diamond Relat. Mater.* **13** 1802

[28] Zhang H, Liu F M, Ding P, Zhong W W and Zhou C C 2010 *Acta Phys. Sin.* 59 2078 (in Chinese)