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ScienceDirect
Diamond & Related Materials 17 (2008) 209–211
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

HPHT synthesis of large single crystal diamond doped with high nitrogen concentration ☆

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Received 23 April 2007; received in revised form 28 November 2007; accepted 6 December 2007
Available online 14 December 2007

Abstract

Large green single crystal diamond with high nitrogen concentration is firstly synthesized by temperature gradient method under high pressure and high temperature (HPHT). Sodium azide (NaN_3) is added as the source of nitrogen to the synthesis system of high pure graphite and kovar alloy ($Fe_{59}Co_{25}Ni_{17}$). The HPHT synthesis condition is 5.4 GPa and 1480 K. The maximum crystal size is 3.2 mm. The infrared absorption spectra indicate that the nitrogen concentration in the green large single crystal diamond reaches 1520 ppm in the form of single substitution, which is close to that in nature diamond, and several times higher than that in the man-made Ib large single crystal diamond previously.

Keywords: Single crystal diamond; High nitrogen concentration; Synthesis; HPHT

1. Introduction

Nitrogen is the most familiar impurity in diamond. In general, based on the concentration and form of nitrogen in crystal, the diamonds are classified into types Ia (IaA and IaB), Ib, IIa and IIb. Types IaA and IaB diamonds are corresponding to nitrogen atoms with pairs atoms (A aggregates) and four atoms accompanying vacancy (B aggregates), respectively, in which the concentration of nitrogen is commonly about 2×10^3 ppm; While type Ib diamond contains nitrogen with a single substitution form, in which the concentration of nitrogen is commonly about 200 ppm [1,2]. Type II diamond contains few nitrogen atoms which are undetectable with a Fourier transform infrared spectroscopy (FTIR) [1,2]. It is of interest to know the limits of solution of nitrogen in diamond in both natural and synthetic diamond; the results of this paper indicate that at least about 1500 ppm nitrogen can be contained in a Ib synthetic crystal grown from the Fe–Co–Ni–C system.

Generally it is supposed that natural diamond is formed in the HPHT environment, deep in the Earth. Most of natural diamonds are type Ia diamonds, however, almost all the synthetic diamonds belong to type Ib diamonds. Because synthetic diamond is so remarkably different from natural diamond in the forms and concentration of nitrogen, for a long time it has been thought that natural diamond has an entirely different growth mechanism from that of synthetic diamond.

However, up to now, there are few reports on the HPHT synthesis of large single crystal diamond which contains the same nitrogen concentration as that in nature diamond. Though, during the works of Kanda et al. [2] and Borzdov et al. [3], diamonds with several thousand ppm nitrogen have already been synthesized successfully in quite high pressure(higher than 7.0 GPa), but all of the crystals shapes are incomplete, and the diamonds are in Ia type. For synthesized Ib diamonds, according to reports, the highest concentration of nitrogen in synthesized perfect diamond

☆ This work was supported by the NSFC of China (50572032).
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0925-9635/$ - see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.diamond.2007.12.018

is 800 ppm [4]. It is obvious that the nitrogen concentration in synthesized Ib diamonds is much less than in Ia diamonds. Furthermore, Cherenko's result indicates that the form of nitrogen in type Ib diamond can be transformed into the form in type Ia under appropriate temperature and pressure conditions [5]. So, if we can synthesize Ib type diamonds with the same concentration of nitrogen as that in nature diamond, we will be able to fabricate 'natural diamond' in laboratory. So, it is very important to synthesize large single crystal Ib diamond with high concentration of nitrogen, which is helpful not only to understand the original mechanism of natural diamond but also to extend the use of synthetic diamond.

In our previous studies, under high pressure of 5.0–5.8 GPa, we have successfully synthesized high-concentration-nitrogen diamond single crystal in Ib type with small size (only 0.5 mm in diameter), and the concentration of single substituted nitrogen impurities achieves 2.5×10^3 ppm [6]. However, the crystals are so small in size that many characters of crystals are difficult to measure. So, in this work, we aim to synthesize high-concentration-nitrogen large single crystal diamond by temperature gradient method under HPHT.

2. Experimental

The synthetic experiments were carried out in a cubic anvil HPHT apparatus (SPD-6×1200). The sample assembly for diamond synthesis by HPHT is shown in Fig. 1. The pressure was estimated by the oil press load, which was calibrated by a curve that was established based on the pressure-induced phase transitions of bismuth, thallium, and barium. The temperature was determined from a relation between the temperature and input power, which had been calibrated using a Pt6%Rh–Pt30% Rh thermocouple [7].

High pure graphite was used as the carbon source, kovar alloy was used as a catalyst, and NaN_3 (99.99%) was used as a solid nitrogen additive. Synthesis experiments were carried out at 1400–1500 K and 5.2–5.6 GPa for 2–20 h. {111} crystal face was selected as the growth face. The most suitable synthesis conditions are 5.4 GPa and 1480 K, under which a series of synthesis experiments for different synthesis time from 2 to 20 h were carried out. Large single crystal diamond crystals with high concentrations of nitrogen are synthesized.

The collected samples were treated in acids to isolate the grown diamond and the metal solvent catalyst. Then, the diamond crystals were boiled in the mixture of H_2SO_4 and HNO_3 to remove the impurities remained on the surfaces of the crystals. The final crystals were observed with an optical microscopy. The concentrations of nitrogen in diamond were measured by a Fourier transform infrared (FTIR) spectrometer.

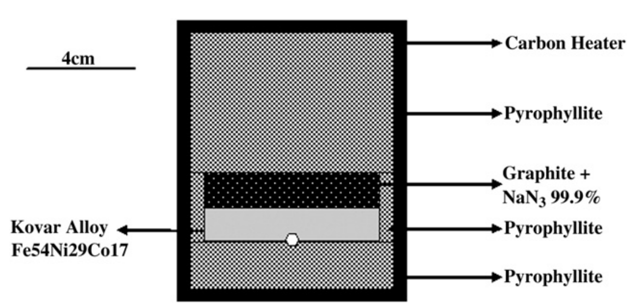

Fig. 1. The assembly for large single crystal diamond synthesized by HPHT.

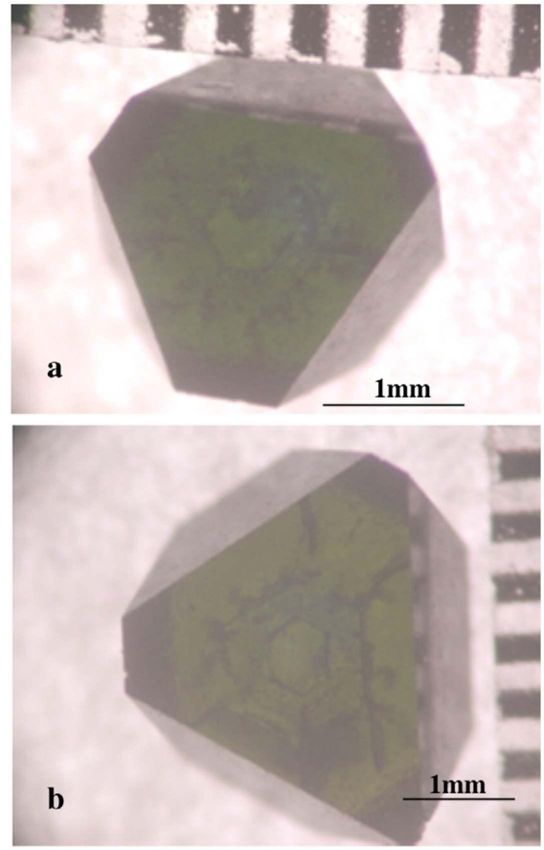

Fig. 2. Photographs of diamond crystals synthesized with FeCoNi alloy and NaN_3 additive. (a) 11.5 h, (b) 19.5 h.

For the infrared absorption measurements, a Bomem M110 Fourier transform infrared spectrometer fitted with a Spectra Tech IR-PLANTM microscope was used. The IR beam size was limited to a 150 μm square aperture so as to pass only the diamond crystals.

3. Result and discussion

3.1. The characters of diamond crystals synthesized with NaN_3 additive

Fig. 2 shows crystals of different growth time: (a) 11.5 h, (b) 19.5 h. The crystal a is 2.5 mm in diameter, 0.9 mm in height, 11.0 mg in weight, and the average growth rate is 0.956 mg/h. The crystal b is 3.2 mm in diameter, 1.2 mm in height, 25.9 mg in weight, and the average growth rate is 1.33 mg/h.

From the photographs of diamond crystals shown in Fig. 2, it can be seen that the color of the crystals has already become very green because of the NaN_3 additive, which induces a lot of nitrogen atoms to be introduced into diamond crystals, thus causing lots of color centers. The crystals have a good quality

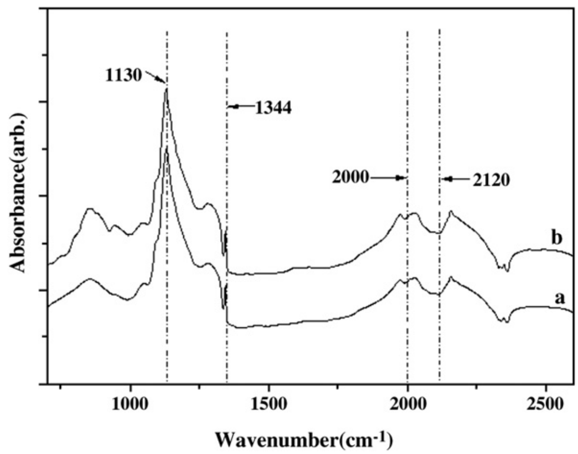

Fig. 3. FTIR spectra of diamonds synthesized for different time: (a) 11.5 h, (b) 19.5 h.

and perfect crystal shape without obvious pits, inclusions and other defects. The crystal face is mainly {111}.

3.2. The concentrations of nitrogen in diamond

Fig. 3 shows the infrared absorption spectra of crystals. The concentration of nitrogen impurity can be calculated based on the data of infrared absorption spectra [1,8–11]. Type Ia diamonds can be classified into types IaA and IaB. In type IaA diamonds the nitrogen impurities exist in the form of alternative atomic pairs (A aggregates), which corresponds to a FTIR absorption peak at 1282 cm^{-1} [8–11]. In type IaB diamonds the nitrogen impurities exist as tetrahedral forms (B aggregates), which corresponds to a peak of absorption at 1185 cm^{-1} [8–11]. However, in type Ib diamonds, the nitrogen impurities are single substituted atom forms, which corresponds to the peaks of absorption at 1130 cm^{-1} and 1344 cm^{-1} [8–11].

From the typical infrared absorption spectra in Fig. 3 it can be seen that there are no obvious peaks at 1282 cm^{-1} and 1185 cm^{-1}. The single substituted atom forms of nitrogen impurities (type Ib) can be detected in the one-phonon region of the spectra [1]. In an ideal spectrum, the concentration of nitrogen in type Ib diamond is proportional to the intensity of absorbance in 1130 cm^{-1}, and the proportion is 25 [12]. According to Davies [1], the absorption coefficient at 2000 cm^{-1}, where a dip is present, is 1.23 mm^{-1} for all diamond in room temperature. So the absorption intensity at 2000 cm^{-1} can be used to normalize the intensity of the one-phonon region related to nitrogen impurity. Whereas the baseline is much curve between 700 cm^{-1} and 2600 cm^{-1}, we used the dip at 2120 cm^{-1} to instead of the intensity of 2000 cm^{-1} to reduce the error cause by the curve of the baseline. As comparing with intensity at 2000 cm^{-1}, it can be achieved that the depth of the dip corresponds to 5.5 cm^{-1}. So we can calculate the nitrogen concentration using the following formula [6].

$$N_c(\text{ppm}) = \mu(1130\ \text{cm}^{-1})/\mu(2120\ \text{cm}^{-1}) \times 5.5 \times 25 \qquad (1)$$

In formula (1), μ (1130 cm^{-1}) and μ (2120 cm^{-1}) representing the absorption intensities of 1130 cm^{-1} and the dip at 2120 cm^{-1}. The concentration of nitrogen calculated from the FTIR spectra in Fig. 3a is 1520 ppm for the crystal in Fig. 2a, and that in Fig. 3b is 1200 ppm for the crystal in Fig. 2b.

4. Summary

In summary, green large single crystal of Ib diamonds with high nitrogen concentrations have been first successfully synthesized by adding sodium azide (NaN_3) to the system of high pure graphite and kovar alloy catalyst. The maximum size is 3.2 mm in diameter. The highest concentration of nitrogen achieves 1520 ppm, which is the highest concentration of nitrogen in large single crystal diamonds and close to that in nature diamonds. The nitrogen in the diamonds is almost in single substitution states. Further HPHT treatment of these high-concentration-nitrogen diamond crystals may induce the synthesis of 'nature diamonds'.

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