# Synthesis and characterization of p-type boron-doped IIb diamond large single crystals*

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High-quality p-type boron-doped IIb diamond large single crystals are successfully synthesized by the temperature gradient method in a china-type cubic anvil high-pressure apparatus at about 5.5 GPa and 1600 K. The morphologies and surface textures of the synthetic diamond crystals with different boron additive quantities are characterized by using an optical microscope and a scanning electron microscope respectively. The impurities of nitrogen and boron in diamonds are detected by micro Fourier transform infrared technique. The electrical properties including resistivities, Hall coefficients, Hall mobilities and carrier densities of the synthesized samples are measured by a four-point probe and the Hall effect method. The results show that large p-type boron-doped diamond single crystals with few nitrogen impurities have been synthesized. With the increase of quantity of additive boron, some high-index crystal faces such as {113} gradually disappear, and some stripes and triangle pits occur on the crystal surface. This work is helpful for the further research and application of boron-doped semiconductor diamond.

**Keywords:** boron-doped, type-IIb diamond, temperature gradient method, semiconductor

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## 1. Introduction

Generally, diamonds are classified into types Ia, Ib, IIa and IIb on the basis of their concentrations and forms of nitrogen and boron. Nitrogen in type-Ia and type-Ib diamonds is in aggregated or isolated form, respectively. Type-IIa diamond is the pure crystal which contains an undetectably small concentration of nitrogen, while type-IIb diamond contains boron. Because about 98% of natural diamonds are of type Ia, the proportions of natural type II (include type-IIa and type-IIb) diamonds are small in natural diamonds. However, the reserve of natural type-IIb diamond, which is about one-thousandth of the reserve of natural type-II diamond, is much less than those of diamonds of other types.[1−3] Type-IIb diamond is a promising material for p-type wide-gap semiconductor due to its high carrier mobility, high thermal conductivity and extreme elastic properties. The boron impurity substitutes for the carbon atom in a diamond lattice and creates the acceptor level near the top of a valence band with an activation energy of 0.37 eV. At higher boron concentration diamond possesses the superconducting property.[4−7] Therefore it is significant to synthesize type-IIb diamond.

Type-IIb diamond is p-type semiconductor. Due to its small covalent radius, boron is easily incorporated into the diamond lattice. Boron atoms substitute for the carbon atoms if the doping is low and they are able to occupy interstitial positions at the high doping level. Type-IIb diamond can be synthesized by chemical vapour deposition (CVD) and high pressure and high temperature (HPHT) methods including film growth method (FGM)[8,9] and temperature gradient method (TGM). The former method is mostly adopted by researchers at present.[10−14] Therefore only type-IIb diamond film has been applied into semiconductor apparatus. While coarse grain diamond obtained by FGM is not suitable for making semiconductor apparatus,[15] TGM is a better option to grow large type-IIb diamonds for their applying to semiconductor.

Owing to outstanding properties of large type-IIb diamond, the research results of large type-IIb dia-

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mond have been reported,[4−7] recently. But the crystal surface textures and the electric properties of the large type-IIb diamonds for a particular growth system have not been reported by now. In the present paper high-quality large type IIb diamonds are synthesized on the basis of growing high quality type IIa large diamonds by TGM.[16,17] Namely, the additive Ti/Cu as nitrogen getter is added into cell at HPHT, at the same time boron is added into the cell. The crystal morphologies, the crystal surface textures and the electrical properties of the synthetic diamond crystals are studied. In addition, the synthetic large diamonds are ascertained to be of type IIb by the micro FTIR.

## 2. Experiment

The synthesis experiments of large diamond single crystals were carried out by TGM in a china-type cubic anvil high-pressure apparatus at $\sim$ 5.5 GPa and $\sim$ 1600 K. The schematic diagram of growth cell in graphite heater is shown in Fig. 1. High-purity graphite was used as carbon source and $Fe_{55}Ni_{29}Co_{16}$ (wt%, abbr. FeNiCo) alloy was adopted as alloy solvent. High-purity Ti/Cu (1.51 wt% in FeNiCo alloy) and amorphous B powder were used as additives for synthesizing type-IIb large diamonds. High-quality diamonds obtained by FGM, each with about 0.6 mm in size, were used as the seeds. The {111} facet of seed was used as the growth sector simultaneously. In order to compare the properties of diamonds, the growth conditions of synthetic diamonds are maintained to be consistent except for the quantity of additive boron.

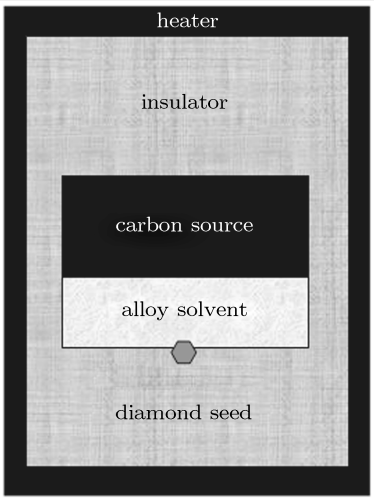



**Fig. 1.** Schematic diagram of diamond growth cell.

The principle of TGM is that diamond can dissolve from a source in an upper region at higher temperature and crystallize on a diamond seed in a lower region at lower temperature, because the solubility of diamond is dependent on temperature.[16,17] The growth rate of diamond is proportional to the temperature gradient along the axis in the growth cell. The temperature gradient along the axis is determined by the structure of the growth cell. Namely, the growth rate of diamond is controlled by adjusting the structure of the growth cell.

The synthetic pressure is determined from the relationship between the cell pressure and the oil press load, which is established based on the pressure-induced phase transition of bismuth (Bi), barium (Ba) and thallium (Tl). The temperature is determined from the relationship between the temperature and the input power, which is calibrated using a Pt6%Rh-Pt30%Rh thermocouple.[18]

The crystal morphology and surface texture of the synthetic large diamond single crystals were observed by using an optical microscope (OM) and a scanning electron microscope (SEM) respectively. The nitrogen concentration ($N_c$, in $cm^{-1}$) and the boron concentration ($B_c$, in $cm^{-1}$) in diamond were measured by micro Fourier transform infrared (FTIR) technique on a BRUKER IFS 66V/S spectrometer fitted with a Hyperion 3000 microscope.[19] The electrical property of large diamonds was tested by a four-point probe and the Hall effect method.[10,11]

## 3. Results and discussion

### 3.1. Morphologies and surface textures of large synthetic diamonds

In order to avoid the effects of growth rates on the properties of synthetic diamonds, the growth rates of different diamonds were maintained to be consistent within about 1.200 mg/h. Namely the growth rates of samples (A), (B) and (C) (see Fig. 2) were 1.201 mg/h, 1.200 mg/h and 1.200 mg/h respectively. With the increase of quantity of additive boron in the cell of growing type-IIa large diamond, the colour of the synthetic diamond became darker gradually (See Fig. 2(A) 0 wt%, Fig. 2(B) 0.2 wt%, Fig. 2(C) 0.6 wt%, where the percentage refers to the quantity of boron in FeNiCo alloy) and its morphology varies obviously. The sample (A) of type-IIa diamond (in Figs. 2(A) and 2(a)) shows multifaceted exteriors in its morphology and there is a transition facet between two dominant {111} and {100} facets, such as {110} and {113} . There is no obvious change in the morphology of type-IIb diamond sample (B) (see Figs. 2(B) and

2(b)) when the quantity of boron in FeNiCo solvent alloy is 0.2 wt%. There is obvious variation in the morphology of diamond sample (C) (see Figs. 2(C) and 2(c)), on which the transition facet of resembling type IIa disappears, when 0.6 wt% quantity of boron is added into the alloy. As a result, there are simple-facets (only {111} and {100}) in morphology of sample (C).

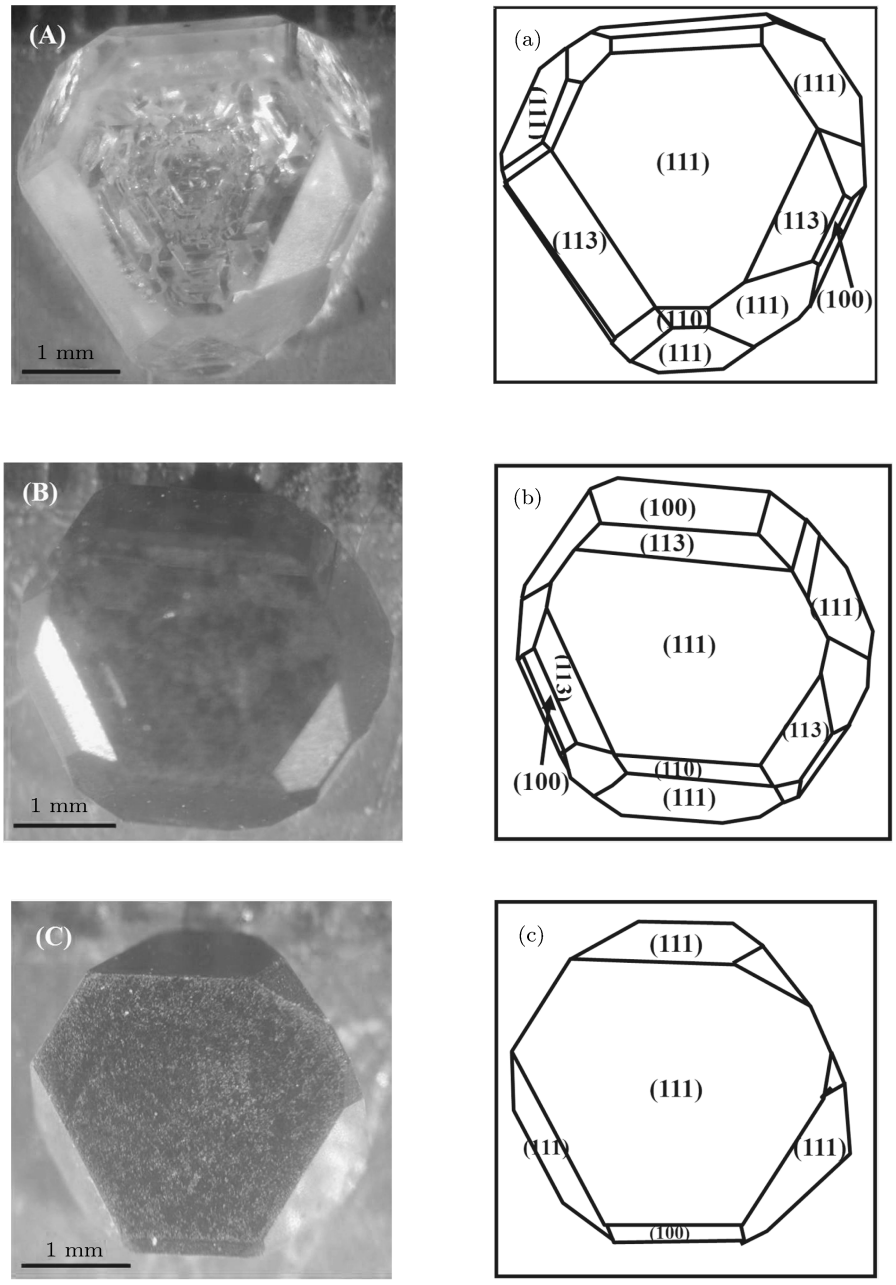



**Fig. 2.** The OM and morphology images of large diamond crystals synthesized with different quantities of boron additive: 0 wt% (A), 0.2 wt% (B), and 0.6 wt% (C). The morphology images in panels (a), (b) and (c) are corresponding to panels (A), (B) and (C), respectively.

These variations in morphology have been reported by Strong *et al.* in their paper.[20] But there remained some doubt whether impurities in the growth environment influenced crystal morphology through absorption on specific crystal faces and affected the growth rates of those faces. The results showed whether those faces appeared were determined by their growth rates.[20] Therefore, due to the additive quantity of boron, there appeared the variation in the growth habit of type IIb crystal which made the growth rate in the region of these

transition facets faster so these facets disappeared.

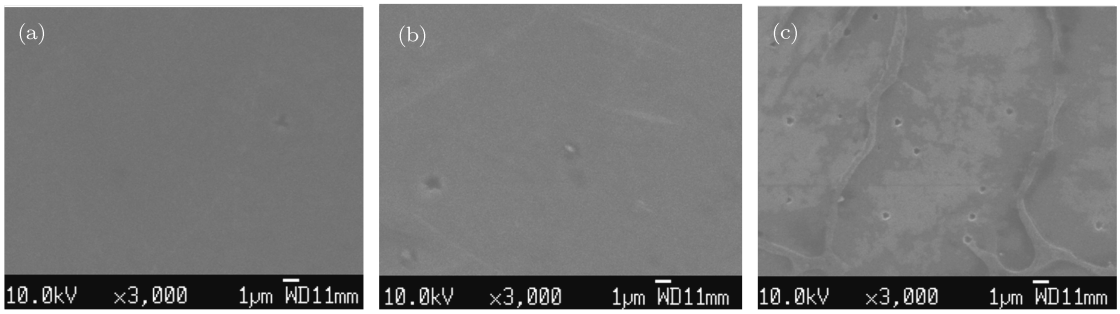



**Fig. 3.** SEM images of large diamond crystals synthesized with different quantities of boron additive: 0 wt% (a), 0.2 wt% (b), and 0.6 wt% (c).

It can be seen that with the quantity of boron increasing, the surface of the dominant facet {111} on the large type-IIb large diamond becomes coarse. In order to detect the surface change on the synthetic diamond crystals, the SEM was used to probe the surfaces of the diamonds with different quantities of additive boron in FeNiCo alloys of 0 wt%, 0.2 wt%, 0.6 wt%, respectively. The centre on the biggest {111} facet of each sample on Fig. 2 was selected to be detected by using SEM, and the SEM images of the diamond surface are seen in Fig. 3. It is observed that the surface of the type IIa diamond exhibits a perfect surface without any defect as indicated in Fig. 3(a). On the contrary, the surface of the type-IIb diamond with a boron quantity of 0.2 wt% shows a few striations and small pits as shown in Fig. 3(b). We clearly observe raised stripes and many big pits with the shape of down pyramid on the {111} facet of the type-IIb diamond with a boron quantity of 0.6 wt% as seen in Fig. 3(c).

The phenomena are similar to those of synthetic diamonds with doped boron, obtained by FGM.[15] Zhang *et al.*[15] have explained the phenomena of the diamond with doped boron by the bald-points model. Namely, when boron was doped into the synthetic diamond, on the {111} face, the lattice sites where boron atoms substituted for carbon atoms would become bald-points in the growth process. Therefore, with the quantity of boron increasing, there would be excessive bald-points on the surface of diamond and these bald-points disturbed the growth of diamond, which resulted in a great many defects on the {111} facet.[15] Although the type-IIb large diamond is different from the boron-doped diamond which is grown by FGM, we can also explain the phenomena of defects on {111} facet of the type-IIb large diamond by the bald-points model.

## 3.2. FTIR analyses of synthetic diamond crystals

To measure the $N_c$ values in synthetic diamonds, the three diamond samples in Fig. 2 have been characterized by micro FTIR in Fig. 4. Due to the different distributions of Nc and Bc atoms in different growing phases of large synthetic diamond, the centre on the biggest {111} facet of each sample in Fig. 2 was selected to be measured by micro FTIR.

In order to calculate $N_c$ and $B_c$ values in diamond from FTIR absorption spectra, the calculation formulae of $N_c$ and $B_c$ values are given as follows:

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

where $\mu(1130\ \text{cm}^{-1})$ and $\mu(2120\ \text{cm}^{-1})$ are the intensities of the peaks located at 1130 $\text{cm}^{-1}$ and 2120 $\text{cm}^{-1}$ respectively,[19] and $B_c$ is calculated by the calculation formula of the uncompensated acceptor concentration (UAC) in the type-IIb diamond, i.e.,[4]

$$[B_c - N_c] \approx 1.6 \times 10^{17} \times \alpha_{1290}, \quad (2)$$

where $\alpha_{1290}$ (in $\text{cm}^{-1}$) is absorption coefficient at 1290 $\text{cm}^{-1}$.

In order to compare the $N_c$ values in these diamond samples, the conditions of these samples synthesized at HPHT were maintained to be consistent except for the quantity of additive boron. It can be seen in Fig. 4(a) that the absorption peaks of 1130 $\text{cm}^{-1}$ and 1344 $\text{cm}^{-1}$ in diamond sample (A) are undetectable, which shows that the $N_c$ value in the synthetic diamond with Ti/Cu (without boron additive) is less than 1 ppm according to formula (1). Corresponding diamond sample of Fig. 4(a) is characterized

to be the type-IIa diamond.

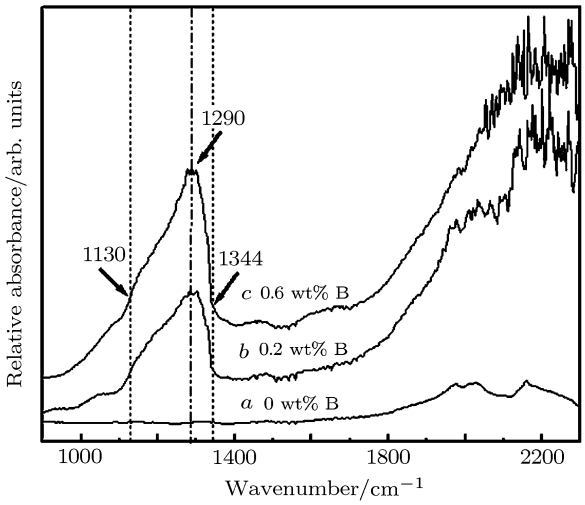



**Fig. 4.** FTIR absorption spectra of large diamond crystals synthesized with different quantities of boron additive: 0 wt% (a), 0.2 wt% (b), and 0.6 wt% (c).

The infrared absorption spectra of diamond samples (B) and (C) in Fig. 2 correspond to curves $b$ and $c$ in Fig. 4. Figure 4 shows the characteristic peaks at 1290 $cm^{-1}$ of boron on the curves. Because the synthesis conditions of diamond samples (B) and (C) are consistent with that of sample (A) except for the quantity of boron doped, we may deduce that the absorbed peaks at 1130 $cm^{-1}$ and 1344 $cm^{-1}$ of curves $b$ and $c$ are also undetectable. Therefore, the $N_c$ values in diamond samples (B) and (C) are less than 1 ppm. The $B_c$ values in diamond samples (B) and (C) are characterized by the characteristic peak at 1290 $cm^{-1}$. Therefore, diamond samples (B) and (C) in Fig. 2 have the same characteristics as the type-IIb diamond.

### 3.3. Electrical properties of synthetic diamond crystals

The electrical properties of diamond samples (A), (B) and (C) are tested by a four-point probe and the Hall effect method.[10,11] The results of the measurements are shown in Table 1.

**Table 1.** Electrical properties of large diamonds.

| sample | quantity of boron additive | p/n | resistivity/Ω·cm | Hall coefficient/$cm^3 \cdot c^{-1}$ | Hall mobility/$cm^2 \cdot (Vs)^{-1}$ | carrier density/$cm^{-3}$ |
|---|---|---|---|---|---|---|
| 1 [Fig. 2(A)] | 0 | | $2.923\times10^{10}$ | $4.447\times10^{17}$ | $1.221\times10^{8}$ | $1.403\times10^{4}$ |
| 2 [Fig. 2(B)] | 0.2% | p | 4348 | $2.087\times10^{11}$ | $4.653\times10^{7}$ | $2.990\times10^{11}$ |
| 3 [Fig. 2(C)] | 0.6% | p | 1498 | $5.236\times10^{9}$ | $3.495\times10^{6}$ | $4.768\times10^{12}$ |

As can be seen from Table 1, with the increase of quantity of additive boron in the cell, the carrier densities of these samples become bigger gradually, while their resistivities, Hall coefficients and Hall mobilities turn smaller gradually. The sample (A) of the large type-IIa diamond is an insulator because its resistivity arrives at $2.923\times10^{10}$ Ω·cm. The characteristics of the samples (B) and (C) are of p-type semiconductor because of the additive boron. The parameter of the sample (B) in semiconductor is inferior to that of the sample (C). These results indicate that the boron is doped into the diamond effectively.

## 4. Conclusions

The boron is added into the cell of growing high-quality large type-IIa diamond for synthesizing high-quality large type-IIb diamond by means of TGM at HPHT. The increase of doped boron leads to not only darkening the diamond, but also changing the morphology and the micro-texture on the surface of large type-IIb diamond compared with those of large type-IIa diamond. According to the results from FTIR absorption spectra, the synthetic large diamond is type-IIb diamond. It is believed from the measured electrical property that the characteristic of semiconductor in the synthetic large type-IIb diamond is of p-type.

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