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Effects of additive boron on HPHT diamond single crystals grown by TGM

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In this work, under pressure 5.4 GPa and temperature 1250–1400°C, large gem-diamond single crystals with perfect shape and different content of additive boron were synthesized using temperature gradient method. High-purity boron powders were added as boron source into the graphite powder, and the effects of additive boron on crystal growth habit were investigated in detail. The relationship between the growth rate and the amount of additive boron was studied. The scanning electron microscopy was employed to study the morphology of boron-doped diamond crystals. Raman spectroscopy and Hall measurements were used to investigate the crystal structures and the carrier concentration, respectively. The results show that with the increase of the content of boron added into graphite powder, the crystal growth rate and the carrier concentration increase firstly, and decrease afterwards, and the zone-center phonon line at 1332 cm^{-1} has small shift to lower energy. The defects occur on the crystal surface when excessive boron is added in the synthesis system.

HPHT, boron-doped diamond, catalyst, carrier concentration

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It is well known that there are a lot of impurities in diamonds synthesized by high-pressure and high-temperature (HPHT). Different impurities have different influences on the properties of diamond crystals [1–3]. For example, by doping phosphorus and boron, n-type and p-type diamond crystals can be synthesized, respectively. The diamond semiconductor is expected to be the high-speed, high temperature and high-power electronic-device due to its high elastic modules, high melting point, chemical inertness, high thermal conductivity, and wide band gap. Boron is one of the most common doped elements in diamond synthesized by CVD and HPHT [4,5]. Boron-doped diamond has been proved to be semiconductor [6,7] or superconductor [8,9]. It is undoubted that boron-doped diamond is one of the most promising materials for many applications [10–14].

The synthesis and properties of boron-doped diamond, which are the foundation and precondition of application, are very important for the related research. Today, boron-doped diamond single crystals can be synthesized using CVD method or HPHT growth. Ramamurti et al. [15] grew boron-doped diamond single crystal using microwave plasma CVD. Abbaschian et al. [16] synthesized large size boron-doped diamond single crystals under HPHT by temperature gradient method using Fe-Ni alloy catalysts. Boron-doped diamond crystals were synthesized by Li et al. [17] and Zhang et al. [18] by adding h-BN and amorphous

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boron to the system of Fe-Ni-C, respectively.

Although some work on the synthesis and properties of boron-doped diamond has been completed by many researchers, up to date, the carrier concentration of boron-doped diamond single crystals, the effects of additive boron on crystal quality and growth rates, have not been reported systematically. In this work, the diamond crystal with perfect shape and different content of boron doped in graphite powder has been synthesized. The scanning electron microscopy (SEM) was employed to study the morphology of boron-doped diamond crystals. Raman spectroscopy and Hall measurements were used to investigate the crystal structure and electrical properties. This work might be helpful to the further study on the boron-doped diamond.

1 The experiments

The experiments were carried out in a cubic anvil high-pressure and high-temperature apparatus (SPD-6×1200) using temperature gradient method (TGM) under pressure 5.4 GPa and temperature 1250–1400°C. The sample assembly for the synthesis experiments is shown in Figure 1. High-purity graphite was used as carbon source, and NiMnCo alloy ($Ni_{75}Mn_{16}Co_9$) was used as catalyst/solvent. High-purity boron powders were added into the graphite powder as boron source, and the content of additive boron was in the range of 0.5 wt%–2.5 wt%. In addition, high-quality seed crystals with a (100) seed surface of about 0.5 mm×0.5 mm were used to prevent the formation of dislocation bundles in the grown crystal. A graphite tube was introduced as a heater. To figure out the effect of boron, two kinds of diamond crystals were synthesized. One sample was synthesized from NiMnCo-C system, and the other sample was synthesized from NiMnCo-C-B system. 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.

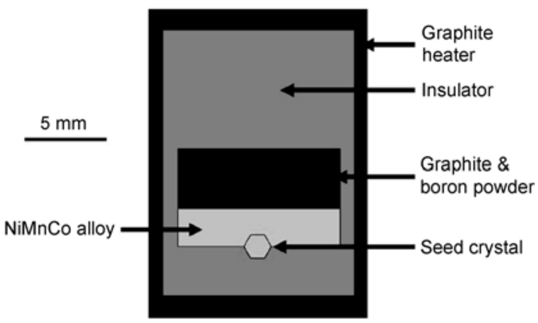

Figure 1 Sample assembly for diamond growth using temperature gradient method.

The collected samples were disposed in a bottle of boiling mixture of H_2SO_4 and HNO_3, and then observed with an optical microscope and the SEM. The weight and the size were measured by an electron scale and a vernier caliper, respectively.

2 Results and discussion

2.1 Surface morphology

Four samples in the order of increasing content of additive boron are labeled as Figures 2(a)–(d). The defects of the diamond crystals increase with increasing boron content in graphite powder. Figures 2(a)–(d) are the SEM images of samples (A)–(D). It could be found that when the content of additive boron was less than 1.5 wt%, the diamond surface was smooth and flat (Figures 2(a) and (b)). When 2.0 wt% boron or 2.5 wt% boron is added in the synthesis system, caves will appear on the surfaces of the synthetic crystals frequently, just as shown in Figures 2(c) and (d). Therefore, it is much more difficult for the growth of large high boron-doped diamond single crystal than that of general type-Ib diamond crystal. For the synthetic boron-doped diamond single crystal under HPHT, boron can incorporate into diamond lattice, and boron together with carbon can form B-C covalence bond. A boron atom can form three B-C covalence bonds, but a carbon atom can form four B-C covalence bonds. Therefore, the appearance of boron will destroy the structure of diamond lattice, and the defects will increase when a mass of boron is added into the synthetic system.

We believe that the synthetic method of adopting solvent/catalyst and HPHT is propitious to the formation of steady B-C covalence bond which makes boron incorporate into diamond lattice. As with nitrogen, the incorporation of boron varies with the growth sector: the take-up rate is much higher in the (111) sectors than in the other sectors [19]. The uneven colors of boron-doped diamond crystal, just as shown in Figures 2(A) and (B), can testify this. The colors of synthetic type-Ib diamond crystals are light yellow or yellow, whereas the colors of synthetic boron-doped diamond crystals, which can be seen in Figures 2(A)–(D), turn to gray or black. By cutting and polishing, the surface of roughcast diamond can be disposed. Figure 3(a) is the optical photo of cut and polished type-Ib diamond crystal. We can see that the color of the crystal is yellow. Cut and polished boron-doped diamond crystal is shown in Figure 3(b), and the color of the crystal is gray. The color of cut and polished boron-doped diamond crystal testifies that boron has entered into diamond crystal.

2.2 Growth rates

According to the weight of diamond crystals and growth

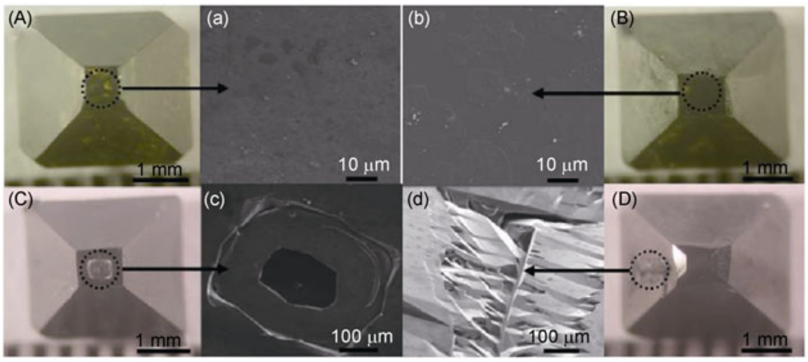

Figure 2 Optical photos and SEM images of the diamond crystals grown with different added amounts of boron. (A) 0.5 wt%; (B) 1.5 wt%; (C) 2.0 wt%; (D) 2.5 wt%. (a)–(d) are the SEM images of samples (A)–(D).

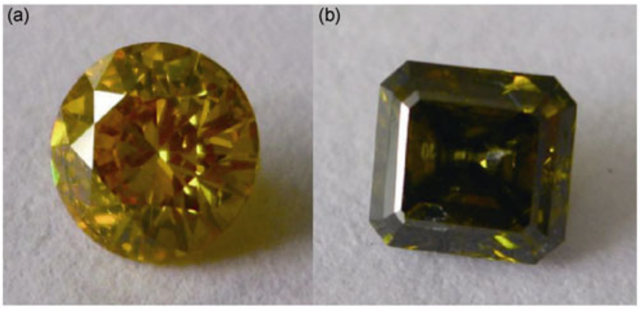

Figure 3 Optical photos of cut and polished diamond crystals. (a) Type-Ib diamond; (b) boron-doped diamond.

time, the average growth rates of general type-Ib diamond crystals were calculated in the paper [20]. In our experiment, when 12 hour growth time was certain, the relationship between the growth rate and the amount of additive boron was studied, and the results are shown in Figure 4. It can be seen that when the amount of additive boron is less than 1.5 wt%, the crystal growth rate increases obviously when boron enters into diamond crystal. When the added content of boron is 1.5 wt%, the crystal growth rate reaches 5.96 mg/h. The result might be caused by the increase of carbon solubility.

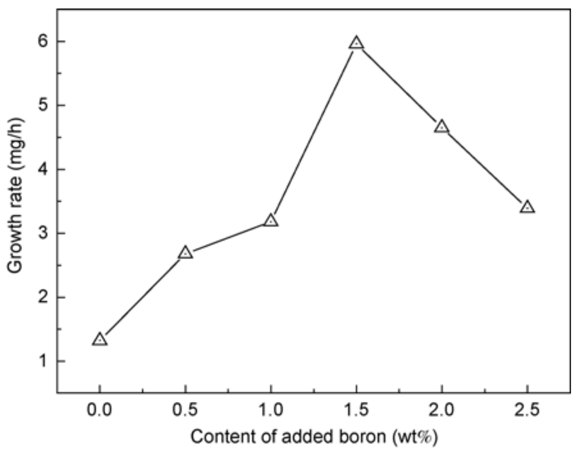

Figure 4 Curve of growth rate versus the content of added boron.

The carbon solubility in melting line and diamond/graphite equilibrium line both move downwards by the increase of added amount of boron, so the carbon solubility will increase. The increase of carbon solubility leads to the high speed of carbon atom separating from metal. Therefore, the growth rate of boron-doped diamond crystal becomes quick.

As the content of additive boron varies from 1.5 wt% to 2.5 wt%, the growth rate will decrease. The foregoing result indicates that the defects of the diamond crystals increase when the added amount of boron increases. Because synthesized crystals in low growth rates can gain high-quality diamond crystals, when the amount of additive boron is very big (more than 1.5 wt%), the growth rates must be reduced to grow high-quality boron-doped diamond crystals. Furthermore, the reduction of growth rate can be attributed to the existence of the limit carbon solubility.

2.3 Raman spectroscopy

As a nondestructive method, Raman spectroscopy is commonly used in characterizing the structure and quality of synthesized diamond crystals. Raman spectra were measured at room temperature in a range of 1000–2000 cm^{-1}. The excitation source of a 785 nm laser beam was focused to a spot in the centers of (100) faces. Figure 5 is the room-temperature Raman spectra of four samples: A: 0 wt% boron; B: 0.5 wt% boron; C: 1.5 wt% boron; D: 2.5 wt% boron. The result indicates that zone-center phonon line at 1332 cm^{-1} has small shift to lower energy with increasing boron content in carbon source. The first-order zone-center phonon line is observed at 1332 cm^{-1} in type-Ib diamond crystal (sample a). For samples b and c, the shifts are about 0.2 and 1.3 cm^{-1}, respectively. The shifts of the samples c and d are almost the same.

As substituting atoms, boron atoms can incorporate into diamond lattice. As covalent radius of boron (0.88 Å) is only slightly larger than that of carbon (0.77 Å), boron doping leads to expansion of the cubic diamond lattice [9]. Therefore, the structure of diamond lattice will change also, and the change is the reason why zone-center phonon line

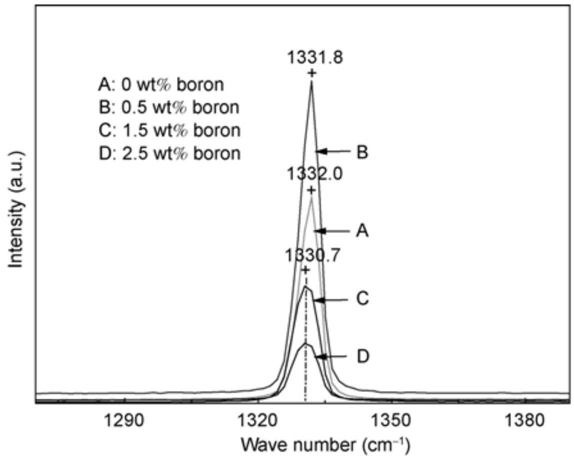

Figure 5 Raman spectra of the diamond crystals grown with different added amounts of boron.

shifts to lower energy.

2.4 Carrier concentration

By hall measurement, using four probes method (van der Pauw method), the carrier concentrations of boron-doped diamond crystals were investigated. It is well known that type-Ib diamond crystals are good insulators. In our studies, the results showed that synthetic boron-doped diamond crystals were all p-type semiconductor. Figure 6 is the relationship between carrier concentration and boron content in graphite powder. The carrier concentration increases when the content of additive boron increases from 0 wt% to 2.0 wt%. When the amount of added boron reach 2.0 wt%, the diamond crystal, with carrier concentration of 4.935×10^{18} cm^{-3}, can be synthesized. By continuing increase of boron content in graphite powder, the carrier concentration will decrease.

When boron content in graphite powder is less than 2.0 wt%, the increase of carrier concentration, by increasing boron content, can attribute to the amount of cavity carriers increasing. We know that B and N, which determine the electrical properties of synthetic boron-doped diamond crystal, are two kinds of main impurity in synthetic diamond crystal. In ref. [21], the concentrations of nitrogen in boron-doped diamond crystals were calculated by a Fourier transform infrared (FTIR) spectra, and the results indicated that the concentration of nitrogen decreased with the increasing boron content in synthetic system. Therefore, when the content of additive boron exceeds 2.0 wt%, the decrease of carrier concentration by increasing boron content in graphite powder can not be attributed to the variety of nitrogen impurity. We believe that, the decrease is possibly due to the fact that B and N can be produced to BN under HPHT which can decrease the concentration of boron in the sample. Another reason may be the defects increasing which can restrain carrier transferring.

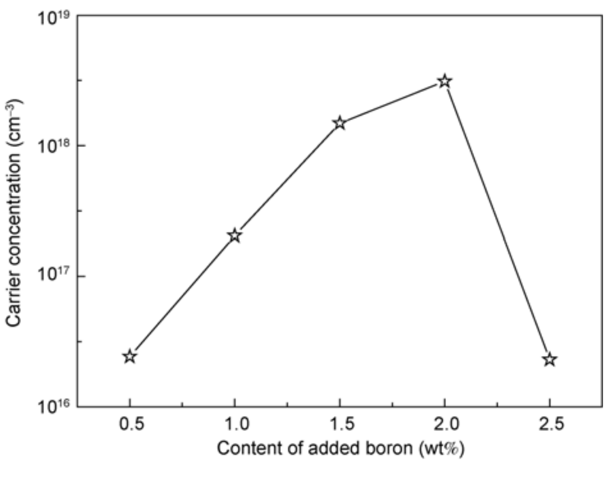

Figure 6 Carrier concentration vs. content of boron added into the graphite powder.

3 Conclusions

Large Boron-doped diamond single crystals with different content of boron added into graphite powder were synthesized under HPHT. The results show that boron can be incorporated into diamond lattice. The surface defects increase by the increase of added amount of boron. With the increase of the content of boron added into the graphite powder, the crystal growth rate and the carrier concentration increase firstly, and decrease afterwards, and the zone-center phonon line at 1332 cm^{-1} has small shift to lower energy.

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