Synthesis of n-type semiconductor diamond single crystal under high pressure and high temperature

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Abstract. In this paper, diamond single crystal co-doped with sulfur and boron was successfully synthesized at the fixed pressure of 6.0 GPa and temperature range of 1535 K. Sulfur was detected in the co-doped diamond by Fourier Transform Infrared Spectroscopy (FTIR) and the corresponding characteristic peak located at 848 cm\textsuperscript{-1}. Interestingly, Hall effect measurements indicated that the diamond co-doped with sulfur and boron exhibited n-type semiconductor behaviour. Furthermore, the Hall mobility and carrier concentration of the co-doped diamond higher than those of the boron-doping diamond.

1. Introduction
Diamond is an attractive candidate for electronic device applications due to its superior characters, such as a high critical electric field, high carrier mobility and the extremely high thermal conductivity, which are important for establishing semiconductor-based devices to run under extreme conditions. P-type semiconductor diamond can be realized by the addition of boron (B) additive in synthesis system. \[1\] Even, the electrical transport properties of p-type semiconductor diamond can be significantly enhanced using the method of co-doped with B and hydrogen under high pressure and high temperature (HPHT) conditions. \[2\] However, up to now, it is a challenge for the preparation of n-type semiconductor diamond with the excellent electrical performance because the effective donor elements have not been found.

Diamond is the insulator and nitrogen (N) is regarded as a good donor element in diamond, however, which does not generate a shallow donor state below the conduction band. Both theoretical calculation results and experiments show that the sulfur element can be used as a donor into diamond crystal to synthesize n-type semiconductor diamond. \[3-8\] Nakazawa etc. found that the electrical performance of the obtained diamond film doping with sulfur (S) additive was not stable and the quality of the synthesized diamond film was poor. \[9\] It was speculated that it attributed to the low concentration of S in the obtained diamond because of the larger atomic radius of S element. Therefore, it is difficult to realize the synthesis of n-type semiconductor diamond with a single sulfur doping. Theoretical calculation shows that B
element can promote the involvement of S element in the diamond in the process of diamond growth. [10] Furthermore, it was experimentally confirmed that n-type diamond could be synthesized co-doped with B-S using chemical vapor deposition (CVD) method. [11] However, it needs the further study and understanding of the preparation of n-type semiconductor diamond single crystal co-doped with B and S additives under HPHT conditions.

In this work, the synthesis of n-type semiconductor diamond is investigated with B and S additions under HPHT. It is interesting that the obtained diamond crystal exhibits n-type semiconductor. It is believed that the work may be useful for diamond-device technology and semiconductor physics.

2. Experimental Details

The synthetic experiments were carried out in a China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1200) with a sample chamber 12 mm in diameter. The diamond crystallization was run at a pressure of 6.0 GPa, which was measured at room temperature by the change in resistance of standard substances (thallium and barium) and at high temperature by the graphite-diamond equilibrium. Then, the synthesis temperature was 1535 K, which was calibrated using a Pt6%Rh–Pt30%RH thermocouple with a precision of ±1.5 K. Synthetic diamond (0.6 mm in size) with (100)-oriented was selected as the seed crystal. High-purity graphite was employed as the carbon source and diamond single crystals were grown in Fe$_{64}$Ni$_{36}$-C system. The purities of both B additive and S powders were 99.9 %.

In order to make the diamond separated from the catalyst, the sample treated after HPHT was firstly put in boiling dilute nitric acid for 1 hour. Then, the diamond was adequately boiled in the mixture of H$_2$SO$_4$ and HNO$_3$ to confirm that the remained graphite and other impurities on diamond surfaces were completely cleaned. Then, the obtained crystals were characterized by FTIR. Additionally, the electrical resistivity was measured at room temperature by Van der Pauw (interface converter Keithley kusb-488 from America, Lakeshore 420 Gauss meter and probe) method with a constant magnetic 1 T and the electrical current 1.0×10$^{-4}$ mA.

3. Results and Discussion

The diamond crystallization was run at a fixed pressure of 6.0 GPa and temperature of 1535 K by temperature gradient growth (TGG) method. The experimental parameters of diamond crystallization were summarized in Table 1. Herein, the listed proportion represented the weight ratio of the additive to Fe$_{64}$Ni$_{36}$ catalyst.

| Sample | B (wt.%) | S (wt.%) | Ti (Cu) | Time (h) | Color       |
|--------|----------|----------|---------|----------|-------------|
| a      | 0        | 0        | -       | 8        | Yellow      |
| b      | 0        | 2        | Added   | 24       | Colorless   |
| c      | 0        | 2        | -       | 20       | Yellow      |
| d      | 0.4      | 2        | -       | 20       | Yellow      |
Figure 1. Optical images of diamond crystals

(a) without any additive, (b) with 2 wt.% S and Ti(Cu) additives, (c) with 2 wt.% S additives and (d) with 2 wt.% B and 0.4 wt.% B additives.

Fig. 1 showed the optical images of the typical diamonds grown from the Fe_{64}Ni_{36}-C system under HPHT conditions. All the four samples displayed the dominant (100) faces and minor (111) faces. The typical yellow color of crystal (a) attributed to the incorporated nitrogen impurity remained in the raw materials and the free N coming from the atmosphere. Diamond (b) exhibited colourless due to the addition of N getter Ti(Cu) during the diamond crystallization process, where Ti played the role of N getter and generated TiN by combination reaction. The role of Cu was to decompose the formed TiC to effectively insure that the ability of Ti acted as N getter. Sample (c) synthesized with S additive belonged to yellow. Similarly, diamond (d) obtained from the B and S co-doped system also exhibited yellow. It was probable that the amount of B incorporated into diamond structure was so small that crystal (d) showed yellow rather than blue.

Figure 2. FTIR spectra of the obtained diamond crystals

(a) without any additive, (b) with 2 wt.% S and Ti(Cu) additives, (c) with 2 wt.% S additives and (d) with 2 wt.% B and 0.4 wt.% B additives.

FTIR was well known to be a powerful non-destructive technique for analyzing impurities and investigating chemical bonding structures in diamond. [12-14] The FTIR spectra for the representative diamond crystals were recorded in Fig. 2. The FTIR spectra (a) showed that the diamond crystal contained N impurity in the form of the C-centers (single substitutional N atoms), of which the characteristic absorptions located at 1130 and 1344 cm\(^{-1}\). Inserted in Fig. 2 (b), the characteristic absorptions attributing to N impurities were not found, meaning that
the N concentration valuation of diamond (b) was less than 1 ppm. However, it was observed for curves (a) and (b) that the absorption peaks located at 2920 and 2850 cm\(^{-1}\), which was responsible for sp\(^3\) CH\(_2\)-antisymmetric vibrations and sp\(^3\) -CH\(_2\)-symmetric vibrations in diamond, respectively.\(^{[15,16]}\) The presence of absorption peaks about hydrogen probably originated from the air. In curve (c), the absorption peak of S appeared and located at 848 cm\(^{-1}\) besides the peaks 1130 and 1344 cm\(^{-1}\). However, the absorption of S was not observed in crystal (b). It allowed us to speculate that N impurity could enhanced the incorporation of S into diamond. Displayed in curve (d), the appearance of absorption peaks at 1298 and 848 cm\(^{-1}\) in the FTIR spectra confirmed B and S were simultaneously incorporated into the diamond. The nitrogen concentration of the synthesized crystals could be calculated by the equation \(^{[17]}\)

\[
C_N = (25.0 \pm 2) \times a \text{ (1130 cm}^{-1}\text{)}
\]

The N concentration of the obtained diamond (a), (b), (c) and (d) were 200, 230, 0 and 210 ppm, respectively. Basing on the above results, it was probable inferred that the incorporation of N into diamond structures would be restrained while B, H or S impurities entered into diamond.

In order to understand the electrical properties of the diamond co-doped B and S, Hall effect measurements were performed at room temperature and the corresponding results were listed in Table 2.

| Sample | Resistivity \((10^6 \, \Omega \cdot \text{cm})\) | Hall mobility \((\text{cm}^2 \, \text{v}^{-1} \, \text{s}^{-1})\) | Carrier concentration \((\text{cm}^3)\) | Hall coefficient \(R_H\) \((\text{cm}^3)\) |
|--------|---------------------------------|-----------------|-----------------|-----------------|
| a      | -                               | -               | -               | Insulator       |
| b      | -                               | -               | -               | Insulator       |
| c      | 51.329                          | 23.067          | 5.278           | -7.590×10^8     |
| d      | 9.808                           | 64.225          | 9.922           | -6.299×10^8     |

(a) without any additive, (b) with 2 wt.% S and Ti (Cu) additives, (c) with 2 wt.% S additives and (d) with 2 wt.% B and 0.4 wt.% B additives

Table 2 showed that crystals (a) and (b) uniformly displayed the insulator. In terms of crystal (a), although N existed in diamond (a), N was in a deep level so that crystal (a) was the insulator. Diamond (b) exhibited the performance of insulator because there were no impurity defects relating with B or S. It was an interest of that the Hall coefficients of diamond (c) and (d) were negative values, indicating that the synthesized crystals belonged to n-type semiconductor. The resistivity of crystal (c) was 51.329×10^6 \(\Omega \cdot \text{cm}\). However, the resistivity of crystal (d) reduced to 9.808×10^6 \(\Omega \cdot \text{cm}\) due to the introduction of B additive on the premise of the fixed sulfur addition content in the two synthesis systems. Furthermore, both the carrier mobility and concentration values of diamond co-doped with B and S were higher than those of the prepared diamond (c). It was well known that B was the shallow acceptor in diamond structures and introduced a B-related electronic state in the gap closing to the top of the vacancy band. Correspondingly, the B-doping diamond should exhibit p-type semiconductor characteristics. However, the obtained crystal co-doped with B and S demonstrated the n-type semiconductor. Therefore, the S addition played the key of the transformation of B-doping diamond from p-type to n-type semiconductor, which could be considered by the following
two possible factors. The one was that the superfluous electrons providing by S donors made up for the vacancies producing from B acceptors in the dynamic equilibrium process. The rest of the electrons resulted in the increasing of the concentration in the conduction band, which led the final diamond to showing n-type semiconductor. Another possible consideration was that B and S combined to form a composite donor as a whole during the process of diamond crystallization. The understanding of the transformation mechanism needed the further study in detail for this.

4. Conclusion
N-type diamond semiconductor was successfully synthesized in Fe Ni-C system with B or S additive under HPHT conditions. N concentration of diamond would be restrained to a certain extent when B or S entered into the obtained diamond. The electrical conductivity of diamond co-doped with B and S was significantly improved than that of diamond doping with S on the premise of B addition content was the same.

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