Synthesis of N-type semiconductor diamonds with sulfur, boron co-doping in FeNiMnCo-C system at high pressure and high temperature*

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A series of diamonds with boron and sulfur co-doping were synthesized in the FeNiMnCo-C system by temperature gradient growth (TGG) under high pressure and high temperature (HPHT). Because of differences in additives, the resulting diamond crystals were colorless, blue-black, or yellow. Their morphologies were slab, tower, or minaret-like. Analysis of the x-ray photoelectron spectra (XPS) of these diamonds shows the presence of B, S, and N in samples from which N was not eliminated. But only the B dopant was assuredly incorporated in the samples from which N was eliminated. Resistivity and Hall mobility were 8.510 Ω·cm and 760.870 $cm^2/V·s$, respectively, for a P-type diamond sample from which nitrogen was eliminated. Correspondingly, resistivity and Hall mobility were 4.211×10^5 Ω·cm and 76.300 $cm^2/V·s$ for an N-type diamond sample from which nitrogen was not eliminated. Large N-type diamonds of type Ib with B–S doping were acquired.

Keywords: large single crystal diamond, high pressure and high temperature, doping, electrical property

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1. Introduction

It is well known that large diamonds exhibit many excellent properties such as extreme hardness, wide-band gap, optical transmission over a wide range, high thermal conductivity, good electrical insulation, and so on.[1–9] Effective doping can modify some of these properties.[10–14] Attempts have been made to dope diamond films using various elements. Phosphorus, sulfur, and boron are considered as potential doping elements.[15,16] Since the addition of B or S is straightforward when forming diamond through chemical vapor deposition (CVD),[16] diamonds doped with either B or S have already been studied. It has been established experimentally that diamond can be synthesized from boron-C, nitrogen-C, and sulfur-C by CVD under high pressure and high temperature (HPHT).[1,17–24] P-type diamond with B doping has been studied longer and has been applied variously, but the pursuit of high quality N-type diamonds with S doping has been disappointing. Some progress has been made in CVD synthesis of diamond with S and a small amount of B added, exhibiting N-type conduction properties.[16,25,26] Co-doping has been proven to be an effective way to incorporate donor dopants for N-type diamond.[18] However, no doped N-type diamond films with high Hall mobility have been reported so far. This may be due to the compensation of donors by defects or residual acceptor impurities. Improvement in diamond's electrical properties is strongly related to the improvement of crystalline perfection, electron surface states, and additive content. Similarly, high quality type Ib and IIa diamonds made by HPHT show potential for semiconductor materials study. However, the effects of B and S incorporated in diamond under HPHT remain unclear.

In this paper, large single crystal diamonds with B and S co-doping were synthesized in a FeNiMnCo-C system by temperature gradient growth (TGG) under HPHT. In addition, a nitrogen getter was added or not, respectively, to the system with both B and S additives to synthesize N-type IIa and Ib doped diamonds. The color and morphology of these diamond samples were investigated. X-ray photoelectron spectroscopy (XPS) measurements were employed to explore the samples synthesized from the FeNiMnCo-C system. The Van der Pauw method was used to detect electrical properties of the diamonds with additives.

2. Experiment

Experiments on diamond crystal growth were carried out by TGG in a China-type cubic anvil high-pressure appara-

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tus (SPD-6×1200) at 5.5 GPa and 1550 K. TGG was carried out under HPHT, graphite became diamond and then was dissolved in a catalyst, and it began to diffuse, driven by the temperature gradient, and then grew on the seed. High-purity graphite was used as the carbon source and $Fe_{39}Ni_{41}Mn_7Co_{13}$ (subscripts for mass percentage, hereafter abbreviated FeNiMnCo) alloy as the solvent catalyst. High-purity Ti/Cu (1.51 wt.% in FeNiMnCo alloy) was introduced for removing nitrogen.[27] The additives, sulfur and boron powder, were placed between two catalyst slices in the amount of 0–2 wt.% (the weight percentage was relative to the FeNiMnCo catalyst). The purity of the above materials was not less than 99.99 wt.%. Simultaneously, a diamond with a well faceted (100) crystal face of 0.6 mm×0.6 mm was used as the seed to synthesize diamond crystal of 3–4 mm. The collected samples were placed in a boiling solution of nitric and sulfuric acid to remove the remaining graphite and catalyst. Then the samples were cleaned several times in boiling deionized water as well.

The synthesis pressure was determined from the relationship between cell pressure and hydraulic load, which was established based on the pressure-induced phase transitions of bismuth (Bi), barium (Ba), and thallium (Tl).[28] The temperature was measured by a Pt6%Rh-Pt30%Rh thermocouple.[29]

An optical microscope was employed to characterize the color, morphology, and inclusions of the synthetic large diamonds. XPS analysis (instrument model: PHI X-tool, x-ray source: Al 1486.6 eV Mono at 21.3 W, step size: 0.1 eV, beam diameter: 201.9 μm, spatial resolution: 100 μm) confirmed the presence of B, S, and N in the diamonds. The resistivity and Hall coefficient were measured at room temperature using the Van der Pauw method (interface converter Keithley kusb-488 from America, Lakeshore 420 Gauss meter and probe) with a constant magnetic field of 1 T and an electrical current of 1.0×10^{-4} mA. The carrier concentration N_c was calculated from the Hall coefficient and resistivity.

3. Results and discussion

3.1. Morphology and color of synthetic diamond crystals

The color and morphology of the synthesized diamonds with nitrogen getter and other additives are displayed in Fig. 1. As shown, the morphology of synthetic diamonds in Figs. 1(a) and 1(b) is dominated by not only the (100) and (111) faces but also the (221) face. Furthermore, it is clear that the crystals are transparent, with no visible pits or inclusions. It is interesting to note that the obtained B–S co-doped diamonds (Figs. 1(c)–1(e)) in the FeNiMnCo-C system are dominated mainly by the (100) and (111) faces. Keeping S at 2 wt.% and increasing the quantity of B, the morphologies of the synthesized diamonds vary from slab to tower, and even minaret. It is consistent with the research results of Zhang that with increased B content, the growth region of the (111) face becomes wider while the region of the (100) face becomes narrower.[30] These changes of morphology are caused by the addition of B and S, which changes the V region of diamond growth in the FeNiMnCo-C system. It is clear that the synthetic diamond crystals stay colorless with the addition of only S, but turn out blue black with the addition of B and S. If B and S are added to the FeNiMnCo-C system, even with 0.2 wt.% B, the resulting diamond crystals are blue black rather than colorless. With increased boron content, the resulting diamond crystals are black and tend to be imperfect, even under the same conditions of growing high-quality diamonds. We deduce that the characteristics of the diamond synthesized in a FeNiMnCo-C system are obviously influenced by the simultaneous incorporation of B and S.

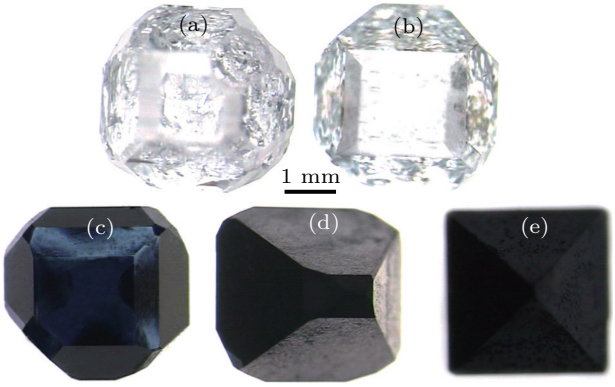


Fig. 1. (color online) Photographs of large diamonds synthesized with different contents of sulfur and boron (nitrogen getter: Ti and Cu (1.51 wt.%), (a) with 0% S, (b) with 2% S, (c) with 0.2% B and 2% S, (d) with 0.8% B and 2% S, (e) with 1.2% B and 2% S).

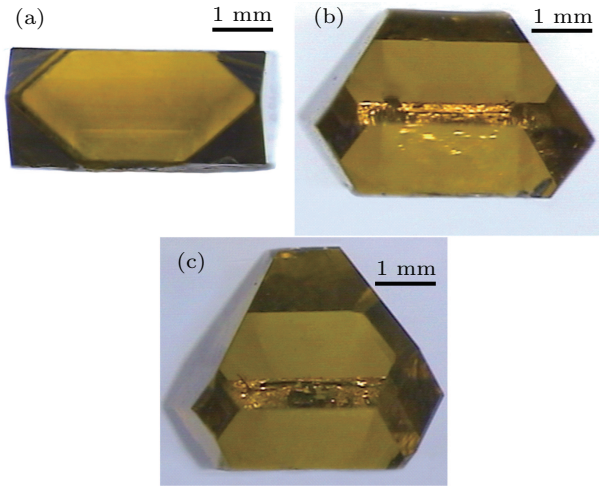


Fig. 2. (color online) Photographs of large diamonds synthesized with different contents of sulfur and boron ((a) with 0.2% B and 2% S, (b) with 0.8% B and 2% S, (c) with 1.2 % B and 2% S).

Certain amounts of B and S were added in the FeNiMnCo-C system without nitrogen getter to synthesize diamond, and three superior crystals (as shown in Fig. 2) were obtained. The morphologies of the diamonds vary from slab to tower, even minaret. These changes are similar to those of diamonds in Fig. 1. It is clear that the crystals are bright yellow

without visible pits or inclusions. The yellow color of the diamonds does not differ obviously with 2% S and 0.2%, 0.8%, 1.2% B added respectively. There are two reasons for this phenomenon; one is the N content in the diamonds and the other is the small amount of B. If the amount of B is high enough, the color of diamonds is blue, or even black.[31]

3.2. XPS spectra of diamonds

In order to determine whether the additives exist in the diamond structure, measurement of the XPS C 1s region was carried out separately to detect the C 1s spectra of diamonds with various additive contents. In order to make up for insufficiencies of some selected samples for XPS test results, all samples in Figs. 1(a)–1(e) and 2(f)–2(h) were analyzed. The C 1s spectra in Fig. 3(a) have peaks at 284.73 eV and 285.13 eV for C–C bonding (284.70 eV and 285.10 eV), as previously reported.[30,34] The peaks at 285.28 eV and 285.51 eV in Fig. 3(a) can be identified as combinations of C–C and C–N bondings (285.20–285.70 eV) according to the NIST XPS database (NXD). Likewise, the peaks appear in Fig. 3(b) at 284.10 eV and 285.00 eV for C–C bonding as previously reported.[32] In Fig. 3(b), the peaks at 285.51 eV and 285.63 eV can be identified as combinations of C–C and C–N bondings according to NXD. Unfortunately, we have not found C–S (283.40–283.70 eV) bonding in Fig. 3(a) or Fig. 3(b). In fact, nitrogen was only vestigial in the sample, as nitrogen was eliminated with Ti and Cu.

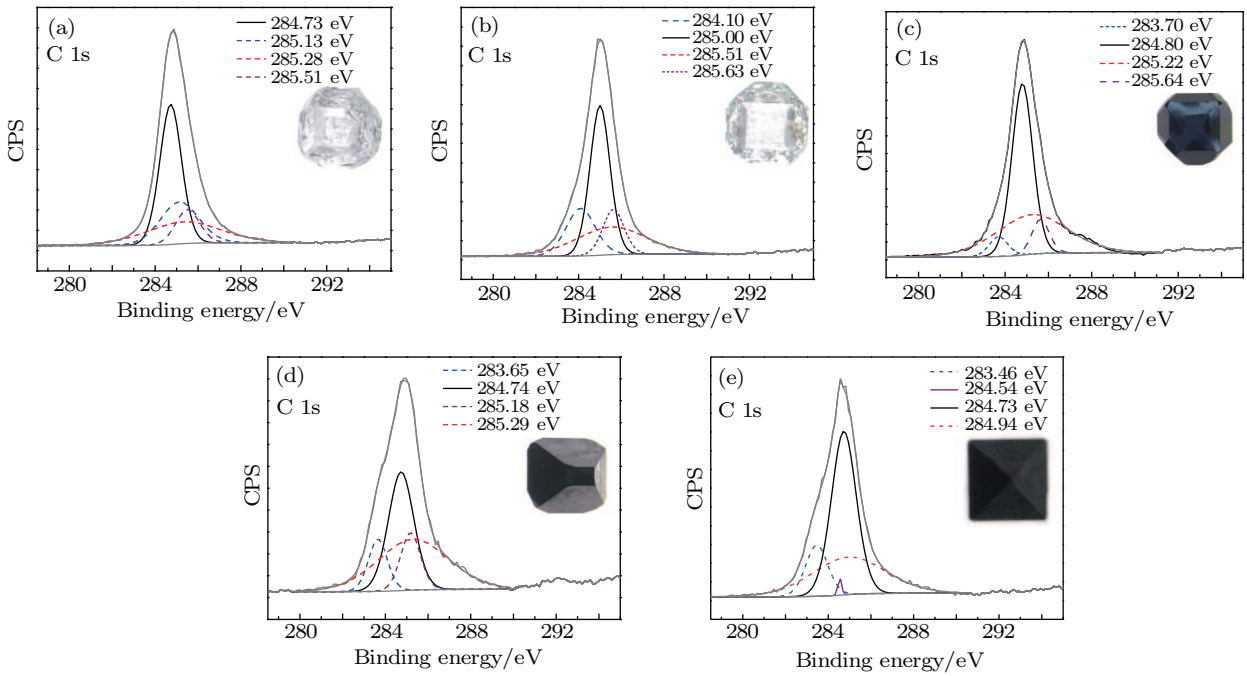


Fig. 3. (color online) Fitted curves together with the measured XPS C 1s spectra of diamonds ((a) with 0% S, (b) with 2% S, (c) with 0.2% B and 2% S, (d) with 0.8% B and 2% S, (e) with 1.2% B and 2% S).

In Fig. 3(c), the C 1s spectral peaks at 284.00 eV and 285.22 eV can be confirmed as C–C bonding. The C 1s spectra peaks at 285.64 eV can be identified as a combination of C–C and C–N bondings according NXD. It is interesting that the C 1s spectral peaks change obviously with B and S doping. The C 1s spectral peaks at 283.70 eV (in Fig. 3(c)) can be regarded as a combination of C–B (283.00–283.70 eV) and C–S bondings, as previously reported.[33] In Fig. 3(d), the C 1s spectral peaks at 284.74 eV and 285.18 eV can be confirmed as C–C bonding.[30,34] The peak at 285.29 eV can be identified as a combination of C–C and C–N bondings according to NXD. The peaks at 283.65 eV (in Fig. 3(d)) can be regarded as a combination of C–B and C–S bondings. In Fig. 3(e), one peak 283.46 eV at the lowest binding energy can be regarded as a combination of C–B and C–S bondings. The small peak at 284.54 eV can be confirmed as C=C bonding, as previously reported.[33] The peaks at 284.73 eV can be confirmed as C–C bonding. The C 1s peak in Fig. 3(e) is shifted to the left obviously due to B and S doping, the highest binding energies at 284.94 eV can also be regarded as a combination of C–C and C–N bondings. In Figs. 3(c)–3(e), the peaks at the lowest binding energies shift to the left as 283.70 eV, 283.65 eV, 283.46 eV and the intensity increases gradually with the increase of B doping.

The XPS analysis of typical samples in Figs. 2(f)–2(h) without nitrogen getter is shown in Fig. 4. The C 1s spectra in Fig. 4(f) have peaks at 284.29 eV and 285.02 eV for C–C bonding. The peaks at 285.21 eV can be identified as a combination of C–C and C–N bondings, the peaks at 283.33 eV (in Fig. 3(d)) can be regarded as a combination of C–B and C–S

bondings. It is obvious that the bonding situation of C 1s spectra in Figs. 4(g) and 4(h) is similar to that in Fig. 4(f). But the peaks at the lowest binding energies shift to the right on the whole as 283.33 eV, 283.67 eV, 283.57 eV, and the intensity change is not obvious with the increase of B doping.

In summary, C–C chemical bonds can be identified in the XPS spectra of all the diamond samples. A small amount of N remains in the samples shown in Figs. 4(a)–4(c). In addition, B or S atoms may exist in samples shown in Figs. 4(a)–4(c).

We also used XPS to detect whether S atoms exist in the structure of the doped diamonds. As shown in Figs. 5(a)–5(d), S is not found in the structure of the samples in Figs. 1(a)–1(c), while the S 2p spectra of the samples in Figs. 1(d)–1(e) also show no evidence that S atoms exist in these diamonds. It is possible that the low concentration of S in the diamonds was below the detection threshold of the XPS equipment. However, the S 2p spectra suggest that S atoms exist in the structure of the sample in Fig. 2(c), as shown in Fig. 5(d). Simultaneously, the S 2p spectra of the samples in Figs. 2(a) and 2(b) also show that S atoms exist in the diamonds. Therefore, it can be shown from the above results that S is not found in the diamond samples in Figs. 1(a)–1(e) with nitrogen getter but is found in the diamond samples in Figs. 2(a)–2(c) without nitrogen getter. That is, S enters diamonds containing N easier than it enters diamonds without N. Possibly, N is beneficial for S participating in diamond structure, or it is simply difficult to incorporate S in diamond. This is mainly due to S having a bigger atomic radius than that of N, making it difficult for S alone to go into the diamond structure. However, N in diamond distorts the lattice of the diamond, allowing S to easily go into the diamond structure.

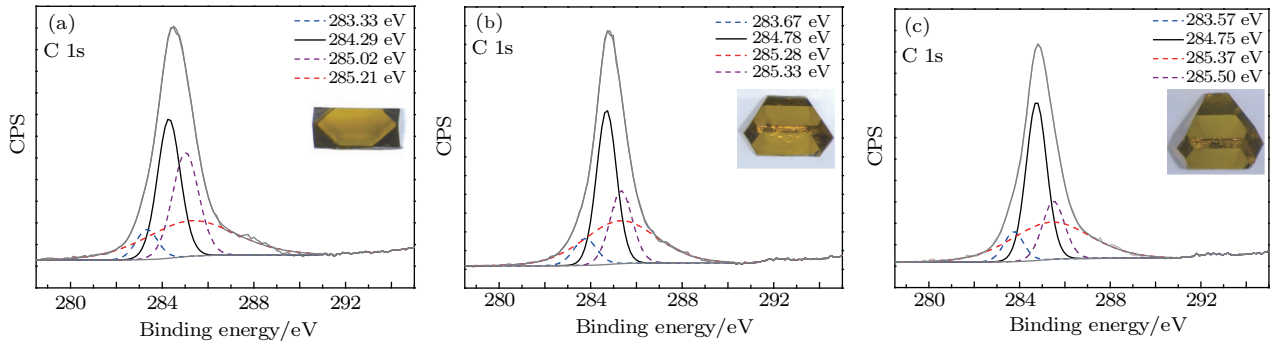


Fig. 4. (color online) Fitted curves together with measured XPS C 1s spectra of diamonds ((a) with 0.2% B and 2% S, (b) with 0.8% B and 2% S, (c) with 1.2 % B and 2% S).

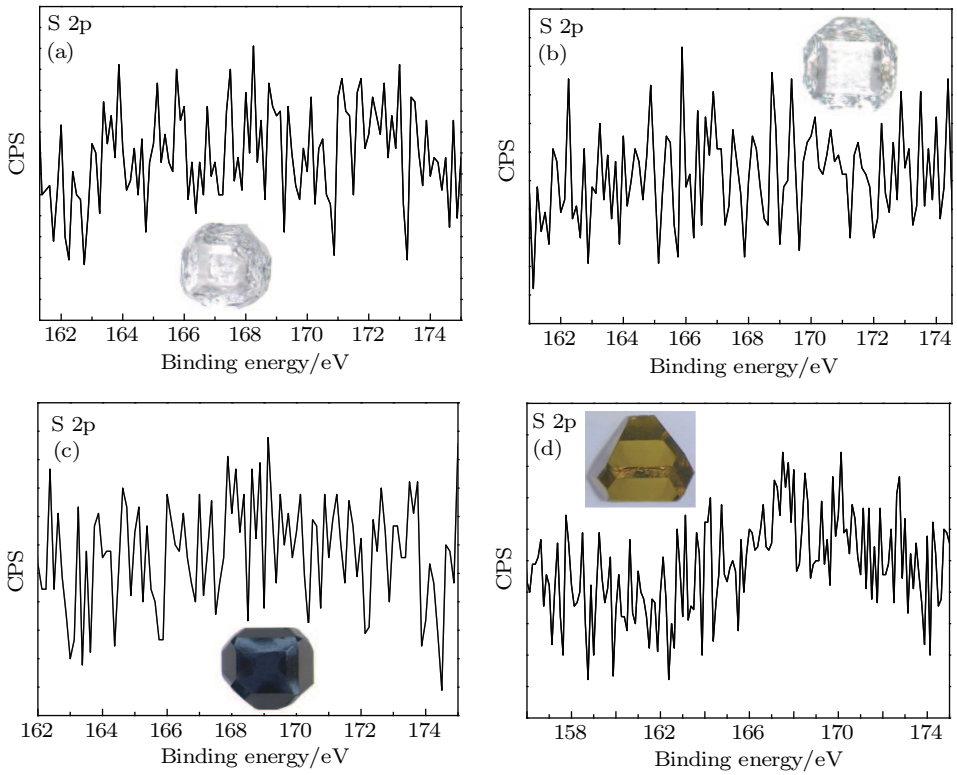


Fig. 5. (color online) XPS S 2p spectra of diamonds in (a) Fig. 1(a), (b) Fig. 1(b), (c) Fig. 1(c), (d) Fig. 2(h).

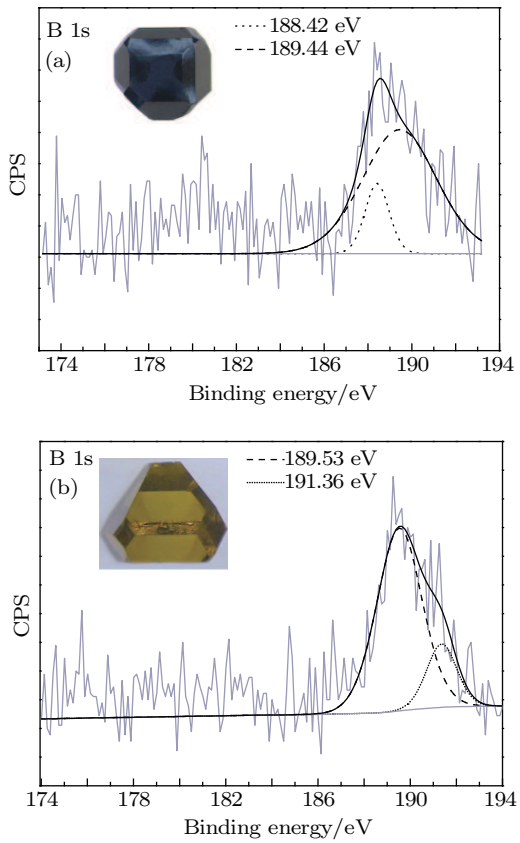


Fig. 6. (color online) Fitted curves together with measured XPS B 1s spectra of diamonds in (a) Fig. 1(c) and (b) Fig. 2(h).

In addition to the XPS spectra of S 2p, the XPS B 1s region was also analyzed to detect the presence of B, which is useful for further study of the structures of the diamonds. The spectra with binding energies of 188.42 eV in Fig. 6(a) and 189.53 eV in Fig. 6(b) for B–N bonds were reported.[35] In addition, the B 1s spectrum in Fig. 6(a) at 189.44 eV for B–C was reported.[35] Furthermore, the binding energy of the B 1s spectrum around 191.36 eV in Fig. 6(b) can be assigned to B–S and B–N bonds according to the NXD. The bonding situations of B 1s spectra of the samples in Figs. 1(d)–1(e) and 2(a)–2(c) are similar to those of the samples in Figs. 1(c) and 2(c), respectively. As a whole, the XPS results indicate that B is incorporated into the diamonds in Figs. 1(c)–1(e) and 2(a)–2(c). The spectra of Figs. 3–6 reveal that limited S content is incorporated in the samples in Figs. 2(a)–2(c), but none is incorporated in the samples in Figs. 1(a)–1(e). Sulfur does not easily enter into the diamond structure. Therefore, S did not go in the diamonds doped B and S with nitrogen getter. When nitrogen is not removed from diamond, the N can cause crystal lattice distortion in diamond then S easily gets into the diamond crystal lattice.

3.3. Electrical properties of synthetic large diamond crystals

In order to understand the effects of B and S on the electronic properties of diamond, Hall coefficient and resistivity measurements were performed at room temperature. The electrical transport properties of diamonds were measured by the Van der Pauw method. The experimental results of the measurements are presented in Table 1. The reference sample of Fig. 1(a) has no B or S added. With nitrogen eliminated from the diamond, the crystal is colorless, as is typical of type IIa diamond. With small amounts of B additive, the Hall coefficient of the sample in Fig. 1(c) is 2.709×10^{8}. With the amount of B up to 0.8 %, the resistivity of the sample in Fig. 1(d) is 15.856 Ω·cm, the Hall coefficient is smaller, 1.367×10^{4} cm^3/c, and the Hall mobility is 862.134 cm^2/V·s. Moreover, with the amount of B up to 1.6%, both the Hall coefficient and resistivity decrease for the sample in Fig. 1(e). However, without eliminating nitrogen from the diamonds, the Hall coefficients for the samples in Figs. 2(a)–2(c) are negative. Furthermore, compared to the samples in Fig. 1, the resistivity of the samples in Fig. 2 are much higher. Nevertheless, the conduction type of diamonds in Fig. 2 is N-type. When doped with 2% S and 1.2% B, the Hall mobility of the sample in Fig. 2(c) is 76.300 cm^2/V·s at room temperature.

Table 1. Test results of electrical properties of the crystals.

Sample	Sulfur additive/wt.%	Boron additive/wt.%	R_H/(cm^3/c)	ρ/Ω·cm	μ_H/(cm^2/V·s)
Fig. 1(a)	0	0	3.789×10^{18}	3.103×10^{10}	1.221×10^{8}
Fig. 1(b)	2	0	1.646×10^{18}	2.012×10^{10}	8.181×10^{7}
Fig. 1(c)	2	0.2	2.709×10^{8}	61.323	4.418×10^{6}
Fig. 1(d)	2	0.8	1.367×10^{4}	15.856	862.134
Fig. 1(e)	2	1.2	6.475×10^{3}	8.510	760.870
Fig. 2(a)	2	0.2	-2.591×10^{8}	6.132×10^{6}	42.254
Fig. 2(b)	2	0.8	-7.153×10^{7}	1.262×10^{6}	56.680
Fig. 2(c)	2	1.2	-3.213×10^{7}	4.211×10^{5}	76.300

On the basis of these results, we assume that only a very small amount or no S exists in the diamond samples with nitrogen getter. Although in the diamonds with B–S Co-doping, in fact, no S atoms exist. This makes these diamonds P-type. In contrast, we find that both B and S exist in the structure of the samples without nitrogen getter. So the results reveal that the incorporation of S is decided by whether nitrogen is eliminated from the diamonds. The entrance of S into diamonds

(see in Fig. 2) makes them N-type semiconductors.

4. Conclusion

Diamonds were synthesized in a FeNiMnCo-C system at 5.5 GPa and 1500–1600 K. With the addition of S and B, obvious changes took place in the color and morphology of the crystals. It is obvious that the samples were variously colorless, blue-black, or yellow and had a morphology of slab, tower, or minaret. As a whole, analysis of the XPS spectra C 1s, S 2s, S 2p, and B 1s indicates that only B was assuredly incorporated in the samples in Figs. 1(c)–1(e) from which nitrogen was eliminated. However, both B and S were assuredly incorporated in the samples in Fig. 2 from which nitrogen was not eliminated. P-type and N-type conductivities of diamonds were detected by the Van der Pauw method. When nitrogen getter was added into the system with both B and S doping, the conduction type of synthesized type IIa doped diamonds was P-type. In contrast, the conduction type of synthesized type Ib doped diamonds was N-type.

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