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Investigation of low-resistivity from hydrogenated lightly B-doped diamond by ion implantation

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Abstract
We have implanted boron (B) ions (dosage: 5×10^{14} cm^{-2}) into diamond and then hydrogenated the sample by implantating hydrogen ions at room temperature. A p-type diamond material with a low resistivity of 7.37 mΩ cm has been obtained in our experiment, which suggests that the hydrogenation of B-doped diamond results in a low-resistivity p-type material. Interestingly, inverse annealing, in which carrier concentration decreased with increasing annealing temperature, was observed at annealing temperatures above 600 °C. In addition, the formation mechanism of a low-resistivity material has been studied by density functional theory calculation using a plane wave method.

Keywords: diamond, hydrogenation, low resistivity, plane wave method

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diamond has been extensively investigated both theoretically and experimentally because of its unique structural properties and important technological applications. In particular, owing to its chemical immunity and negative electron affinity, it is rapidly becoming a candidate material for field emission devices [1, 2]. To realize diamond devices, low-resistivity p-type and n-type materials must be fabricated. In addition, electron field emission (FE) from diamond materials is interesting, which is the key element of cold-cathode field emission displays (FEDs) [3]. A study has found that the reduction in the resistivity of p-type diamond can increase emission efficiency [4]. Consequently, it was necessary to obtain a low-resistivity p-type diamond material.

The boron impurity in diamond has been studied for decades, because boron doping can lead to p-type diamond materials [5–13]. Low-resistivity p-type diamond with metallic-type conductivity has been obtained when the boron concentration exceeds the critical value of 2.0×10^{20} cm^{-3} [5, 7, 14]. Although it is known that B-doped diamond for forming p-type semiconductor needs an activation energy of about 0.37 eV, the formation mechanism of low-resistivity diamond materials remains unknown, which is an obstacle for the manufacture of low-resistivity materials [8, 15]. For example, the formation of the low-resistivity contact of field effect transistors (FETs) is still under study [16, 17]. A few studies of heavily B-doped diamond have been performed on the low resistivity and superconductivity of doped diamond [18–29]. Takano *et al* and Mukuda *et al* [30, 31] have investigated the superconductivity and the origin of superconductivity in heavily B-doped diamond by microwave plasma-assisted chemical vapor deposition and ^{11}B-NMR, respectively. Oguchi [32] has studied the electronic

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structure of heavily B-doped diamond with different doping sites by first-principles calculation. The results show that the superconductivity of heavily B-doped diamond is mediated by an electron-phonon interaction. The interstitial B dopant is unstable compared with the substitutional B dopant. Recently, Tsubouchi *et al* [29] have obtained a low-resistivity p-type layer (resistivity: 2.3 mΩ cm) by implanting a high dosage (8.4×10^{16} cm^{-2}) of B ions into diamond. However, to heavily implant B ions into diamond usually requires special methods such as a high-temperature or high-pressure technique, which raises difficulties practically [26, 28, 29, 33, 34]. However, to lightly implant B ions into diamond is much easier. To our knowledge, little work related to low-resistivity materials has been performed on lightly B-doped diamond.

In this work, we attempted to hydrogenate lightly B-doped diamond (estimated maximum B concentration: 8.62×10^{19} cm^{-3}) and then anneal it in the range of 300–630 °C. As a result, we have obtained a low-resistivity (7.37 mΩ cm) material at an annealing temperature of 560 °C, which has the same order of resistivity as heavily B-doped diamond [29].

2. Experiment

A commercial $5 \times 5 \times 0.2$ mm^3 diamond film with a small amount of nitrogen impurity synthesized by high-power DF arc plasma jet CVD was used in the study. The grain diameter is about 50 μm. Prior to ion implantation, it was confirmed that the diamond film has high sufficient resistivity at $\sim 10^{10}$ Ω cm. B ions with 400 keV at a dosage of 5×10^{14} cm^{-2} were implanted into the diamond film at a beam current density of 0. 16 μA cm^{-2} at room temperature. To prevent radiation damage induced by ion implantation, the film was annealed for 1.5 h in vacuum of 10^{-3} Pa at 1450 °C. Then it was washed immediately following the annealing in a boiling acid mixture ($H_2SO_4 : HNO_3 = 9 : 1$) for 1.5 h to remove amorphous carbon. The procedure has been proved to be effective (it will be depicted in detail subsequently). The H ions at a dosage of 1.8×10^{15} cm^{-2} with 140 keV were implanted into B-doped diamond to hydrogenate the sample. The depth profiles of B and H are shown in figure 1 based on TRIM simulation [3, 5]. The largest B concentration is 8.62×10^{19} cm^{-3} at 0.48 μm depth and the largest H concentration is 3.13×10^{20} cm^{-3} at 0.46 μm depth. The density of defects produced by the B and H doses in the sample is lower than the critical defect density $N_c = 10^{22}$ vac cm^{-3} based on TRIM simulation [35]. To prevent damage caused by H ion implantation and to promote the interaction of the B and H ions, one diamond sample was annealed at different temperatures (300–630 °C) sequentially in a quartz tube with an Ar flux of 30 ml min^{-1}. The annealing is described in detail in table 1. After the annealing, the diamond was cleaned in a boiling $H_2SO_4 : HNO_3 = 9 : 1$ solution to remove amorphous carbon. To bare the implanted layer and make contact between the electrode and the implanted layer, the hydrogenated B-doped diamond was etched by reactive ion etching technology. Then indium point contacts were formed at four corners of the sample surface to measure the electronic

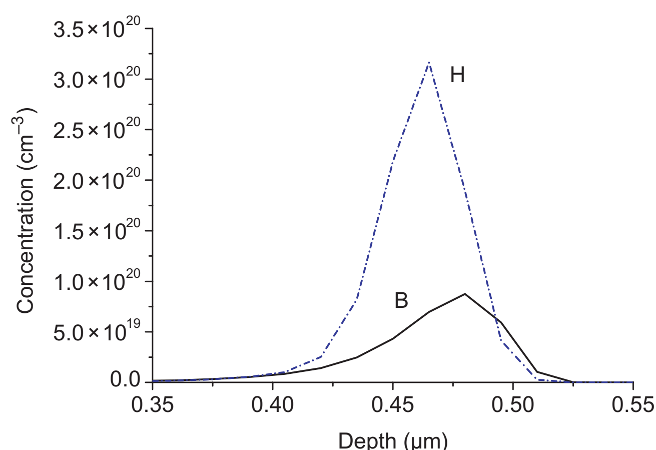

Figure 1. Depth profiles of B and H in diamond based on TRIM simulation. The solid line is the depth profile of B and the dot line is that of H.

Table 1. Parameters of annealing process of film in range of 300–630 °C in quartz tube with Ar flux of 30 ml min^{-1}.

Temperature (°C)	300	350	400	450	500	510	520	530	540
Time (min)	30	30	60	60	60	60	60	60	60
Temperature (°C)	550	560	570	580	590	600	610	620	630
Time (min)	60	60	60	60	60	60	60	60	60

properties of the sample using a four-point probe method in the Van der Pauw configuration at room temperature. The electrode displayed good ohmic I–V characteristics. The sample was characterized by atomic force microscopy (AFM) and Raman spectroscopy. The Nd : YAG laser (532 nm) was used in Raman measurement.

3. Results and discussion

3.1. AFM

Figure 2(a) shows the surface of the original sample (as-grown diamond film), which is quite smooth with a few small thorns and a surface roughness Ra of 4.39 Å, suggesting the good quality of the sample. Figure 2(b) shows the surface of the B-doped sample, which is not smooth with a few small protuberances. The surface roughness Ra is 165.9 Å. The thorns may be intrinsic defects formed during the growth and the protuberances are the defects that resulted from the implantation. Although the sample had a few defects, we believe that the quality of B-doped diamond is good for further research.

3.2. Raman spectroscopy

To confirm the validity of removing amorphous carbon on the sample surface, we show the Raman spectra of diamond in various states in figure 3. The Raman spectrum of the original sample (as-grown diamond film) is shown in line *a*, in which two peaks appear: one at 1332 cm^{-1}, which is the typical eigenpeak of diamond, and the other at 1458 cm^{-1} The original sample has a sufficiently high resistivity at

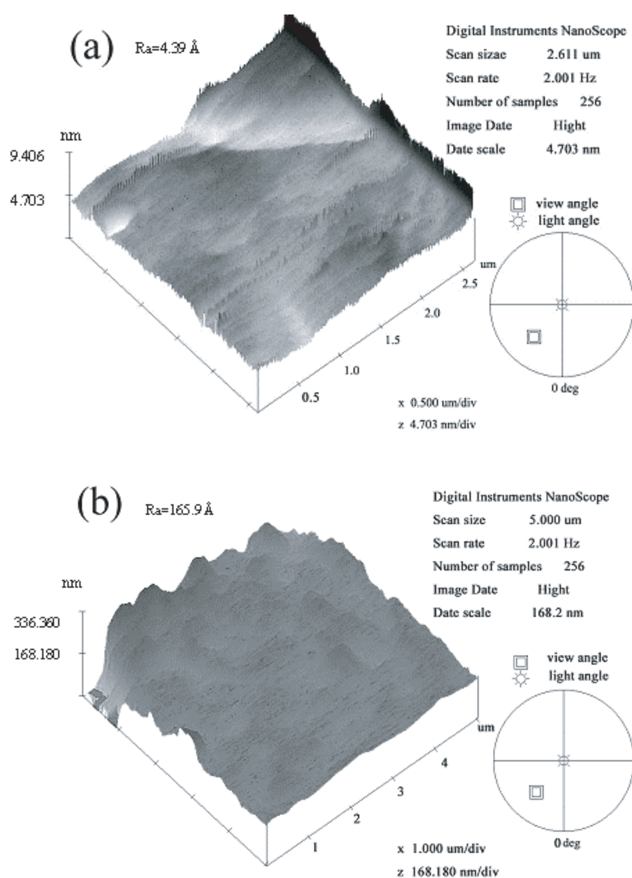

Figure 2. The surface morphologies of diamond (a) and B-doped diamond (b) are shown, as determined by the AFM. The surface of the original sample (a) is quite smooth with small thorns; that of boron-doped diamond (b) is not smooth with a few small protuberances.

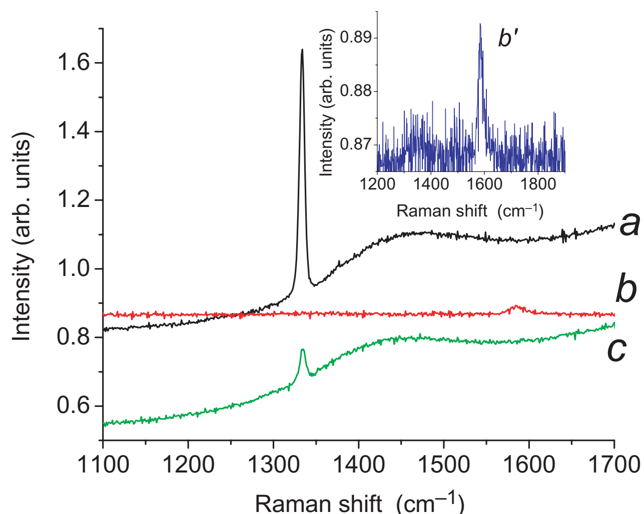

Figure 3. Raman spectra of diamond in various states. Line *a* is the Raman spectrum of the original sample. Line *b* is that of B-doped diamond (annealed at 1450 °C). Line *c* is that of hydrogenated B-doped diamond annealed at 560 °C and then washed in a boiling acid mixture and etched.

$\sim 10^{10}\,\Omega\,$cm (it is mentioned in the experiment section); thus, there is no graphitic amorphous carbon in the original sample. The broad peak at 1458 cm^{-1} in line *a* should be caused by intrinsic defects formed during the growth of the diamond film (as seen in figure 2(a)). According to $C_{nd} = 1/[1+75(I_d/I_{nd})]$ [36, 37], the defect structure content C_{nd} is about 0.89%, where $I_d = 1.62$ and $I_{nd} = 1.1$ are the intensities of the peaks at 1332 and 1458 cm^{-1}, respectively. Such a low percentage of defects will have little influence on the following experiment results and discussion.

Line *b* is the Raman spectrum of the B-doped diamond sample annealed at 1450 °C. There is only a peak at 1587 cm^{-1} (see the 100-fold-enlarged peak *b′* in the inset) in the spectrum. Owing to long-time (1.5 h) annealing at a high temperature (1450 °C), C–C bonds on the surface are reconstructed with more stable sp^2 bonds. Therefore, the peak at 1332 cm^{-1} disappears and the peak at 1587 cm^{-1} appears. Because the characteristic peak of graphite appears at about 1580 cm^{-1}, the surface should be composed of amorphous carbon similar to graphite. The hydrogenated sample was annealed in the range of 300–630 °C and shows special properties at 560 °C (it will be shown and discussed in detail subsequently), so the Raman spectrum of the sample annealed at 560 °C and treated by washing in a boiling acid mixture and etching is shown in line *c*. The peak at 1587 cm^{-1} disappears and two peaks appear at 1332 and 1458 cm^{-1} in the spectrum. The results indicate that there is no amorphous carbon on the surface of hydrogenated diamond, namely, the amorphous carbon was completely removed after the sample was washed in a boiling acid mixture ($H_2SO_4 : HNO_3 = 9:1$). The broad peak at 1458 cm^{-1} in line *c* is similar to that in line *a*, which indicates that the peak may be caused by intrinsic defects and not by the high graphitic amorphous content.

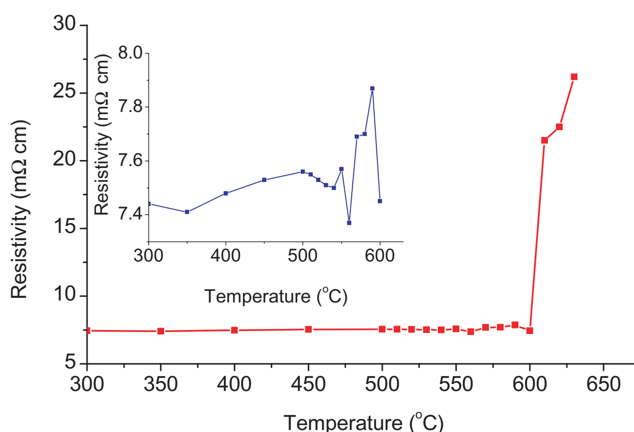

Figure 4. Annealing temperature dependence of resistivity in the range of 300–630 °C. The inset shows the annealing temperature dependence of resistivity in the range of 300–600 °C.

3.3. Hall effect measurement

The Hall effect measurement showed a positive sign of the sample, which indicates that the doped diamond film has a p-type conduction character. Figure 4 shows the annealing temperature (300–630 °C) dependence of the resistivity, which was determined by Hall effect measurement in the Van der Pauw configuration at room temperature. The resistivity is low in the range of 300–600 °C and increases sharply

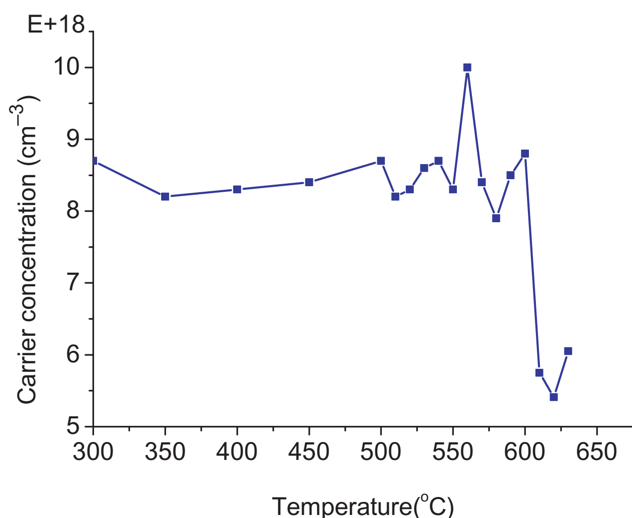

Figure 5. Annealing temperature dependence of carrier concentration in the range of 300–630 °C.

over 600 °C. To further investigate the annealing temperature dependence of the resistivity, the inset in figure 4 shows the resistivity of the sample in the range of 300–600 °C. The resistivity is not sensitive to temperature in the range of 300–500 °C; however, it changes evidently in the range of 550–600 °C and a minimum of 7.37 mΩ cm is reached at 560 °C.

Figure 5 shows the annealing temperature (300–630 °C) dependence of the carrier concentration of hydrogenated diamond. It can be seen that the carrier concentration is quite low and hardly changes in the range of 300–500 °C; however, it changes evidently in the range of 500–600 °C and a maximum of 1.0×10^{18} cm^{-3} is reached at 560 °C. The carrier concentration decreases sharply above 600 °C. From the above analysis, we may conclude that the lowest resistivity 7.37 mΩ cm and the highest carrier concentration 1.0×10^{18} cm^{-3} are reached at 560 °C, which suggest that the use of hydrogenated B-doped diamond enables the formation of a low-resistivity p-type material [29, 38]. Technologically, the production of such low-resistivity p-type material by implantation and hydrogenation techniques would be useful for diamond device processing. In general, the carrier concentration increases with increasing annealing temperature. However, an abnormal phenomenon, that is, the carrier concentration decreases with increasing annealing temperature, may occur in a certain temperature range. This is the so-called 'inverse annealing' phenomenon [39]. For hydrogenated B-doped diamond, the 'inverse annealing' phenomenon occurs when the annealing temperature is over 600 °C (as shown in figure 5). It can result from the exchange reaction between the substitutional B impurities and the interstitial C ones.

3.4. Formation mechanism of low-resistivity material

To determine the formation origin of low-resistivity materials during the hydrogenation of lightly B-doped diamond, we have calculated the electronic structures of

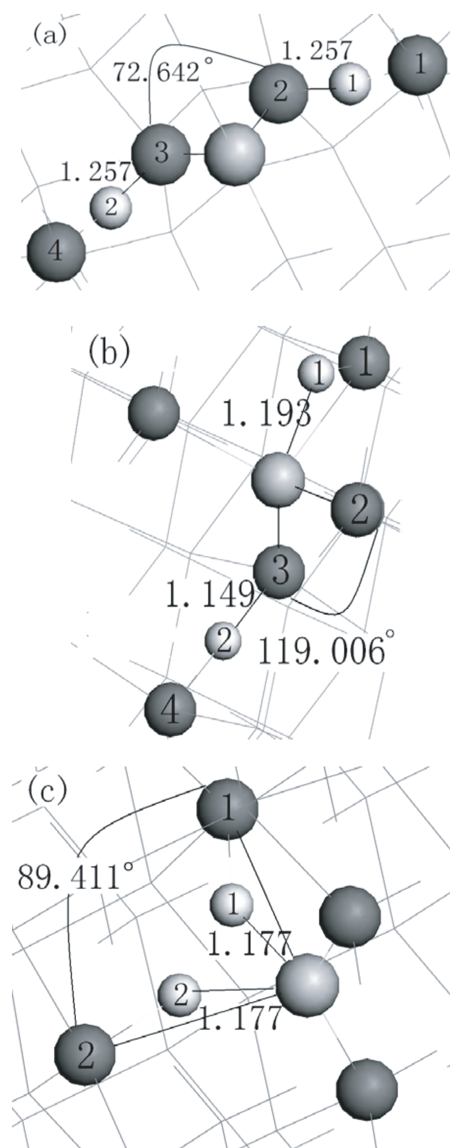

Figure 6. Optimized structures of diamond doped in (B+H) configurations: (a) B–$2H_{cc}$, (b) B–H_{bc}–H_{cc}, and (c) B–$2H_{bc}$. The black, grey and white balls are C, B and H atoms, respectively.

diamond doped with various (B + H) configurations by density functional theory (DFT) calculation. For B and H-doped diamonds, a 64-atom host supercell is used. The calculation was performed using CASTEP codes [40], with conjugated gradient approximation (GGA) and ultrasoft pseudopotentials in reciprocal space. Exchange-correlation potential parametrized by the Perdew–Burke–Ernzerhof scheme (PBE) was used [41]. The energy cutoff for the plane wave expansion was 310 eV. The calculation was performed using the Monkhorst-Pack scheme for sampling in the Brillouin zone with a mesh of $4 \times 4 \times 4$ special k points [42].

Here, we show three optimal (B + H) configurations in figure 6, which are stable according to formation energy (it will be shown in detail subsequently). In the three configurations, B atoms replace C and H atoms in various sites. The first one, B–$2H_{cc}$, is shown in figure 6(a), in which two H atoms, H_1 and H_2, occupy the C_1–C_2 and C_3–C_4 buckled bonds, respectively. The bond lengths of C_2–H_1 and

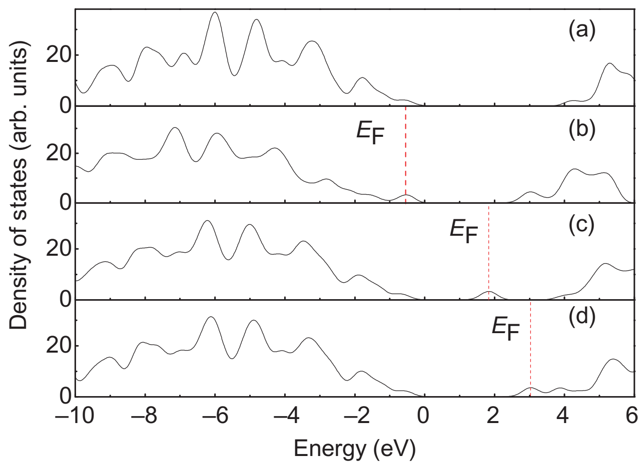

Figure 7. DOSs of (a) pure diamond, (b) diamond with B–$2H_{cc}$ configuration, (c) diamond with B–H_{bc}–H_{cc} configuration, and (d) diamond with B–$2H_{cc}$ configuration. The dot line represents the Fermi level E_F.

C_3–H_2 are about 1.257 Å, and the angle between the C_2–B bond and C_3–B bond is about 72.642°. Figure 6(b) shows the second one, B–H_{bc}–H_{cc}, in which the two H atoms, H_1 and H_2, occupy the C_1–B and C_3–C_4 buckled bonds, respectively. The bond lengths B–H_1 and C_3–H_2 are about 1.193 and 1.149 Å, respectively. The angle between the C_2–B and C_3–B bonds is about 119.006°. The third configuration, B–$2H_{bc}$, is shown in figure 6(c), in which two H atoms, H_1 and H_2, occupy the C_1–B and C_2–B buckled bonds. The bond lengths of B–H_1 and B–H_2 are about 1.177 Å, and the angle C_1–B–C_2 is about 89.411°.

Figure 7 shows the density of states (DOS) of diamond with the three (B+H) configurations. The DOS of pure diamond is shown in figure 7(a) as reference. The DOS of diamond with the B–$2H_{cc}$ configuration (as seen in figure 7(b)) shows that the Fermi level E_F locates in the valence band. It reveals clearly that the B–$2H_{cc}$ configuration induces impurity band mixing with the valence band and the Fermi level lies in the valence band, which results in the doped diamond having a p-type metallic conductivity character. However, figures 7(c) and (d) show that the B–H_{bc}–H_{cc} or B–$2H_{bc}$ configuration introduces deep gap states and that the Fermi level lies in the band gap or near the bottom of the conductivity band, respectively, which indicates that the doped diamond has an insulator character or n-type conductivity character. These results demonstrate that if the B–$2H_{cc}$ configuration is formed in doped diamond, a low-resistivity p-type conductivity will occur. Consequently, we can deduce that it is the formation of the B–$2H_{cc}$ configuration in our sample during the hydrogenation of B-doped diamond, that leads to low-resistivity phenomena.

To investigate the relative stability of (B + H) configurations, the formation energy (E^f) of BH_2 configurations was estimated using [43]

$$E^f = E(C_{63}BH_2) - 63\mu_C - \mu_B - 2\mu_H,$$

where μ_C is the chemical potential of the atoms C obtained from pure diamond. μ_B and μ_H are the chemical potential of B and H impurities, which are obtained from B_2H_6 and H_2, respectively. $E(C_{63}BH_2)$ is the total energy of the supercell with the BH_2 configuration, which can be accurately obtained by first-principles techniques. The results show that the formation energies for the B–$2H_{cc}$ (figure 6(a)), B–H_{bc}–H_{cc} (figure 6(b)), and B–$2H_{cc}$ (figure 6(c)) configurations are about −13.65, −14.16, and −12.82 eV, respectively. This means that the formation energies for various configurations have slight differences, which means each of them may be possibly formed under suitable experimental conditions. The hydrogenation of lightly B-doped diamond is a new and better method of obtaining p-type low-resistivity materials; therefore, many problems still need to be further studied, e.g., controlling the formation of configuration B–$2H_{cc}$ by researching suitable experimental conditions.

4. Conclusions

In summary, we obtained a p-type diamond material with the low resistivity of 7.37 mΩ cm during the hydrogenation of B-doped diamond. By Raman spectroscopy, we confirmed that there are no amorphous carbon on the surface of hydrogenated diamond after the sample is washed in a boiling acid mixture. Furthermore, we deduce that the low-resistivity material is hydrogenated B-doped diamond and not graphite. Our theoretical results suggest that the hydrogenation of B-doped diamond results in a metallic characteristic with low-resistivity p-type conductivity if some B–$2H_{cc}$ configurations form. Technologically, the production of such a low-resistivity p-type material would be useful for diamond device processing. The phenomenon of inverse annealing is also observed at annealing temperatures above 600 °C, which suggests that annealing above 600 °C is unnecessary.

Acknowledgments

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