Large single crystal diamond grown in FeNiMnCo–S–C system under high pressure and high temperature conditions*

He Zhang(张贺)[1], Shangsheng Li(李尚升)[1,†], Taichao Su(宿太超)[1], Meihua Hu(胡美华)[1], Guanghui Li(李光辉)[2], Hongan Ma(马红安)[2], and Xiaopeng Jia(贾晓鹏)[2]

[1] *School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo* 454000, *China*
[2] *State Key Laboratory of Superhard Materials, Jilin University, Changchun* 130012, *China*

(Received 11 April 2016; revised manuscript received 19 July 2016; published online 28 September 2016)

Large diamonds have successfully been synthesized from FeNiMnCo–S–C system at temperatures of 1255–1393 °C and pressures of 5.3–5.5 GPa. Because of the presence of sulfur additive, the morphology and color of the large diamond crystals change obviously. The content and shape of inclusions change with increasing sulfur additive. It is found that the pressure and temperature conditions required for the synthesis decrease to some extent with the increase of S additive, which results in left down of the V-shape region. The Raman spectra show that the introduction of additive sulfur reduces the quality of the large diamond crystals. The x-ray photoelectron spectroscopy (XPS) spectra show the presence of S in the diamonds. Furthermore, the electrical properties of the large diamond crystals are tested by a four-point probe and the Hall effect method. When sulfur in the cell of diamond is up to 4.0 wt.%, the resistance of the diamond is 9.628×10^5 Ω·cm. It is shown that the large single crystal samples are n type semiconductors. This work is helpful for the further research and application of sulfur-doped semiconductor large diamond.

Keywords: large diamond, high pressure and high temperature, sulfur additive

PACS: 81.05.Ug, 07.35.+k, 61.72.U– **DOI:** 10.1088/1674-1056/25/11/118104

1. Introduction

It is well known that diamond is a hard material with extremely excellent properties, such as wide band-gap, high electron mobility and hole mobility, high heat conductivity, and negative electron affinity.[1–15] When the appropriate additive is doped, the electronic properties of semiconductor diamond can be realized.[16–20] Some of the properties may be influenced by the impurities incorporated in the diamond lattice. Both phosphorus and sulfur are considered as the potential doping elements.[9,10,21–28] It has been established experimentally that phosphorus–C and sulfur–C systems are able to synthesize diamond at high pressure and high temperature (HPHT).[10,29] Diamonds with sulfur additive exhibiting n-type properties have been produced by chemical vapor deposition (CVD).[9,27,30] If a large diamond with S doping becomes an n-type semiconductor, then it will be a substantial step towards its application in electronics.

Phosphorus doping for large diamond synthesis at HPHT has been reported.[29] In this paper, a large diamond synthesis was carried out with sulfur powder additive.

2. Experiment

The synthesis experiments were carried out in a China-made cubic anvil high-pressure apparatus by temperature gradient method (TGM). The samples were synthesized under the conditions of pressure at 5.3–5.5 GPa and temperature at 1255–1393 °C. The samples of large diamond are shown in Fig. 2. The raw materials of the experiment were a FeNiMnCo alloy slice and graphite powder with purity not less than 99.99%. The FeNiCo alloy was used as the catalyst in the experiment abroad, while NiMn was used in China. In the experiment, it was found that composite catalyst FeNiMnCo with certain percentages of both alloys is better for synthesizing diamond. The additive elemental sulfur powder (99.99% purity) was placed between the catalyst slices with the amount of 1.0–4.0 wt.%. High grade hexoctahedron diamond single crystal with well faceted (100) crystal face of 0.6 mm×0.6 mm was used as the seed.

The synthetic pressure was determined from the relationship between the cell pressure and the oil pressure, which was established based on the pressure induced phase transition of bismuth (Bi), barium (Ba), and thallium (Tl). The temperature was measured using a Pt6%Rh–Pt30%Rh thermocouple.[7,31] Then, the collected samples were placed in a boiling solution of nitric acid and sulfuric acid to remove the remnant graphite and catalyst. An optical microscope was used to observe the color, morphology, inclusions, and surface characteristics of the large diamond crystals. X-ray photoelectron spectroscopy (XPS) was applied to confirm the presence of S in the diamonds. Raman spectroscopy (RENISHAW inVia 2400 grating, 532 laser resolution: 1 cm^{-1}) was used to check the qual-

*Project supported by the National Natural Science Foundation of China (Grant No. 51172089), the Education Department of Henan Province, China (Grant No. 12A430010), and the Fundamental Research Funds for the Universities of Henan Province, China (Grant No. NSFRF140110).

†Corresponding author. E-mail: lishsh@hpu.edu.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

ity of the large diamond crystals. The electrical resistivity was measured at 25 °C by LSR-3 using the Van der Pauw method. The Hall coefficient was measured using the Van der Pauw method with a constant magnetic field of 1 T and an electrical current of 1.0×10^{-4} mA. The carrier concentration was calculated from the Hall coefficient, assuming a single carrier model as a Hall scattering factor of unity.

3. Results and discussion

3.1. Pressure and temperature conditions required for large diamond growth from the FeNiMnCo–S–C system

Firstly, the experiments were performed under the conditions of pressure at 5.5 GPa and temperature at 1306 °C (Table 1). The growth time that ranges from 20.5 h to 28.5 h was long enough to synthesize diamond crystals of size 3–4 mm. In the absence of S in the growth system at 5.5 GPa, the morphology of the large diamond crystals shows that they are mainly composed of (100) crystal faces. There is an obvious change in the morphology of the large diamond with S doping. The faces of the diamond crystal with 1.0 wt.% S additive include not only (100) but also (111). When the sulfur additive is up to 2.0 wt.%, the morphology of the large diamond crystals shows that they are mainly composed of (111) faces with minor (100) faces. When the sulfur additive increases further, the morphology of the large diamond crystals always displays (111) faces. With sulfur additive increases, the quality of the crystal decreases and crystal defects can be found. The faces of the diamond tend to (111) with the increase of the sulfur additive.

Table 1. Experimental results of large diamond growth from the FeNiMnCo–S system at 5.5 GPa.

Sulfur additive/wt.%	Growth time/h	Temperature/°C	Morphology
0	20.5	1306	(100)
1.0	21.6	1306	(100)+(111)
2.0	24.0	1306	(100)+(111)
3.0	24.0	1306	(111)
4.0	28.5	1306	(111)

The region of diamond growth is a V-shape region bounded by the solvent–carbon eutectic melting line and the diamond–graphite equilibrium line in the carbon-melt system.[22,23,29] To further explore the change of the V-shape region (the pressure–temperature (P–T) phase diagram of carbon), we employed both 0 wt.% and 1.0 wt.% of sulfur additive at pressures between 5.3–5.5 GPa (Table 2). As we know, the processing time significantly affects the morphology. For example, the morphologies of the diamonds with growth time of 10 h and 50 h are different under the same conditions. So the growth time was set between 9.5 h and 10 h. In the growing system with 0 wt.% sulfur additive, the temperature range is about 1286–1393 °C, and the morphology of the large diamond crystals shows that they are mainly composed of (100) crystal faces, (100)+(111) crystal faces, and (111) crystal faces, respectively. When the additive sulfur is 1.0 wt.%, the temperature ranges from 1267 °C to 1350 °C at a pressure of 5.5 GPa. Then, in the growing system with 1 wt.% sulfur additive, the temperature range is about 1255–1320 °C, and the morphology of the large diamond crystals shows that they are mainly composed of (100)+(111) crystal faces and (111) crystal faces at the pressure of 5.3 GPa.

Table 2. Experimental results of large diamond growth from the FeNiMnCo–S system.

Pressure/GPa	Sulfur additive/wt.%	Growth time/h	Temperature/°C	Morphology
5.5	0	9.5	1286	(100)
		9.5	1306	(100)
		9.5	1314	(100)+(111)
		9.5	1335	(100)+(111)
		9.5	1393	(111)
5.5	1.0	10.0	1267	(100)
		10.0	1285	(100)
		10.0	1306	(100)+(111)
		10.0	1324	(100)+(111)
		10.0	1350	(111)
5.3	1.0	10.0	1255	(100)+(111)
		10.0	1275	(100)+(111)
		10.0	1305	(111)
		10.0	1320	(111)

The experimental results on crystallization of carbon phases in the FeNiMnCo–S–C system are summarized in Fig. 1. The addition of S additive into the growing system results in the V-shape region moving to the lower left (curve a moves towards curve b in Fig. 1). Namely, the temperature and pressure requirement for the synthesis of diamond in the FeNiMnCo–S–C system is lower than that in the FeNiMnCo–C system. The most probable reason for this is that the elements in the FeNiMnCo–S system may interact with each other under the HPHT conditions and the characteristics of the FeNiMnCo alloy solvent have been changed by S. Generally, the temperature and pressure conditions of crystal growth may

decrease with S doping, and the energy which is required for the large diamond growing also decreases.

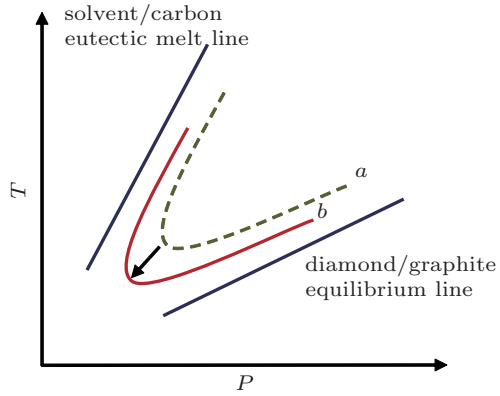


Fig. 1. (color online) Schematic of the movement of the V-shape region (the V-shape region of *a*: diamond growth from FeNiMnCo–C system; V-shape region of *b*: diamond growth from FeNiMnCo–S–C system).

3.2. Effects of additive S on the morphology and inclusions of large diamond

There are five kinds of sulfur-contained samples, corresponding to the sulfur contents of 0 wt.%, 1.0 wt.%, 2.0 wt.%, 3.0 wt.%, and 4.0 wt.%, respectively (Fig. 2). All the samples were synthesized under conditions of 5.5 GPa and 1306 °C (Table 1). Then, the large diamonds were observed under optical microscope (Fig. 2). For clearly demonstrating the internal station of the large diamonds, the corresponding side photos were also taken, such as Fig. 2(a′) corresponding to Fig. 2(a). For the non-transparent diamond in Fig. 2(e), the corresponding side photo was not taken. As shown in Figs. 2(a) and 2(a′), the crystal synthesized without any additive is yellow and has no inclusions. The large diamond obtained in the presence of 1.0 wt.% additive sulfur is yellower in color and no visible inclusions are observed. When the sulfur additive is up to 2.0 wt.%, the large diamond is a deep yellow and visible inclusions trapped in the large diamond crystal are noticed, which is shown in Figs. 2(c) and 2(c′). As shown in Figs. 2(d) and 2(d′), when the additive sulfur is up to 3.0 wt.%, the large diamond has a cluster inclusion and the transparency weakens. It can be seen from Fig. 2(e) that when the sulfur additive is up to 4.0 wt.%, the large diamond is of poor quality with dark color and pits in the (111) faces. In summary, the content of inclusions in the diamond increases with the increase of the sulfur additive.

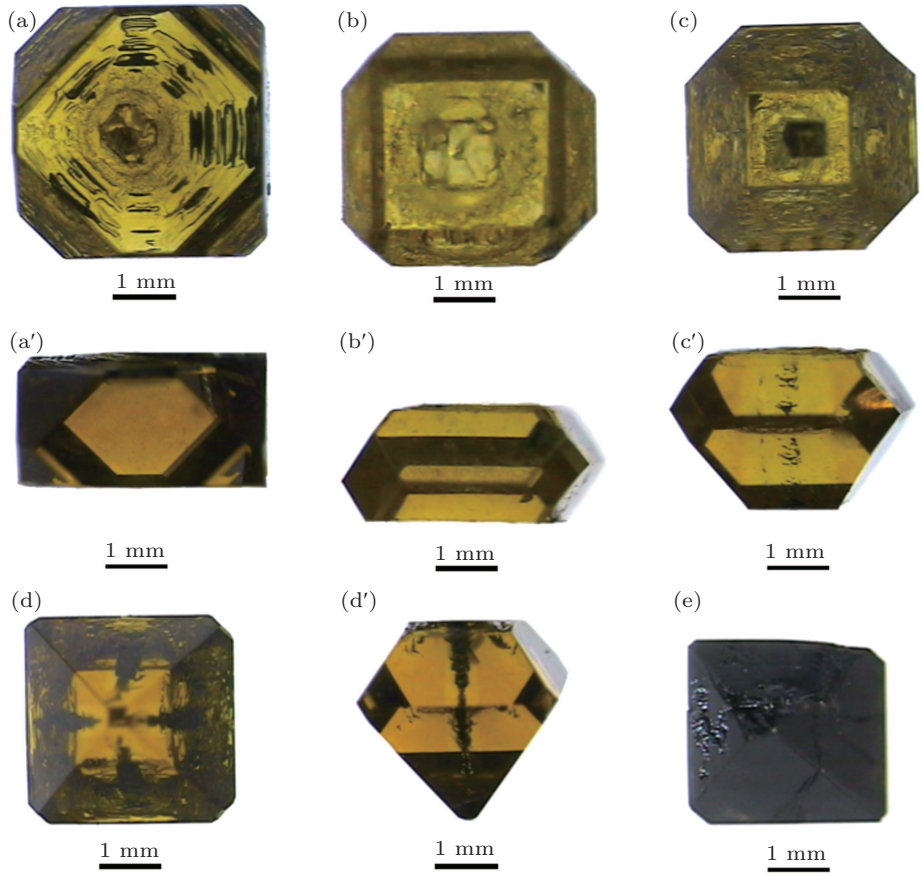


Fig. 2. (color online) Photographs of large diamonds synthesized with different amounts of sulfur additive: (a) and (a′) 0%, (b) and (b′) 1%, (c) and (c′) 2%, (d) and (d′) 3%, (e) 4%.

In order to analyze the surface characters of the synthesized diamonds, SEM photographs with a magnification of 2000 were taken. Figure 3 shows the results of the typical crystals corresponding to those in Fig. 2. It is evident from the photographs in

Fig. 3(a) for the (111) surface and Fig. 3(A) for the (100) surface of the crystal in Fig. 2(a) that these surfaces are flat. It is found in Figs. 3(B)–3(D) that the (100) surfaces of the corresponding crystals are flat. However, the relevant (111) surfaces appear to have some lines, which conforms to the mechanism of crystal growth.[15] The defect parts of the crystal in Fig. 2(e) are partial enlarged, a lot of triangle pits and gaps are discovered. From the SEM images, the produced diamond crystals show good quality, expect for the crystal in Fig. 2(e).

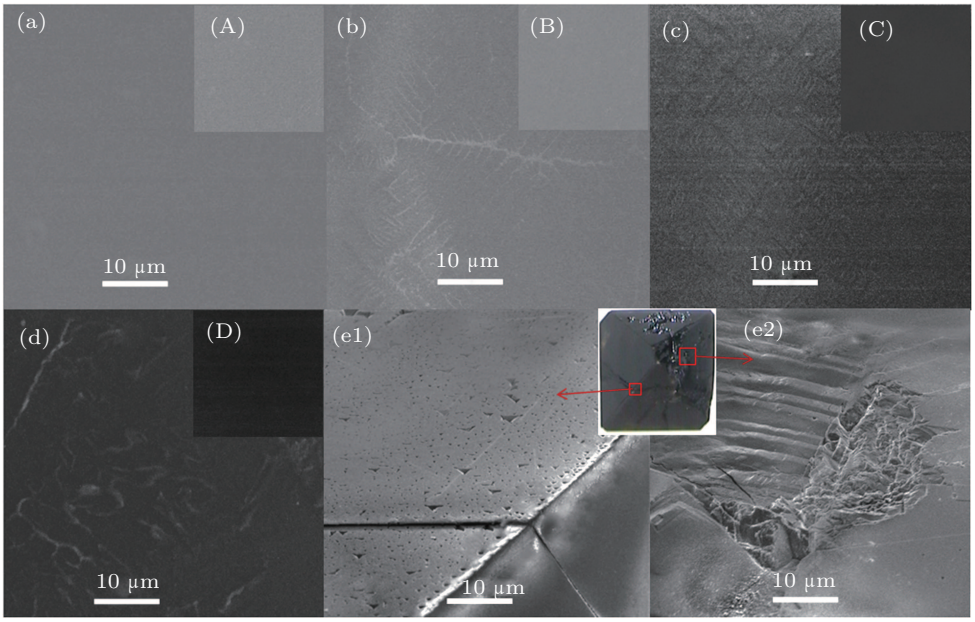


Fig. 3. (color online) SEM images of large diamonds synthesized with different amounts of sulfur additive: (a) and (A) 0%, (b) and (B) 1%, (c) and (C) 2%, (d) and (D) 3%, (e1) and (e2) 4%; (A)–(D) for (100) surfaces, and (a)–(e) for (111) surfaces.

3.3. XPS spectra and Raman spectra of the large diamonds

XPS was applied to check whether the S element existed in the structure of the obtained diamonds. The XPS spectrum for the S doped diamond with 2 wt.% S is displayed in Fig. 4. From the XPS spectrum of C 1s shown in Fig. 4(a), it is found that the spectrum can be suitably resolved into three signals with binding energies of 284.11 eV, 284.40 eV, and 284.53 eV, respectively. By taking many factors into account, the deconvolution peak at 284.11 eV can be regarded as C–C bonding according to the NIST XPS database. Since the C 1s peaks of C–N (over 1 ppm of nitrogen exist in the diamond), C–C, and C–S center at 284.40 eV according the NIST XPS database, the deconvolution peak at 284.4 eV can be regarded as a combined contribution from the C–N, C–C, and C–S bondings. It was reported that the C 1s spectra have peaks at 284.60 eV for C–C bonding.[3,24,32] Because the peak at 284.53 eV is extremely close to that at 284.60 eV, it can be attributed to C–C bonding. The spectrum of S 2p (as shown in Fig. 4(b)) can be resolved into two signals with binding energies of 164.09 eV and 163.14 eV, respectively, which can be attributed to S–S, C–S (164.00 eV) bonds according to the literatures[33–35] and the NIST XPS database. In other words, the XPS spectra indicate that the S element is incorporated into the diamonds.

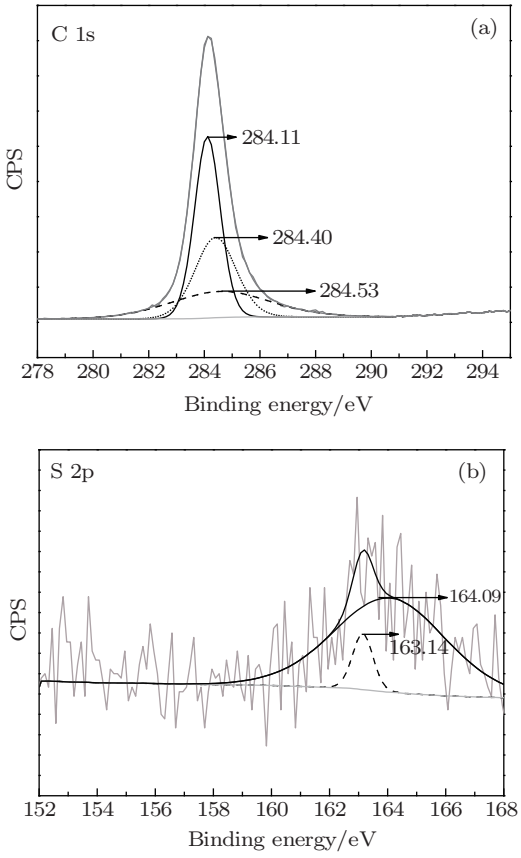


Fig. 4. XPS spectra of the diamond with 2 wt.% S: (a) C 1s, (b) S 2p.

For the CVD of large diamond, the full width at half maximum (FWHM) of the Raman spectral line is usually used to judge the degree of the large diamond crystal integrality, and the location of the spectral peak is used to estimate the magnitude of the residual stress. In fact, this method has been used to evaluate the quality of the large diamond single crystal synthesized by the HPHT method.[24] The large diamond FWHM of the Raman peaks is calculated by Gaussian simulation (the Gaussian simulation curve is the closest to the Raman curve). The results of the measurements are shown in Fig. 5.

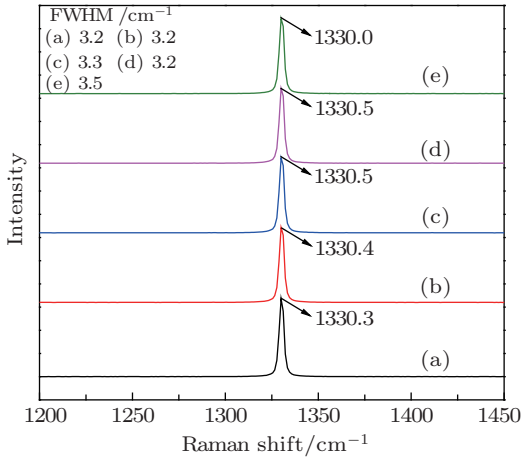


Fig. 5. (color online) Raman spectra of large diamonds synthesized with different amounts of sulfur additive: (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 4%.

Generally, the characteristic peak of natural diamond is 1331–1346 cm^{-1}, while the characteristic peak of the theoretically perfect large diamond is 1332.5 cm^{-1}.[24] In our experiments, the peak position and FWHM for the large diamond without sulfur doped are 133.3 cm^{-1} and 3.2 cm^{-1}, respectively. The peak is related to many factors, such as the room temperature and the testing lattice perfection of the large diamond. In general, the higher the peak displacement of the structure of the large diamond, the more deviation from the cubic structure, namely, the internal stress is larger.

It can be seen from Table 3 that, with the increase of the quantity of sulfur additive in the cell, the Raman FWHM of the large diamond gradually becomes larger. Namely, the crystallization degree of the large diamond decreases. That is to say, the introduction of additive sulfur reduces the quality of the large diamond crystal. The testing temperature is 25 °C and the quality of the samples is good. So, the presence of sulfur in the large diamond is possibly the cause for the increase of the Raman FWHM.

Table 3. Raman peak position and FWHM of large diamond with different amounts of S additive.

Sample	Sulfur additive/wt.%	Peak position/cm^{-1}	FWHM/cm^{-1}
(a)	0	1330.3	3.2
(b)	1.0	1330.4	3.2
(c)	2.0	1330.5	3.3
(d)	3.0	1330.5	3.3
(e)	4.0	1330.	3.5

3.4. Electrical properties of the large diamond crystals

The electrical properties of the large diamond crystals are tested by a four-point probe and the Hall effect method, the schematic diagram is shown in Fig. 6. The results of the measurement are listed in Table 4. The Hall coefficients of the samples doped with S are negative, while that of the sample without S is positive. This indicates that the conduct type of the diamonds doped with S is n-type.

Table 4. Test results of the electrical properties of the crystals.

Sample	Sulfur additive/wt.%	Resistivity/Ω·cm	Carrier density/cm^{-3}	Hall coefficient/cm^3·C^{-1}
(a)	0	2.923×10^{10}	1.403×10^{4}	4.455×10^{14}
(b)	1.0	5.381×10^{6}	6.132×10^{9}	-1.019×10^{9}
(c)	2.0	2.031×10^{6}	1.031×10^{11}	-6.062×10^{7}
(d)	3.0	1.312×10^{6}	2.923×10^{11}	-2.138×10^{7}
(e)	4.0	9.628×10^{5}	1.116×10^{13}	-5.600×10^{5}

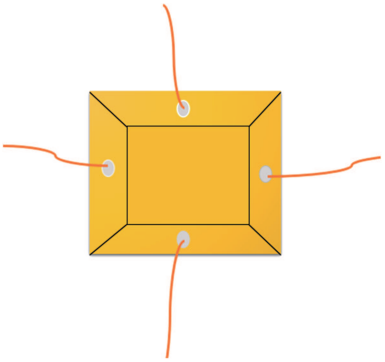


Fig. 6. (color online) Schematic of the test method with a four-point probe.

As can be seen, the resistance 2.923×10^{10} Ω·cm of the large diamond is obviously larger compared with that of the sulfur doped diamond. Simultaneously, the carrier density 1.403×10^{4} cm^{-3} of the large diamond is distinctly smaller. It can be seen that the carrier densities of these samples gradually become larger with the increase of the sulfur additive, while their resistances become gradually smaller. It is universally acknowledged that the synthetic large diamond without any additive is an insulator with a resistance greater than 10^{8} Ω·cm. The electrical properties of the synthetic large diamond change after sulfur doping. The resistance becomes 5.381×10^{6} Ω·cm

with 1 wt.% sulfur doping. When the additive sulfur is up to 4.0 wt.%, the experimental resistance is 9.628×10^5 Ω·cm. With the H_2S additive, a n-type conductivity of the sulfur-doped diamond thin films with resistance 1.82 $\Omega^{-1}\cdot cm^{-1}$ was obtained by Wang.[18] The carrier concentration at room temperature of the S-doped film was 1.4×10^{13} cm^{-3} reported by Mikka,[20] which is close to 1.116×10^{13} cm^{-3} obtained by us. In consideration of the probable presence of the S–S, C–S bonds, the n-type behavior of the diamond doped with S is given in terms of the certain activated electron donation, which is relevant to S. Therefore, the synthetic doped crystal is determined to be an n-type semiconductor, the change of the electrical properties after doping provides the basis for the further synthesis of n-type semiconductor.

4. Conclusion

Large diamond crystals have been synthesized in the FeNiMnCo–S–C system with sulfur additive under HPHT conditions. The increase of the sulfur additive not only deepens the color of the large diamonds but also changes the morphology of the large diamonds. The pressure and temperature conditions of large diamond synthesis decrease with the increase of additive sulfur. The XPS results indicate that S has been incorporated into the diamond. According to the Raman spectra, the increase of sulfur content reduces the quality of the large diamond crystals. The electrical properties of the large diamond crystals changing with the amount of sulfur indicate that they can be n-type semiconductors. These experiments provide the basis of further synthesis of diamond of n-type semiconductor.

Acknowledgment

We thank Cailong Liu and Yong Li for profound discussions and comments.

References

[1] Ulbricht R, Hendry E, Shan J, Heinz T F and Bonn M 2011 *Rev. Mod. Phys.* **83** 543
[2] Strong H and Chrenko R 1971 *J. Phys Chem.* **75** 1838
[3] Zhang J, Ma H, Jiang Y, Liang Z, Tian Y and Jia X 2007 *Diamond Relat. Mater.* **16** 283
[4] Zheng Y J, Li Y T, Jia X P, Ma H A and Zhou L 2009 *Chin. Phys. B* **18** 333
[5] Burns R, Hansen J, Spits R, Sibanda M, Welbourn C and Welch D 1999 *Diamond Relat. Mater.* **8** 1433
[6] Sumiya H, Toda N, Nishibayashi Y and Satoh S 1997 *J. Cryst. Growth* **178** 485
[7] Sun S, Jia X, Yan B, Wang F, Chen N and Li Y 2014 *CrystEngComm.* **16** 2290
[8] Zhang Z, Jia X, Sun S, Liu X, Li Y and Yan B 2013 *Int. J. Refract. Met. Hard Mater.* **38** 111
[9] Sakaguchi I, Mikka N, Kikuchi Y, Yasu E, Haneda H and Suzuki T 1999 *Phys. Rev. B* **60** R2139
[10] Palyanov Y N, Borzdov Y M, Khokhryakov A, Kupriyanov I and Sobolev N 2006 *Earth Planet. Sci. Lett.* **250** 269
[11] Li Y, Jia X, Hu M, Yan B, Zhou Z and Fang C 2012 *J. Refract. Met. Hard Mater.* **34** 27
[12] Goss J, Briddon P, Jones R and Sque S 2004 *Diamond Relat. Mater.* **13** 684
[13] Chao F, Jia X P, Chen N, Li Y D, Chen L C, Guo L S and Ma H A 2015 *Acta Phys. Sin.* **64** 128101 (in Chinese)
[14] Chao F, Jia X P, Yan B M, Chen N, Li Y D, Chen L C, Guo L S and Ma H A 2015 *Acta Phys. Sin.* **64** 228101 (in Chinese)
[15] Zhang H, Li S S, Su T C Hu M H, Zhou Y M, Fan H T, Gong C S, Jia X P, Ma H A and Xiao H Y 2015 *Acta Phys. Sin.* **64** 198103 (in Chinese)
[16] Goss J P, Eyre R J and Briddon P R 2008 *Phys. Status Solidi.* **245** 1679
[17] Chun Q Z and Lei L 2015 *Chin. Phys. B* **24** 018101
[18] Yong W and Zeng Y 2014 *Plasma Sources Sci. Technol.* **16** 255
[19] Gu C Z, Wang Q, Li J J and Xia K 2013 *Chin. Phys. B* **22** 098107
[20] Nishitani-Gamo M, Yasu E, Xiao C, Kikuchi Y, Ushizawa K, Sakaguchi I, Suzuki T and Ando T 2000 *Diamond Relat. Mater.* **9** 941–947
[21] Nesladek M 2005 *Semicond. Sci. Technol.* **20** R19
[22] Palyanov Y N, Kupriyanov I, Borzdov Y M, Sokol A and Khokhryakov A 2009 *Cryst. Growth Des.* **9** 2922-6
[23] Palyanov Y N, Kupriyanov I N, Sokol A G, Khokhryakov A F and Borzdov Y M 2011 *Cryst. Growth Des.* **11** 2599
[24] Yan B, Jia X, Fang C, Chen N, Li Y and Sun S 2016 *J. Refract. Met. Hard Mater.* **54** 309
[25] Sque S, Jones R, Goss J and Briddon P 2004 *Phys. Rev. Lett.* **92** 017402
[26] Nakamura T, Ohana T, Hagiwara Y and Tsubota T 2009 *Phys. Chem. Chem. Phys.* **11** 730
[27] Hasegawa M, Takeuchi D, Yamanaka S, Ogura M, Watanabe H and Kobayashi N 1999 *Jpn. J. Appl. Phys.* **38** L1519
[28] Gupta S, Martíez A, Weiner B R and Morell G 2002 *Appl. Phys. Lett.* **81** 283
[29] Hu M H, Bi N, Li S S, Su T C, Zhou A G and Hu Q 2015 *Chin. Phys. B* **24** 038101
[30] Petherbridge J, May P, Fuge G, Rosser K and Ashfold M 2002 *Diamond Relat. Mater.* **11** 301
[31] Li S S, Mu H A, Li X L, Su T C, Huang G F and Li Y 2011 *Chin. Phys. B* **20** 028103
[32] Sun S S, Jia X P, Zhang Z F, Li Y, Yan B M, Liu X B and Ma H A 2013 *J. Cryst. Growth.* **377** 22
[33] Fleutot S, Dupin J C, Renaudin G and Martinez Hervé 2011 *Phys. Chem. Chem. Phys.* **13** 17564
[34] Zhichang L, Licheng L, Wenming Q, Lang L and Mochida I 1999 *J. Mater. Sci.* **34** 6003
[35] Zhang Y J, Mi C, Yang L, Deng W F, Tan Y M, Ma M and Xie Q J 2014 *Chem. Commun.* **50** 6382