Effect of FeS doping on large diamond synthesis in FeNi–C system*

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The large single-crystal diamond with FeS doping along the (111) face is synthesized from the FeNi–C system by the temperature gradient method (TGM) under high-pressure and high-temperature (HPHT). The effects of different FeS additive content on the shape, color, and quality of diamond are investigated. It is found that the (111) face of diamond is dominated and the (100) face of diamond disappears gradually with the increase of the FeS content. At the same time, the color of the diamond crystal changes from light yellow to gray-green and even gray-yellow. The stripes and pits corrosion on the diamond surface are observed to turn worse. The effects of FeS doping on the shape and surface morphology of diamond crystal are explained by the number of hang bonds in different surfaces of diamond. It can be shown from the test results of the Fourier transform infrared (FTIR) spectrum that there exists an S element in the obtained diamond. The N element content values in different additive amounts of diamond are calculated. The XPS spectrum results demonstrate that our obtained diamond contains S elements that exist in S–C and S–C–O forms in a diamond lattice. This work contributes to the further understanding and research of FeS-doped large single-crystal diamond characterization.

Keywords: HPHT, large single-crystal diamond, FeS doping

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1. Introduction

Diamonds with graphene, carbon nanotubes, and so on are allotropes of carbon. Each carbon atom of diamond crystal in the sp^3 hybrid orbit with four adjacent carbon atoms forms a carbon-carbon covalent bond, so diamond has many unique proprieties such as high hardness, high melting point, etc. In the 1950s, Bundy announced the first success in synthetic diamond,[1] which opened the door to exploring the applications of diamond in various fields such as modern industry, national defense, science and technology, mechanical processing, and electronic appliances.[2,3] Generally speaking, compared with traditional semiconductors, the diamond semiconductor possesses extremely excellent performances, such as wide band-gap, high thermal conductivity, and high dielectric breakdown field strength.[4–6] In order to improve the above characteristics, the influences of doping elements on the quality and properties of diamond and the related mechanism have been studied. These studies are helpful for controlling the quality of diamond synthesis so that the application scope of semiconductor diamond can be widened.

Pure diamond is an insulator. If it is successfully doped with some suitable impurity elements such as an acceptor or donor, the synthesized diamond will become a semiconductor. It can be indicated from the theoretical calculations of the first principles that N-type elements (N, P, As, Sb), S-type elements (S, Se, Te), and sulfur hydride as impurity defects in diamonds can provide donor levels.[7] In addition, the theoretical calculations based on atom superposition and the electron delocalization molecular-orbital method demonstrate that BS and NS in di-vacancy sites in diamond will provide shallow donor levels.[8] Kato *et al.* studied n-type thin film diamond with P doping.[9] It pointed out that the optimal ratio of methane to P vapor was able to grow a smooth, high-quality P doped film. John *et al.* discussed the synthesis, characteristics, and functions of B doping diamond, who pointed out that B doping diamond is an ideal electrical material.[10] Sally *et al.* reported that BS co-doping can promote the incorporation of S into diamonds with n- and p-type semiconductor properties, forming a p–n junction.[11] Hu *et al.* pointed out that the annealing temperature of 800 °C made P doping nanodiamond film a good n-type electrical conductor.[12] On the other hand, with the deepening of research on the doping of diamond thin films, a great many researches have been done on the doping modification of HPHT synthetic diamond. In order to improve the electrical properties of semiconductor diamond synthesized under HPHT, the effects of these impurities on the

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diamond quality, crystal growth rate, growth temperature, and semiconductor properties were observed in the process of diamond growth by doping different impurities. Additive impurities are both singly doped and co-doped, in which the additive elements mainly are B, S, N, P, etc. Palynaov *et al.* studied the nucleation kinetics of Mg and P doping diamond under HPHT, and they pointed out that the factors affecting the diamond nucleation and growth were pressure, temperature, and growth time.[13,14] Li *et al.* reported type-IIb B doping large diamond with P-type semiconducting properties; they pointed out that the crystal shapes tends to be single, and small pitting corrosion appears on the surface as the B content increases.[15] Gong *et al.* reported type-Ib P doping diamond with n-type semiconductor properties, and they pointed out that the diamond surface became rough and the growth rate decreased as the P content increases.[16]

Sakaguchi *et al.* successfully synthesized S doping thin-film diamonds with n-type semiconductor properties by the chemical vapor deposition method.[5,17] Yu *et al.*[18] and Sato and Katsura[19] used sulfur as a nonmetallic catalyst to synthesize type-Ib diamond under HPHT. However, the synthetic diamonds had incomplete crystal morphologies, small sizes, and a large number of growth defects on the surface. Zhang *et al.* reported that type-Ib or IIa with single-S doping and BS co-doping high-quality large diamonds with n- or p-type semiconductor properties were synthesized.[20,21] It is pointed out that there is no change in the color of type-Ib with S or BS co-doping. In contrast, the color of type-IIa diamond changes from colorless to blue and black with the increase of additive B content. The natural type-Ia diamond was based on the kimberlite as a growth environment, in which the sulfides were contained and played an important role in the growth of natural diamond.[22] Taking into account FeS as a sulfide consisting of Fe and S, both of which can be used as a synthetic diamond catalyst, FeS was used as an additive to explore the effects of FeS on single-crystal diamond synthesis under HPHT.

2. Experiment

The experimental equipment was a homemade cubic anvil HPHT apparatus (CHPA SPD6 ×1200). The sample synthesis pressure was about 5.6 GPa and the synthesis temperature was about 1370 °C. The synthesized pressure for diamond was determined from the relationship between oil pressure and chamber pressure, which was based on high pressure phase change resistance established by the bismuth (Bi), barium (Ba), and thallium (TI). The synthesis temperature was measured based on the calibration of Pt.6% Rh–Pt 30% Rh thermocouple. The source of carbon was highly pure natural graphite powder (99.9% purity). The FeNi alloy slice (the weight ratio of Fe:Ni is 64:36) was used as the catalyst in the experiment. The additive ferrous sulfide (FeS) powder (99.9% purity) was evenly tiled between the first layer and the second layer of the four catalyst layers with a 0%–2% weight ratio of FeS– to carbon source. Under the effect of heat convection, FeS is uniformly dispersed in the molten catalyst. The (111)-surface single crystal diamond was selected to use as the seed. The schematic diagram of diamond growth cell is shown in Fig. 1.

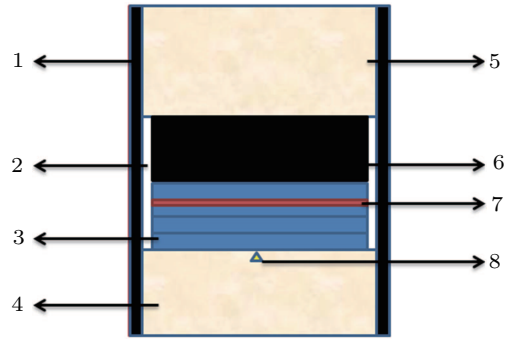


Fig. 1. (color online) Schematic diagram of diamond growth cell. 1: graphite heater; 2: ZrO_2+MgO sleeve; 3: FeNi metal catalyst; 4, 5: ZrO_2+MgO pillar; 6: carbon source; 7: FeS powder; 8: seed crystal.

The synthesized sample was firstly boiled with dilute nitric acid to remove the catalyst alloy coating on the crystal surface and then boiled with a certain mixture of concentrated sulfuric acid and concentrated nitric acid to remove residual graphite and catalyst. The morphology, color, inclusions, and surface morphology of synthesized crystal were observed by optical microscope (OM) and scan electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR) (BrukerOptics/IFSHyperion 3000M) was used to ascertain whether C, N, and S are existent. The XPS measurements were used to detect the existence and state of S in the diamond lattice by the PHI X-tool instrument. The S concentration of diamond was counted by calculating the areas of S2p peak relative to C1s peak.

3. Results and discussion

In order to observe the influence of FeS doping on the diamond quality, large diamonds with different additive dosages are synthesized under the same temperature and pressure. It can be seen in Table 1 that there exists a relationship among the content of FeS, color, and quality of diamond obtained in FeNi-C system.

Table 1. Experimental results of larger diamonds synthesized in the FeNi-C system.

FeS additive /wt%	Growthtime /h	Temperature /°C	Inclusions	Results
0	12	1370	little	light yellow
0.5	12	1370	little	gray yellow
0.7	12	1370	little	gray yellow
1	12	1370	little	gray green
1.5	12	1370	little	gray green
2	12	1370	a little	gray yellow

3.1. Effect of FeS additive amount on shape of large diamond

According to the growth of V-shaped diamond, it is easy to know that controlling the growth temperature at a certain pressure can change the shape of abrasive grade diamond (Film Growth Method, Abbreviated FGM) from cubic to cubic-octahedral to octahedron.[23–25] In contrast, the shapes of large single-crystal diamonds by TGM at different temperatures are plate, tower, and spire. In this paper, a large single-crystal diamond with plate shape is synthesized at 1370 °C and 5.6 GPa. Large diamonds are synthesized with different amounts of FeS doping (see Table 1), and their corresponding photos are shown in Fig. 2. As shown in Fig. 2, the (100) plane of diamond generally refers to a tetragonal or octagonal plane, while the (111) plane generally refers to a triangular or hexagonal plane. Under the same temperature and pressure, when the amount of additive FeS is 0%, the crystal shape is plate, and the (100) faces and (111) faces are dominated. When the amounts of additive FeS are 0.5%, 0.7%, 1%, and 1.5%, the (100) face disappears and the (111) face is dominated. While the amount of additive FeS increases to 2%, the (100) face completely disappears and the (111) face is dominated. This phenomenon is in consistence with experimental results given by Huang, Li and Chen *et al.*[15,23,26,27] In their experiments, the (111)-surface single-crystal diamonds were used as seeds. When the amount of additive N or B or S reaches a certain value, the (100) face disappears and the (111) face is dominated in the diamond shape. On the whole, the results can be explained by the specific surface energy.[26] The incorporation of FeS into diamond lattices makes the specific surface energy of the (100) faces larger than that of the (111) faces. If the rate of carbon atoms transported into the seed crystals is constant, the energy required to migrate the carbon atoms into the seed to form the (100) faces is greater than that to form the (111) faces. Therefore, (100) faces will preferentially disappear by the law of "the fast surface submerged and the slow surface exposed".[4,28]

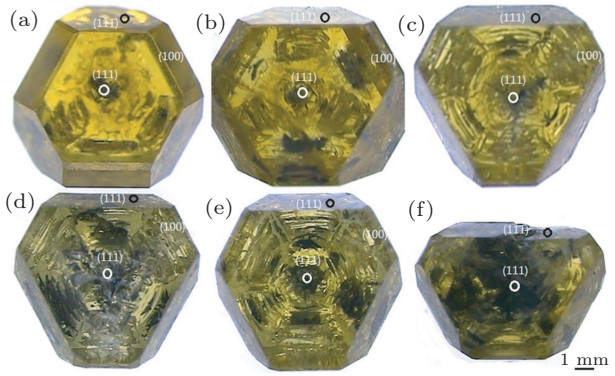


Fig. 2. (color online) OM photographs of large diamonds synthesized with different amounts of FeS: (a) 0%, (b) 0.5%, (c) 0.7%, (d) 1%, (e) 1.5%, and (f) 2%.

Zhang *et al.*[29] used the bald-point model to explain the mechanism of the effects of B doping on the (100) faces and (111) faces of diamond, which can be used to explain the similar phenomena in this study. As shown in Fig. 3(a), one carbon atom is bonded to three adjacent carbon atoms on the (111) surface. As shown in Fig. 3(b), one carbon atom is bonded to two adjacent carbon atoms on the (100) surface. According to Fig. 2, with the increase of FeS content, the (100) face of diamond gradually disappears and the (111) face is dominated. When S replaces the carbon atoms on the (100) or (111) face in the form of positive tetravalent, its number of dangling bonds is different. On the (100) face, one positive tetravalent sulfur substitutes one carbon atom to bond two adjacent carbon atoms, while two additional dangling bonds can bind other carbon atoms. In contrast, only one dangling bond can be bonded to other carbon atoms on the (111) face. Then the effects of dangling bond on the transportation and bonding of carbon atoms between the (100) face and the (111) face will be different. The number of dangling bonds of the (100) face is more than that of the (111) face. Then the growth rate of the (100) face will be greater than that of the (111) face.[15,23,26] Therefore, with the increase of FeS content, the (100) face disappears gradually and the (111) face is prominent.

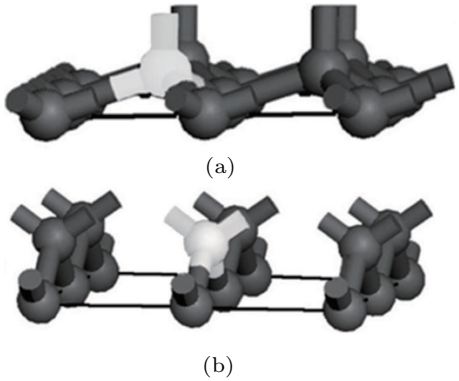


Fig. 3. Substitution of sulfur atom (white) for carbon atom (black) on (111) and (100) surfaces of diamond.

3.2. Effects of FeS additive amount on color and inclusions of large diamond

There are six diamonds doped by FeS with different amounts of 0%, 0.5%, 0.7%, 1%, 1.5%, and 2%, respectively (seen in Fig. 2). It can be seen from Fig. 2(a) that the large diamond without additive FeS is light yellow in color and has high quality. The large diamonds doped by FeS with amounts of 0.5% or 0.7% are gray-yellow in color, both of which have no pitting corrosion on their smooth surfaces of diamonds with few inclusions inside (seen Figs. 2(b) and 2(c)). It can be seen from Figs. 2(d) and 2(e) that the colors of the large diamonds with FeS doping amounts of 1% and 1.5% are gray-green in color and have some pitting corrosions on the coarse surfaces with visible inclusions inside. As seen in Fig. 2(f), the large diamond obtained by 2% doping FeS is gray-yellow in color and has some cracks on the coarse surfaces with lots of inclusions inside. In a word, with the increase of the amount of FeS

doping, the color of the diamond crystal changes from yellow to gray-green and even to gray-yellow. This result is similar to that of Gheeraer *et al.*,[30] who synthesized S-doped diamond thin films by chemical vapor deposition. Besides, the crystal color change is also similar to that of Chen *et al.*,[31] who synthesized S-doped large diamonds by TGM.

The large diamonds synthesized are type-Ib diamonds with a light yellow color, in which the N atoms existed in the form of a single substitute atom.[32] With increasing the amount of additive FeS, a number of S atoms may enter into the diamond lattice as well. The nuclear electron distributions of the N and S are different. When they are illuminated, the electron absorbs part of the energy to produce a transition from the low energy ground state to the high energy excited state. As a result, the color changes of large diamond doping FeS is observed. The un-doped type-Ib large diamond is light yellow in color. With the amount of FeS doping increasing, the color of diamond changes from gray-yellow to gray-green. Obviously, inclusions are seen at the amount of 2% FeS, which may be due to too much S destroying the diamond lattice.

3.3. Effects of FeS additive amount on surface morphology of large diamonds

In order to further observe the crystal surface morphology, the SEM photographs are taken under a magnification of 2000 times. The SEM images for the front and side surfaces of large diamonds in Fig. 4 correspond to those OM photos in Fig. 2. Taking Fig. 2(a) for example, the (111) plane in the middle of diamond is regarded as the front surface. The (100) plane on the right side and the (111) plane on the top side of the diamond are both side surfaces. In the SEM images, the front surfaces and the side surfaces correspond to the central part of the (111) plane, marked by white and black ovals in Fig. 2, respectively. Figures 4(a) and 4(b) and figures 4(c) and 4(d) show the morphologies of front and side surfaces of the crystal in Figs. 2(a) and 2(b) respectively. It can be seen obviously from the photographs, that the front surfaces are both smooth without pit corrosion and the side surfaces show dense dots and are slightly convex. It can be seen obviously from the photographs of Figs. 4(e) and 4(f) that the front surface (Fig. 4(e)) presents a few concave triangles and the side surfaces (Fig. 4(f)) contain a few small irregular triangles. The photographs of Figs. 4(g) and 4(h) are corresponding to the front and side surfaces of the crystal in Fig. 2(d), respectively. It can be seen obviously from this photograph that the front surface (Fig. 4(g)) contains many regular triangular waves and the side surface (Fig. 4(h)) shows the layered steps. It can be seen obviously from the photographs (Figs. 4(i) and 4(j) that the front surface (Fig. 4(l)) contains many concave triangles and the side surface (Fig. 4(j)) displays a layered gully. Figures 4(k) and 4(l) are for the front and side surface of the crystal in Fig. 2(f). It can be seen obviously from the photographs that the front surface (Fig. 4(k)) has many concave triangles and the side surface (Fig. 4(l)) shows many small pits. In summary, the changes of the above crystal surface morphologies with the increase of FeS show that it is possible that more S atoms enter into the diamond lattice and thus affects the bonding of C atoms.

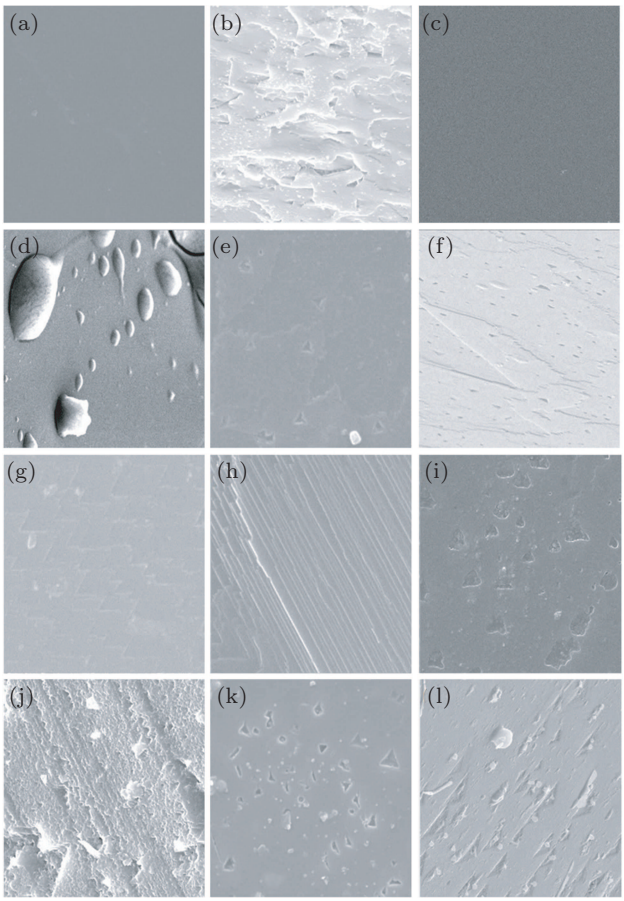


Fig. 4. (color online) SEM images of large diamonds synthesized with different amounts of FeS additive: (a) and (b) 0%, (c) and (d) 0.5%, (e) and (f) 0.7%, (g) and (h) 1%, (i) and (j) 1.5%, (k) and (l) 2%.

From Figs. 2–4, when the amounts of additive FeS are 0.5%, 0.7% 1%, and 1.5%, the (100) face disappears and the (111) face is dominated gradually. A large number of S atoms are transported to the (111) plane, in which C atoms can only bond a limited number of S atoms, which will lead to the accumulation of S atoms and defects caused in the lattice space. The more amounts of FeS are incorporated, the more serious defects are caused. With increasing the amount of FeS, it is also confirmed that the fringes and corrosion pits on the front and side surfaces of the diamond crystals turn gradually serious.

3.4. Analysis of FTIR spectra

The curve *a*–curve *f* in Fig. 5 are infrared absorption spectra of the diamond doping FeS at 0%–2%, corresponding to Figs. 2(a)–2(f), respectively. According to the NIST infrared data, it can be seen from the curves that all of them

have the characteristic peaks of N element with wavenumbers at 1130 cm^{-1} and 1344 cm^{-1}. Besides, there are S–O characteristic peaks each with a wavenumber of 885 cm^{-1} in Fig. 5 (seen curve *b*–curve *f*). The peaks of N atoms are at 1130 cm^{-1} and 1344 cm^{-1} in the ideal type-Ib diamond, of which the N content is calculated according to the formula $N_c = (25.0 \pm 2) \times \alpha$ (1130 cm^{-1}).[33,34] Here, N_c represents the N element content and α (1130 cm^{-1}) represents the value corresponding to the peak 1130 cm^{-1} in the formula. The N_c of each sample is listed in Table 2. As shown in the table, N_c values are similar when diamonds are doped by FeS with amounts of 0%, 0.5%, and 0.7%. It shows that N_c is hardly affected when the additive is a small amount of FeS in diamond synthesis. However, N_c values are lower than that of un-doped diamond when diamond doping FeS amounts are 1% and 1.5%. In contrast, N_c is greater than that of un-doped diamond when the amount of additive FeS is 2%.

Our researcher group has determined the S characteristic peak with a wavenumber of 847 cm^{-1} in the B–S co-doped diamond synthesized in the FeNiCo–C–S system.[35] On the contrary, the S–O characteristic peak with a wavenumber of 885 cm^{-1} is detected in this paper. The distinction between the two characteristic peaks is determined by whether or not the additive boron is used and also by the difference between the two types of additives (S and FeS) and catalyst (FeNiCo and FeNi) to be used.

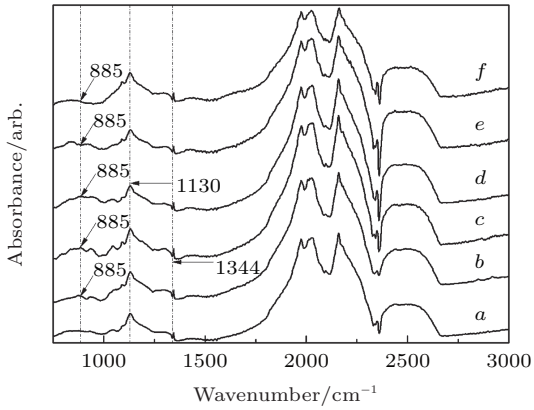


Fig. 5. FTIR absorption spectra of diamonds with FeS content of (a) 0%, (b) 0.5%, (c) 0.7%, (d) 1%, (e) 1.5%, and (f) 2%.

Table 2. N content of diamond doping with different amounts of FeS.

Additive amounts/%	0	0.5	0.7	1	1.5	2
Content of N /ppm	92	90	91	56	72	106

3.5. XPS spectra of diamonds

The XPS measurements are used to detect the existence and state of S in the structure of obtained diamond. Besides, the relative content of the S element is calculated. The XPS results for different amounts of the diamond additive FeS are shown in Fig. 6. In Fig. 6(a) for doping FeS amount of 0.5%, the spectrum of C 1s can be resolved into two signals with binding energies of 284.8 eV and 284.3 eV respectively, which can be attributed to C–S–O and C–C bonds according to the results in the literature and NIST XPS database.[36,37] In Fig. 6(b), it is

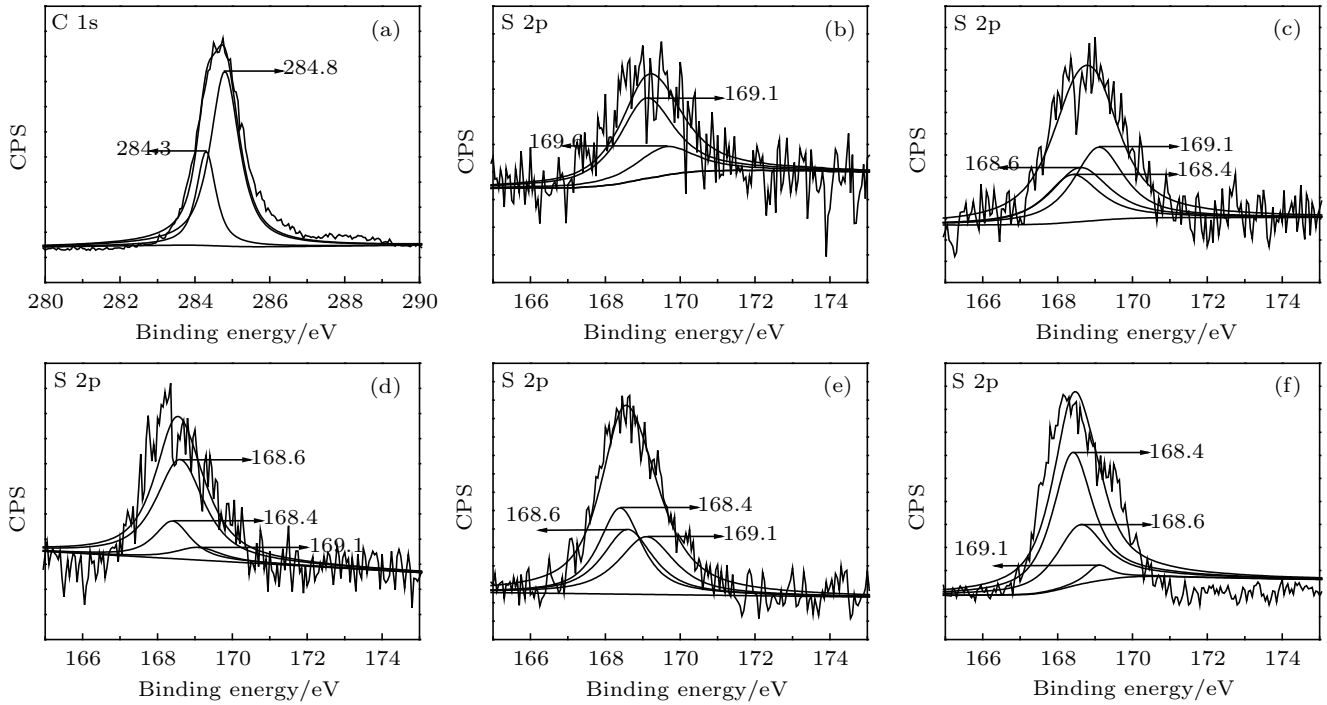


Fig. 6. XPS spectra of the diamond with FeS of 0.5% (a) C 1s, 0.5% (b) S 2p, 0.7% (c) S 2p, 1% (d) S 2p, 1.5% (e) S 2p, and 2% (f) S 2p.

found that the de-convolution of the S 2p spectrum gives 2 peaks centered at 169.1 eV and 169.6 eV, respectively. In Figs. 6(c)–6(f), the de-convolution of S 2p spectrum gives 3 peaks centered at 169.1 eV and 168.4 eV and 168.6 eV, respectively. According to the NIST XPS database,[38–41] the de-convolution peak at 169.1 eV can be contributed from S–C bonding, the peak at 169.6 eV and 168.6 eV are due to S–O bonding, and the peak at 168.4 eV can be attributed to S–C–O boding. The XPS spectrum results demonstrate that our obtained diamonds contain S, C, O elements in lattice structures. After calculating the XPS data, it is found that the concentrations of S relative to C are 0.6%, 0.5%, 1.3%, 6.1%, and 1.2% corresponding to the amounts of doping FeS of 0.5%, 0.7%, 1%, 1.5%, and 2% respectively. When the amounts of additive FeS are 0.5%, 0.7%, 1%, and 1.5%, concentration of S gradually increases. As the amount of additive FeS continues to increase, the concentration of S decreases. This confirms that the inclusions are seen obviously at the amount of 2% FeS, which is due to many S atoms destroying the diamond lattice. As the concentration of S continues to increase, the diamond quality continues to decline. This also shows that the S element has successfully been incorporated into the diamond.

4. Conclusions

In this paper, the effects of FeS doping in the FeNi–C system on single-crystal diamond grown along the (111) plane are investigated. With the increase of FeS content, the face morphology, color, and inclusion of diamond change obviously. It is found that the (111) face of diamond is dominated and the (100) face of diamond disappears gradually with the increase of the FeS content. At the same time the color of the diamond crystal changes from light yellow to gray-green and even gray-yellow. The stripes and pits corrosion on the diamond surface turn worse, correspondingly. According to the FTIR spectrum, there appears an S–O characteristic peak with a wavenumber of 885 cm^{-1}. Besides, the XPS spectra demonstrate that our obtained diamonds contain S, C, and O elements in lattice structures. As the amount of additive FeS increases, the concentration of S atoms increases continuously. In summary, S atoms enter into the diamond lattice, and thus affect the bonding of C atom. This experiment lays a foundation for the further synthesis of sulfide doped large single-crystal diamond.

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