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Co-doping of diamond with boron and sulfur

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Diamond films grown by chemical vapor depositing (CVD), due to their attractive physical and electrical properties, have been recognized as promising material for electronic devices which can operate at high temperatures or in harsh environments. The p-type conductivity has been confirmed for B-doped diamond by gas doping [1]. However, obtaining n-type semiconductor diamond by CVD has proved more challenging, mainly due to the fact that suitable donor atoms are larger than carbon, making incorporation into the diamond lattice unfavorable. Nitrogen has been well characterized as a deep donor with an electronic level at 1.7 eV below the conduction band, but the donor levels are too deep for many electronic applications [2]. Phosphorus-doped diamond films proceed by gas-phase doping during CVD exhibits n-type conductivity [3], but these exhibit poor conductivity making them unsuitable for device applications. Up to now, n-type conductivity with high quality electronic device has not been obtained. Hasegawa *et al.* [4] for the first time succeeded in n-type control by sulfur ion implantation. Their work encourages investigations of H_2S as another possible source of sulfur for *in situ* doping of CVD diamond films. Recently, sulfur has been reported to give n-type conductivity [5], However, its electrical conductivity is very low, and is not suitable for electrical devices. Due to the sulfur's larger covalent radius, a large lattice relaxation in doping S into diamond is created which reduces the solid solubility limit of S and creates defects in diamond. Theoretical calculation results show [6, 7] that B/S pairs are perfect for co-doping into diamond. Co-doping may reduce the lattice-relaxation energy of the crystal due to the p-type smaller atomic radius and n-type larger atomic radius, increasing carrier mobility and making impurity levels shallower. The usefulness of this idea has been experimentally demonstrated for various semiconductors such as GaN, ZnO and so on.

In this study, the experiments were motivated by the possibility of co-doping diamond with sulfur and small quantities of boron. It was expected that boron should facilitate sulfur incorporation into diamond. Co-doping of sulfur and boron was attempted by including dimethyl disulfide and dioxide boron in the source gas, diluted in acetone. The acetone concentration was 0.5%; the S/C atomic ratio in the source gas was 0.005, with a B/S ratio of 0.02. Diamond films were synthesized on a single-crystal n-type (100) Si substrate using the conventional microwave plasma chemical vapor depositing (MPCVD) method.

The amounts of sulfur introduced into the diamond films were quantified by auger electron spectrum technique (AES). The absolute values for the sulfur content of the films were calculated by comparing the areas of selected S peak and C peak, following calibration using sensitivity factors appropriated for each element. When boron was not present, the concentration of sulfur in diamond films was about 0.11 at.%. When boron was added to the source gas, the sulfur concentration increased to 0.15 at.%. This indicated that the addition of boron facilitated sulfur incorporation into diamond. Additionally, it was observed that there was yellow powdery sulfur on the colder parts of the chamber during the CVD process.

The surface morphology of the films was revealed by scanning electron microscopy (SEM) technique. Raman spectroscopy (RS) was used to analyze the various structural phases in the diamond films. For the electrical measurements, the S-doped diamond films were treated in a heated mixture of H_2O_2 and H_2SO_4 (1:1) to oxidize and remove the surface conductive layer. Ohmic contacts were fabricated on the oxidized diamond surface by deposition of Ag (1 μm thick), which was annealed in a vacuum atmosphere at 300 °C for 30 min.The resistance of the films was determined by two point probe measures. The values of film resistance obtained by this method were typically in the range of 10^5–$10^7\,\Omega$, and were then converted to film electrical resistivity by multiplying the films thickness measured by cross-sectional SEM.

Fig. 1 shows the Fourier transform infrared (FTIR) spectrum of B/S co-doped diamond films. Some typical absorption peaks are observed at the wave numbers of 562.0 and 1102.0 cm^{-1}, which are related to the C—S bonds and B—C bonds, respectively. We speculate that CS is the species responsible for the inclusion of S into diamond films.

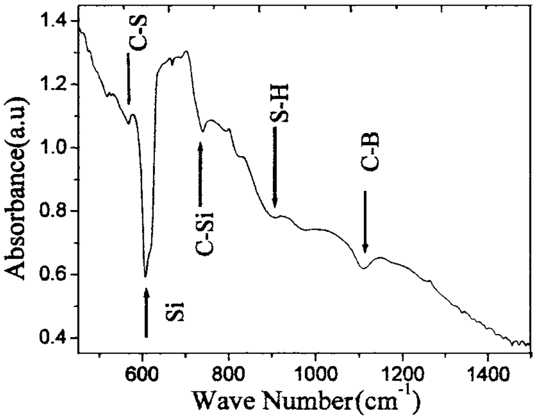

Figure 1 FTIR spectrum for a B/S-codoped sample.

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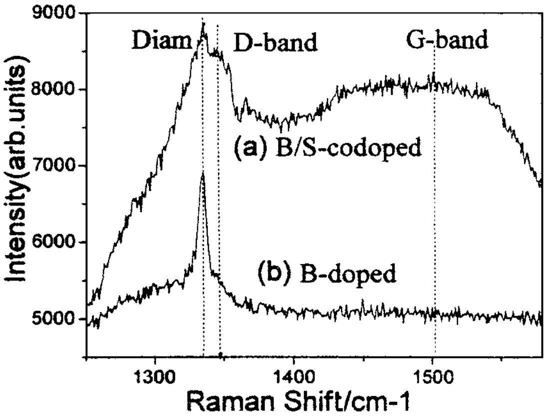
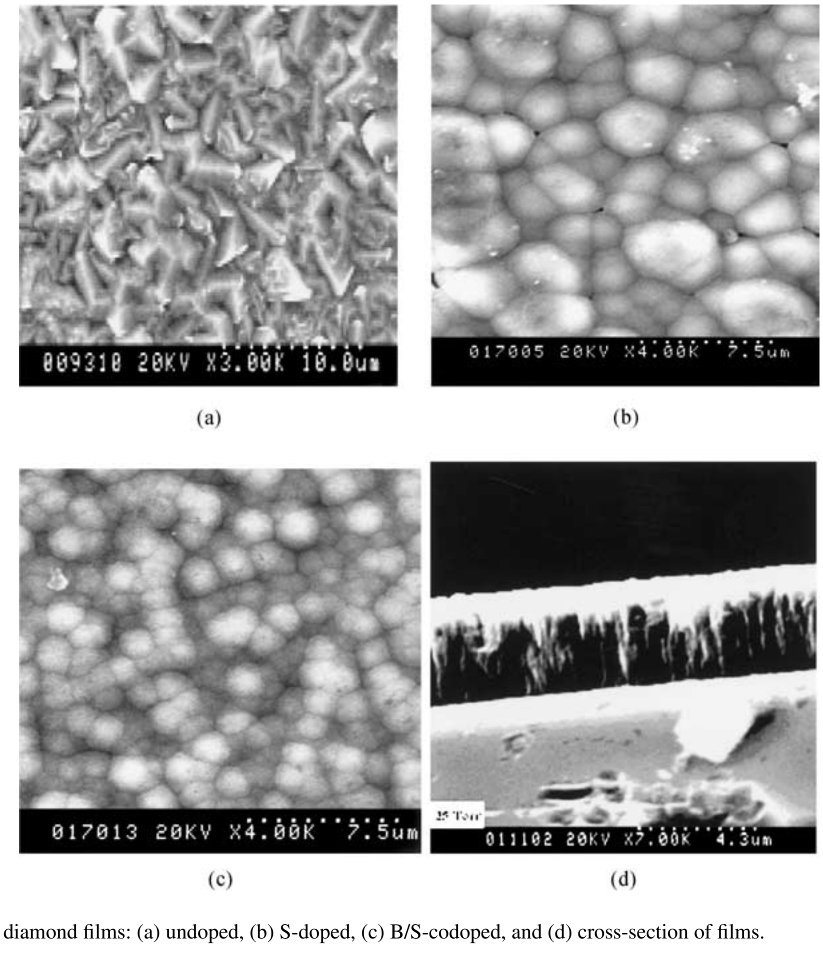


Figure 2 Raman spectra of diamond films: (a) B/S-codoped and (b) B-doped.

The Raman spectrum in Fig. 2a depicted that the B/S co-doped diamond films were composed of crystalline graphite, amorphous sp^2 carbon (or graphitic phase) and crystalline diamond. A strong peak of diamond at about 1332 cm^{-1} in the Raman spectrum confirmed that the films were prodominantly crystalline diamond containing only small amounts of microcrystalline graphitic or amorphous sp^2 carbon components, indicated by broad brands and weak peaks at around 1360 and 1560 cm^{-1}. The typical Raman spectrum of amorphous carbon consists of two broad bands: a D band (D for disordered) at approximately 1350 cm^{-1}, and a G band (G for graphite) at about 1580 cm^{-1} [8]. Fig. 2b showed a Raman spectrum for boron-doped diamond. No observable non-diamond peaks were seen. Therefore, it was speculated that the addition of sulfur during diamond growth tended to promote formation of the sp^2 carbon phases considerably, similar to nitrogen introduced into diamond which induced graphitization of carbon films [9].

Fig. 3 shows SEM images of diamond films grown under different conditions (a) undoped, (b) S-doped, (c) B/S-co-doped. As indicated in Fig. 3a, in the undoped condition the crystals form triangular and rectangular facets. With increasing S incorporation into the films, most of the triangular and rectangular facets disappear (Fig. 3b). And finally the diamond grains change into similar roundish-shaped ones while the surface becomes relatively smoother (Fig. 3c). These findings are consistent with the results that have shown boron improves the crystalline quality of diamond surface [10]. Fig. 3d shows an SEM photo of the film cross-section. The order of the film from top to bottom in Fig. 3d is faceted surface, deposited layer and substrate. The film thickness measured by SEM is about 2.5 μm.

Fig. 4 shows the temperature dependences of the resistivity of sulfur-doped CVD diamond films in the temperature ranges of 300–600 K. As shown in Fig. 4, the liner relationship between log (R) and the inverse temperature, which indicates that the conductivity of the films is thermally activated. The activation energies of conductivity are from 0.39 to 0.52 eV depending on the amount of sulfur in the diamond. For the lone sulfur-doped CVD diamond films, the activation energy of conductivity is determined to be 0.52 eV. But for the B/S



(a) (b)

(c) (d)

Figure 3 SEM image of diamond films: (a) undoped, (b) S-doped, (c) B/S-codoped, and (d) cross-section of films.

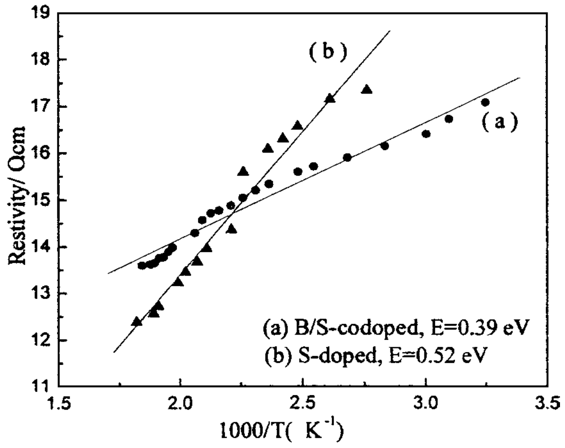


Figure 4 Resistivity curve of diamond films: (a) B/S-codoped and (b) S-doped, as functions of inverse temperature.

co-doped CVD diamond films, the activation energy is decreased to 0.39 eV. This indicates that the conductivity of films is increased with increasing S incorporation into diamond. Unfortunately, Seebeck effect measurements proved unsuccessful due to the high resistivity of the films, so the semiconductor properties of these films remain unclear. It was possible that the enhanced defect density in these polycrystalline film [11], upon sulfur addition to the CVD process, could act as compensating acceptors, soaking up the donated electrons from the S atoms. A theoretical calculation shows that the majority of S atoms should be electrically inactivated in the diamond [12]. Also S atoms may segregate on grain boundaries, as experimentally observed in nitrogen doped diamond. Therefore, the observed small decrease in resistivity may simply reflect the increasing number of grain boundaries or sp^2 carbon content with increasing S incorporation.

In conclusion, the limited amounts of boron facilitate the incorporation of sulfur atoms into diamond. The amount of S atom incorporation into diamond is increased by 1.5 times due to adding limited additions of B atom. With increase of S-incorporation, the activation energy of conductivity decreases from 0.52 to 0.39 eV. The activated energy of 0.39 eV is estimated with S incorporation at levels of up to 0.15%. This study suggests that the existence of the CS bond is responsible for the incorporation of S into the diamond lattice of CVD grown films.

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