

Sulfur: A donor dopant for *n*-type diamond semiconductors

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Evidence for the donor nature of sulfur in diamond was obtained by introducing hydrogen sulfide into the microwave assisted plasma chemical vapor deposition process. The sulfur was successfully doped into homoepitaxial diamond (100) films, which exhibit *n*-type conduction by Hall-effect measurements in the temperature range of 250–550 K. The mobility of electrons at room temperature was $597 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The ionization energy of 0.38 eV was determined by measuring the carrier concentration as a function of temperature. [S0163-1829(99)50828-X]

The use of diamond for electric applications has attracted much attention in conjunction with the development of vapor phase synthesis of diamond films with unique properties. However, the difficulty of producing adequate *n*-type diamond has limited such application to only a few special cases.¹ And while many studies have attempted to synthesize *n*-type semiconducting diamond, to date, such attempts have resulted in *n*-type diamond of very poor quality. To our knowledge, this is the first report of the production of an *n*-type diamond semiconductor of reasonable quality.

It has been well established that boron atoms can be incorporated into diamond lattice to form an acceptor level, meaning that B-doped diamond functions as a *p*-type semiconductor.^{1–3} B-doped diamond homoepitaxial crystals grown by microwave assisted plasma chemical vapor deposition (MPCVD) show quite high carrier mobility of over $1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³ On the other hand, it is hard to obtain reasonably high quality *n*-type semiconducting diamond crystals. The doping of CVD diamond has been investigated by many researchers. From the analogy of donors in silicon, group V and VI elements in diamond are expected to be donor impurities. Nitrogen is a well-known impurity to make very deep levels with the activation energy of 1.7 eV.¹ The level is so deep that N-doped diamonds are good insulators at room temperature. Fujimori *et al.* indicated that doping with phosphorous produces *n*-type diamond films, but that the resistivity of the phosphorous-doped films is too high to be of practical use.⁴ Alexenko and Spitsyn reported *n*-type conduction for P-doped homoepitaxial diamond film.⁵ However, these authors did not characterize the conductivity properties of the film in terms of Hall effect or any other quantitative measurements. Koizumi *et al.* reported that P-doped CVD (111) films produced using PH_3 showed *n*-type conductivity by Hall-effect measurement.⁶ However, the mobility increased with increasing temperature, and the maximum mobility was only $23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These findings of temperature dependence and markedly low mobility indicate that the conduction may be due to the crystal imperfec-

tion. The crystal quality of the P-doped film was low as indicated by the diffused streaky reflection high-energy electron diffraction (RHEED) pattern. Saito *et al.* reported the development of P-doped CVD (111) films by using $\text{P}(\text{C}_2\text{H}_5)_3$ to show *n*-type conduction with a mobility value of $3.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁷ In contrast to the positive association observed by Koizumi *et al.*, Saito *et al.* found that the mobility decreased with temperature. Barber and Yarbrough reported that diamond can be grown by CVD in a sulfur-containing environment.⁸ Although sulfur is known to introduce deep donor levels in silicon^{9,10} and germanium,¹¹ no study has been made of the S doping into diamond crystals.

In this study, homoepitaxial diamond films were deposited on high-pressure and high-temperature synthetic Ib diamond (100) crystals by microwave assisted plasma chemical vapor deposition (MPCVD). The growth conditions are summarized in Table I. We selected H_2S as a dopant because the addition of small amounts of H_2S into the MPCVD system is known to improve diamond crystal quality.¹² The grown diamonds were characterized by confocal micro-Raman spectroscopy, optical differential interference contrast micrography (ODICM), scanning electron micrography (SEM), and reflection high-energy electron diffraction. For the electric measurements, the grown S-doped diamond was treated in a

TABLE I. Growth conditions of the S-doped diamond homoepitaxy.

Gas source	$\text{CH}_4/\text{H}_2\text{S}/\text{H}_2$
CH_4 concentration	1.0%
H_2S concentration	10–100 ppm
(S/C ratio)	1000–10 000 ppm
Total gas flow rate	200 ml min^{-1}
Total pressure	40 Torr
Microwave	2.45 GHz, 300–400 W
Substrate temperature	$830 \text{ }^\circ\text{C}$ measured by optical pyrometer
Substrate diamond	HP-HT Ib diamond (100)

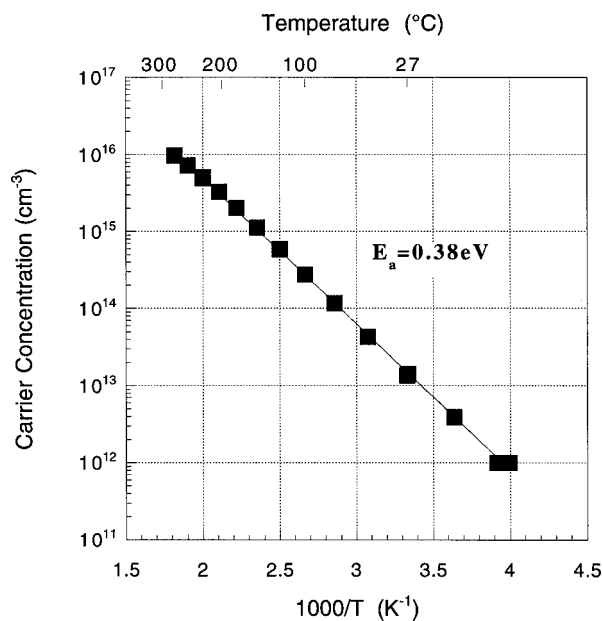


FIG. 1. Carrier concentration of the S-doped homoepitaxial diamond (100) film as a function of reciprocal temperature.

heated mixture of H_2SO_4 and HNO_3 (5:1) to oxidize and remove the surface conductive layer. Ohmic contacts were fabricated on the oxidized diamond surface by evaporation of Ti and Au. Hall-effect measurements were performed with the van der Pauw method in the temperature range of 250–550 K.¹³ Finally, sulfur incorporation was analyzed by particle induced x-ray emission spectroscopy (PIXES) and secondary-ion-mass spectrometry (SIMS). After SIMS measurements, the depth of the craters was measured to determine the film thickness using a Dektak 3030 surface profilometer.

All the S-doped samples showed the negative Hall coefficients, which confirmed that their conduction was of n type. Figure 1 shows the temperature dependence of the carrier concentration of the S-doped film deposited under the condition of 50 ppm H_2S . The carrier concentration increased with increasing temperature from 10^{12} to 10^{16} cm^{-3} . The carrier concentration changes exponentially with the reciprocal temperature. The conductivity of the film was $1.3 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature. The activation energy was estimated to be 0.38 eV from the inclination of the temperature dependence plots.

Figure 2 shows the temperature dependence of the Hall mobility of the sample with 50 ppm H_2S . The carrier concentration depended on the H_2S concentration. But the mobility varied independent from the doping level. The mobility value was maximum at the condition of 50 ppm in this study. This may be due to the difference of the crystal quality grown in the H_2S range of 10–100 ppm. A low H_2S addition increased the crystal quality below 50–60 ppm. In contrast, much higher H_2S addition than 60 ppm decreased the crystal quality.¹² The Hall mobility of the S-doped film with 50 ppm H_2S was $597 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a carrier concentration of $1.4 \times 10^{13} \text{ cm}^{-3}$ at room temperature. Above room temperature, the Hall mobility decreased with increasing temperature approximately with the relationship of $T^{-1.5}$. The mobility of the electrons in type-IIa diamond with nitrogen was esti-

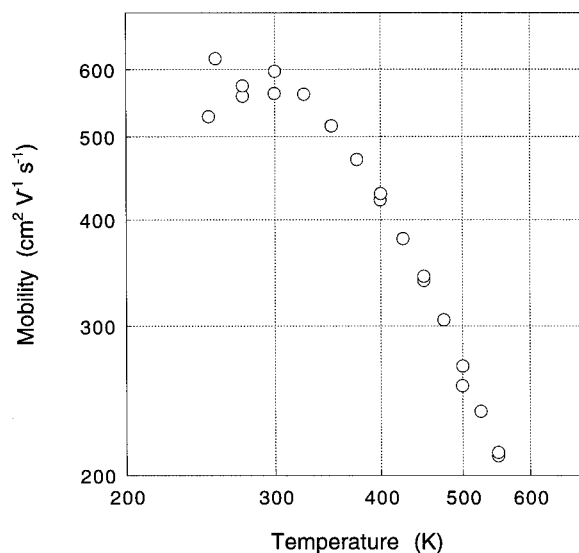


FIG. 2. Hall mobility of the S-doped homoepitaxial diamond (100) film over the temperature range from 250 to 550 K.

ated to be approximately $2000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The observed Hall mobility value of $597 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was reasonably good in comparison with the previously reported results. Koizumi *et al.* reported that P-doped diamond film shows n -type conduction; however, the Hall mobility was a very low $\sim 5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature and then increased with increasing temperature to reach a maximum value of $23 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at around 500 K, the highest temperature used in their study.⁶ In contrast, Saito *et al.* reported n -type conduction with reverse temperature dependence.⁷ However, the dependence was nearly flat and the Hall mobility of their films was also very low ($3.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). They suggested that the very low value of the mobility of the P-doped films should be attributed to scattering by a large amount of unionized P atoms and crystal defects.¹⁴ P-doped diamond tends to have a nondiamond structure¹⁵ and much hydrogen incorporation. Saito *et al.* also reported that the P-doped (111) diamond films contained more defects and more hydrogen than undoped (111) diamond films. Generally, a positive relationship between the Hall mobility and temperature is due to crystal defects scattering, and a negative relation is due to lattice phonon scattering. Recently, Zhu, Kochanski, and Jin suggested that the Fermi level near the conduction band, meaning n -type conduction, can be accomplished by introducing defects into the diamond.¹⁶

In the present study, Raman spectroscopy, ODICM, SEM, and RHEED observation confirmed the S-doped diamond crystal quality. In the confocal Raman spectrum of the S-doped (100) diamond with 50 ppm H_2S , there was a very sharp peak at 1333 cm^{-1} with a very narrow full width at half maximum (FWHM) of 2.6 cm^{-1} , just as in the spectrometer resolution, and also very low background. The FWHM at the sample grown with 100 ppm H_2S was wider than that with 50 ppm H_2S because the sulfur incorporation may cause stresses of the crystal lattice. ODICM and SEM showed almost no features indicative of a flat, uniform surface. Figure 3 shows the SEM picture and RHEED pattern. The SEM picture reveals that the S-doped grown surface was very smooth and had no pits and very little secondary nucleation. A very clear Kikuchi pattern was observed with high

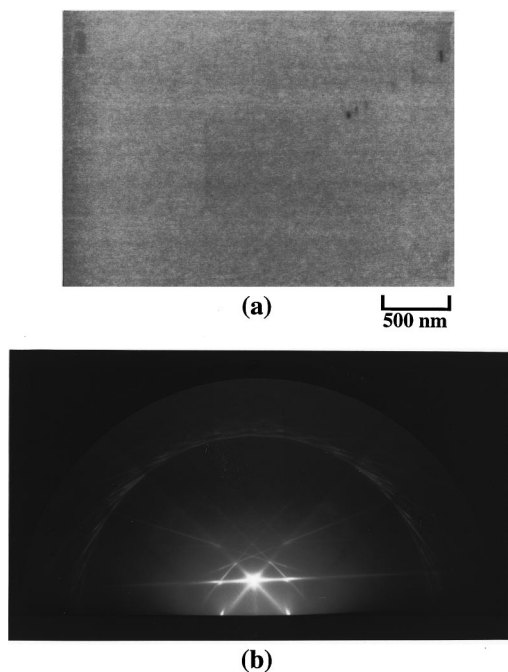


FIG. 3. (a) SEM image of the S-doped (100) homoepitaxial diamond (100) surface. (b) RHEED pattern in the [010] direction of the S-doped homoepitaxial diamond (100) surface. The incident electron beam energy is 30 keV with an angle of approximately 2° .

contrast in the RHEED. In the case of P-doped diamond, no clear Kikuchi pattern has been reported. These findings confirm that the crystal quality of the S-doped film was very high in contrast with that of the P-doped diamond.

Figure 4 indicates the depth profile of ^1H , ^{32}S , and ^{13}C . In order to distinguish ^{32}S from $^{16}\text{O}_2$, high-resolution measurement was conducted. The depth profile reveals that sulfur intensity was constant in the CVD grown layer and larger than that of the substrate. The sulfur concentration was estimated to be a very low 10^{16} – 10^{17} cm^{-3} , although sulfur was uniformly incorporated and no hydrogen was incorporated in the grown layer. The carrier concentration did not reach the saturation level at 300°C . The carrier concentration reached near the concentration of S incorporation 10^{16} – 10^{17} cm^{-3} at 300°C , indicating that the electrical doping efficiency seems very good. The growth rate was calculated to be $0.26 \mu\text{m h}^{-1}$

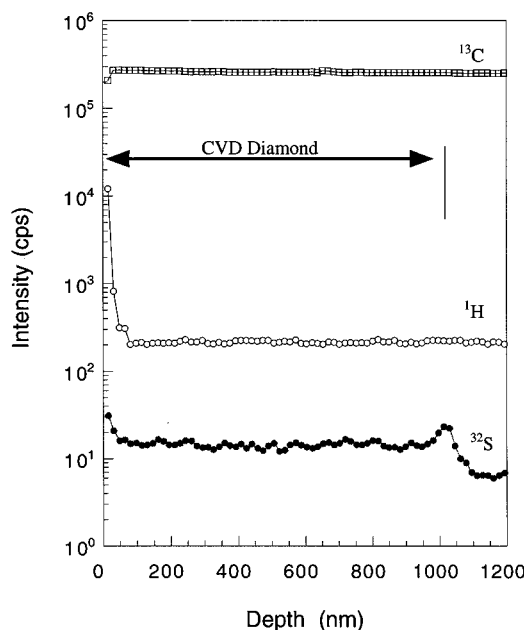


FIG. 4. Depth profiles of impurities in the S-doped homoepitaxial diamond (100) film by SIMS analysis. $^{133}\text{Cs}^+$ with ion energy of 14.5 keV and ion current of 50 nA was used as the primary ion. A modified cooling system was used to reduce the background.

under this condition. PIXES was also conducted for the sulfur analysis of the thick S-doped film of $20 \mu\text{m}$ by use of 2.5 MeV He ion. He-ion-induced x-ray emission was observed at 2.3 keV, suggesting that sulfur was incorporated in the crystal.

In summary, an *n*-type diamond semiconductor was produced from an S-doped homoepitaxial (100) diamond grown by MPCVD using H_2S as a dopant. Hall-effect measurements indicated *n*-type conduction with a mobility value of $597 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. The carrier concentration of the S-doped diamond was $1.4 \times 10^{13} \text{ cm}^{-3}$, and the conductivity was $1.3 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$. The donor level introduced by sulfur was at 0.38 eV below the conduction band.

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