

# EPR study of hydrogen-related defects in boron-doped p-type CVD homoepitaxial diamond films

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## Abstract

Boron-doped p-type single crystalline chemical vapor deposition (CVD) homoepitaxial diamond films were investigated by electron paramagnetic resonance (EPR). Carbon dangling bond defects, which were accompanied by a nearby hydrogen atom, were observed in boron-doped p-type CVD diamond films on a IIA substrate similar to those observed in undoped diamond. This result suggested that the energy level position of the defects is located below the Fermi energy of boron-doped diamond, at around 0.3 eV above the valence-band top. The reason why the Fermi energy could be changed by the incorporation of boron atoms at low density ( $10^{16}$ – $10^{17}/\text{cm}^3$ ) in the film in spite of the existence of the large defect density of EPR centers ( $\sim 10^{18}/\text{cm}^3$ ) is thought to be that the singly occupied electron states of defects are located near the band edge. As for the thermal annealing effect of the defects, it was revealed that the concentration of the defects and the mobility of the p-type film did not change after annealing up to 1200 °C which is much higher than the temperature of boron–hydrogen pair dissociation.

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## 1. Introduction

Diamond has a high potential for optical devices and electronic devices due to its attractive physical and electrical properties [1,2]. As for p-type diamond, high quality single crystalline chemical vapor deposition (CVD) homoepitaxial diamond films have been synthesized [3,4]. Measurements of the Hall effect show that the quality is better than or comparable with that of high-quality natural diamond [3].

In semiconductors, it is well known that both electrical and optical properties are extensively influenced by defects and hydrogen atoms. Therefore, it is important to elucidate their role in diamond for both scientific and practical

reasons. Recently, we observed carbon dangling bond defects accompanying a nearby hydrogen atom in undoped single crystalline CVD homoepitaxial diamond films grown on high-pressure and high-temperature (HPHT) IIA substrates by means of electron paramagnetic resonance (EPR) [5]. It has been reported that defects with a concentration of  $\sim 5 \times 10^{18}/\text{cm}^3$  originate from bulk defects, and not from surface defects or defects localized in nonepitaxial crystallites (NC) [5]. When such a large amount of defects exists in the gap state of semiconductors, it is usually difficult to control the Fermi energy. On the other hand, the Fermi energy of CVD diamond can be changed by incorporating boron atoms at low concentration ranging from  $10^{16}$  to  $10^{17}/\text{cm}^3$  [3,4,6]. These two experimental results seem to be inconsistent. To resolve this contradiction, in this study we investigated the boron doping effect on EPR signals and discussed the position in the gap states of EPR centers. The effect of thermal annealing on the concentration of

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defects and the mobility of the boron-doped film are also reported.

## 2. Experiment

The diamond films used in this study were deposited epitaxially on HPHT IIa diamond (001) substrates ( $2.5 \times 2.5 \times 0.5$  mm). The films were grown in a microwave plasma-enhanced CVD reactor using 0.3%  $\text{CH}_4$  diluted with  $\text{H}_2$ . Doping with boron was carried out by trimethylboron [ $\text{B}(\text{CH}_3)_3$ , TMB] which was also diluted with  $\text{H}_2$ . The TMB/ $\text{CH}_4$  ratio in the source gas was 50 ppm. The gas pressure, total gas flow rate and microwave power were 25 Torr, 400 sccm and 750 W, respectively. The substrate temperature was maintained at 800 °C. The deposition duration was 6 h and the resulting film thickness was approximately 2  $\mu\text{m}$ .

For the electric measurements, in order to remove the high-conductivity layer near the surface, the films were oxidized by an acid mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  at 200 °C for 30 min [7]. Ohmic contacts were fabricated on the oxidized diamond films by evaporating Ti followed by Au/Pt to prevent oxidation of Ti electrodes.

EPR spectra were measured on a Bruker ELEXSYS X-band spectrometer. The microwave frequency was 9.45 GHz. The microwave power and the amplitude of 100 kHz field modulation were 2 mW and 0.05 mT, respectively. The measurement temperature was controlled by using an ESR-900 (Oxford Instruments).

To study the thermal stability, the samples were annealed for 30 min at temperatures between 400 and 1200 °C. The furnace (ULVAC, MR39H/D) was evacuated down to  $1 \times 10^{-6}$  Torr with a turbo molecular pump. The samples were cleaned after annealing in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  solution at 200 °C for 30 min.

## 3. Results and discussion

### 3.1. Observation of EPR spectrum in boron-doped p-type CVD diamond films

The EPR spectrum of the boron-doped p-type films is shown in Fig. 1(a). The  $g$ -value was estimated to be  $2.0026 \pm 0.0001$  which agrees with the  $g$ -value of the carbon dangling bond defects accompanying a nearby hydrogen atom observed in undoped films [5]. No anisotropy of the line shape could be observed. It was confirmed that this signal is not observed in HPHT IIa substrate. The concentration was estimated to be  $\sim 7 \times 10^{18}/\text{cm}^3$  which is similar to the amount of defects in the undoped films observed previously.

The EPR spectrum of the hydrogen related defects observed in undoped CVD diamond films and polycrystalline diamond is well simulated by the sum of the randomly

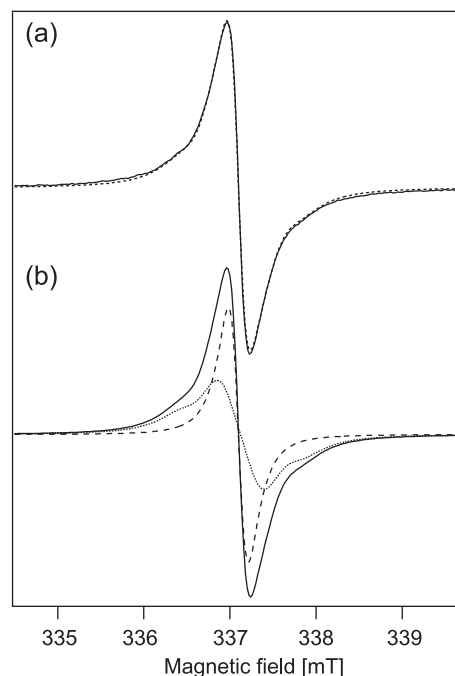


Fig. 1. The EPR spectrum at 150 K and the simulated spectrum of boron doped p-type CVD diamond films. (a) The solid line and the dotted line are the observed spectrum and simulated spectrum, respectively. (b) The dotted line and the dashed line are the randomly oriented spectrum of the H1 center and the additional Lorentzian line, respectively. The solid line is the sum of all lines.

oriented spectrum of the H1 center and additional Lorentzian line [5,8]. In the study of polycrystalline diamond, it is proposed that the H1 center is hydrogen-vacancy complex [8–10]. From its  $g$ -value, the additional Lorentzian line is suggested to be a carbon dangling bond defect. In the study of polycrystalline diamond, the possibility of an H2 center which is also a carbon dangling bond defect accompanying a hydrogen atom with a different distance between a carbon dangling bond and a hydrogen atom was pointed out [8,9]. The simulation spectrum in the boron-doped film is shown in Fig. 1(b). The resonance fields were calculated by first-order perturbation treatment with the effective Hamiltonian:

$$H = \beta_e \tilde{\mathbf{S}} \mathbf{g} \mathbf{B} + \tilde{\mathbf{S}} \mathbf{A} \mathbf{I}_i - g_n \beta_n \mathbf{I}_i \mathbf{B}, \quad (1)$$

where  $\mathbf{g}$  and  $\mathbf{A}$  denote the  $g$ -matrix and the hyperfine matrix, respectively. Other symbols have usual meanings. The details of the calculation of transition probabilities of the allowed and the forbidden transitions were described in a previous study [9] and a text book [11]. The reported hyperfine parameters ( $A_{\parallel} = 27.5$  MHz,  $A_{\perp} = -5.5$  MHz) of the H1 center were used for the randomly oriented spectrum with a Lorentzian line shape with half width at half maximum (HWHM) of 0.3 mT. The HWHM of the additional Lorentzian line is 0.2 mT. As shown in Fig. 1, the spectrum in the boron-doped film is well simulated by

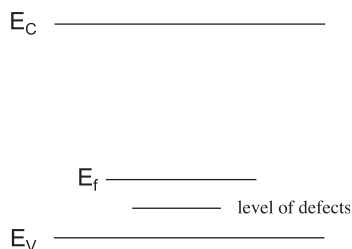


Fig. 2. Energy level scheme for the defects in boron doped diamond.  $E_C$ ,  $E_V$ , and  $E_f$  are the energy level positions of the conduction band minimum, valence band maximum and Fermi level, respectively.

the randomly oriented spectrum of the H1 center and the additional Lorentzian line. This indicates that the observed defects are the same as the defects observed previously in undoped CVD diamond films. The integrated intensity of the randomly oriented spectrum was about twice as large as that of the additional Lorentzian.

As pointed out in the previous study of undoped films [5], the absence of anisotropy of the line shape could not be reproduced from the simulation by using the EPR parameters of the H1 center, unless the orientation is disordered and/or the hyperfine parameters have a wide distribution due to site-to-site variations of the structure. Thus, the structure of the defects in homoepitaxial CVD diamond film might be different from that described by the reported EPR parameters of the H1 center in polycrystalline diamond.

### 3.2. Energy level of defects in the band gap

The Hall mobility of the boron-doped p-type CVD diamond film at room temperature was measured to be  $790 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with carrier concentration of  $4.2 \times 10^{14} / \text{cm}^3$ . In this boron-doped diamond film, it can be calculated that the Fermi energy is located at around 0.3 eV above the valence-band top. The concentration of boron atoms in this study is considered to be much smaller than that of carbon dangling bond defects ( $\sim 7 \times 10^{18} / \text{cm}^3$ ). This is because the concentration of boron atoms is estimated to range from  $10^{16}$  to  $10^{17} / \text{cm}^3$  by secondary ion mass spectroscopy (SIMS) in the boron-doped film synthesized in our laboratory under almost the same conditions [3,6].

In the study of undoped films, it was revealed that the defects were distributed uniformly in the depth direction. It is reasonable to consider that the defects in boron-doped p-type film are also distributed uniformly in the depth direction, because the EPR spectra and EPR center concentrations in undoped and boron-doped films are similar. In this situation the energetic position of EPR centers can be discussed within the framework of a simple semiconductor band structure. Because EPR can be detected for localized unpaired spins, the EPR centers of the carbon dangling bond defects observed in this study should be of a singly occupied electron state and located

below the Fermi energy. In this study, the EPR centers were observed both in undoped and boron-doped diamond in the same manner. Therefore, it is pointed out that the energy position of unpaired spins is located below the Fermi energy of boron-doped diamond, at around 0.3 eV above the valence-band top as shown in Fig. 2. It is considered that the reason why the Fermi energy could be changed by incorporating boron atoms at low density ( $10^{16}$ – $10^{17} / \text{cm}^3$ ) in the film in spite of the existence of the large defect density of EPR centers ( $\sim 10^{18} / \text{cm}^3$ ) is that the singly occupied electron states of defects are located near the band edge. By the same logic, it is also suggested that the doubly occupied electron states of the spin centers are above the Fermi energy of undoped films. The energy position difference between singly occupied and doubly occupied electron states is caused by the Coulomb repulsion between electrons in the defects.

### 3.3. Effect of thermal annealing on the concentration of defects and mobility of the boron-doped film

The effect of thermal annealing on the concentration of the defects was investigated. Both the signal intensity and the line shape of the EPR spectrum did not change after annealing up to  $1200^\circ \text{C}$  as shown in Fig. 3. This result agrees with the previous work in undoped films [5]. In boron-doped diamond, passivation of boron acceptors by hydrogen atoms through the formation of a hydrogen–boron pair has been reported [12,13]. From SIMS and infrared (IR) studies, it was shown that the hydrogen–boron pair dissociates at  $700^\circ \text{C}$  [14]. The present results indicate that the carbon dangling bond defects accompanying hydrogen atoms are much more stable than the hydrogen–boron pairs. High-temperature thermal stability of the EPR center observed in this study was also confirmed by the stable Hall mobility up to  $1200^\circ \text{C}$ .

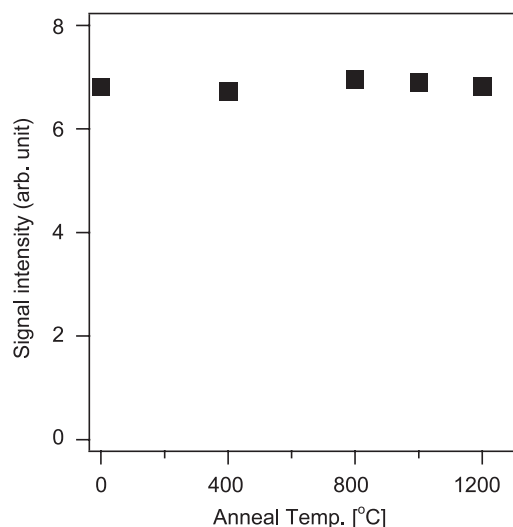


Fig. 3. Annealing temperature dependence of the signal intensity of the defects.

#### 4. Conclusion

The EPR signal at  $g=2.0026\pm0.0001$  was observed in boron-doped p-type single crystalline CVD homoepitaxial diamond films. This resonance was assigned to carbon dangling bond defects accompanying hydrogen atoms. From the analysis of the spectrum, the defects are the same as the defects distributed uniformly in the depth direction in undoped diamond films. The singly occupied electron state of defects is thus located below the Fermi energy in the boron-doped p-type diamond films. It is concluded that the reason why the Fermi energy could be changed by incorporating boron atoms in the film in spite of the large amount of defects is due to the shallow singly occupied electron state of defects. The annealing measurements revealed that the concentration of the defects and the mobility of the p-type film did not change after annealing up to 1200 °C which is much higher than the temperature of boron–hydrogen pair dissociation.

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