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Electron spin resonance characterization of phosphorus-doped CVD diamond films

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Electron spin resonance technique has been applied to characterize defects and to determine local structure of phosphorus in phosphorus-doped (111)-homoepitaxially grown CVD diamond films. Dominant defects have *g*-value similar to that of the H1 center in polycrystalline CVD diamond, however, are not accompanied with a unique nearby hydrogen atom. These defects are likely to be located near substrate/epilayer interface. New phosphorus related center with a tetragonal symmetry has been found.

1 Introduction

Establishment of n-type doping technique is essential for the realization of diamond-based electronic devices. Phosphorus is a promising candidate for n-type dopant of diamond. We have successfully synthesized phosphorus-doped diamond films by microwave plasma-assisted chemical vapor deposition (CVD) using PH_3 as a dopant source [1, 2]. The results of Hall-effect measurements indicated n-type conduction of phosphorus-doped films with an activation energy of 0.6 eV. Cathodoluminescence spectroscopy [3], photoconductivity measurements [4] and infrared absorption spectroscopy [5] supported the phosphorus donor level which is located at 0.6 eV below the bottom of the conduction band ($E_c - 0.6$ eV). These results demonstrated that phosphorus does act as a donor in diamond.

Theoretically predicted donor level of substitutional phosphorus is $E_c - 0.2$ eV both by using the *ab initio* method [6] and by the effective mass approximation [5] and $E_c - 0.37$ eV by first-principle calculation [7]. The donor levels obtained experimentally are considerably deeper than the calculated ones. A possible reason may be attributed to a lattice relaxation around the phosphorus atom. It is important to elucidate the local structure of phosphorus donors in diamond for an understanding of the n-type conductivity.

Electron spin resonance (ESR) method is a powerful technique to identify impurities and point defects by supplying detailed microscopic information of structure and electronic wavefunction. In ESR, phosphorus-related centers are expected to exhibit hyperfine interaction of ^{31}P nucleus ($I = 1/2$, natural abundance 100%). Several phosphorus-related ESR centers have been reported in synthetic diamond powders [8], implanted diamond films during CVD process [9], high-pressure and high-temperature synthetic diamond from phosphorus catalyst [10], implanted IIa diamond [11], and homoepitaxial diamond films

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[12]. However, none of these phosphorus-related spectra have been established to be arising indeed from the unpaired electrons bound to shallow phosphorus donors.

In polycrystalline CVD diamond, the ESR spectrum labeled H1 (g = 2.0028) which accompanies a pair of partially resolved satellites of hydrogen nuclear spin-flip transitions (the spacing of 1.25 mT at the microwave frequency of 9.6 GHz) is commonly observed with a typical concentration of ~1×10^{18} cm^{-3} [13–15]. The hydrogen hyperfine interaction with the isotropic part $a_{\text{iso}} = -5.5$ MHz (–0.20 mT) and the anisotropic part b = 11.0 MHz (0.39 mT) was determined from simulating the microwave frequency dependence of the lineshape including the intensity ratio between the satellites and the primary line and the satellite separation [14, 15]. The H1 center was attributed to a carbon dangling bond accompanied with a hydrogen atom ~0.2 nm away.

Doping requires incorporation of phosphorus atoms at a desired site in the lattice without accompanying a defect such as a lattice vacancy and/or other impurity such as hydrogen. The improvement of both the mobility and the doping efficiency requires lowering the concentration of unwanted defects. In this work, we have applied ESR technique to characterize defects and to search phosphorus related centers in phosphorus-doped (111)-homoepitaxial CVD diamond films.

2 Experimental

Phosphorus-doped diamond thin films were grown epitaxially on both surfaces of synthetic type IIa diamond (111) substrate with dimensions of $2 \times 2 \times 0.5$ mm^3 by microwave plasma-assisted CVD. The source gas was 0.05% CH_4 diluted with H_2. Doping with phosphorus was carried out by adding PH_3 in the source gas. The PH_3/CH_4 ratio in the source gas was 100 ppm. The gas pressure, the total gas flow rate, the substrate temperature, and the growth duration were 100 Torr, 1000 sccm, 900 °C, and 20 h, respectively. The phosphorus concentration and the resultant film thickness were estimated to be 2×10^{18} cm^{-3} and 10 µm, respectively. After the growth, the phosphorus-doped diamond films were chemically treated in a solution of $NaClO_3$ in HNO_3 at 200 °C for 3 h to remove contaminations.

Conventional ESR measurements were performed with a Bruker E500 *X*-band spectrometer by varying the temperature between 10 K and room temperature using an Oxford Instruments ESR-900 cryostat. Pulsed ESR and pulsed ENDOR measurements were carried out using a Bruker Elexsys E580 spectrometer and an Oxford ER4118CF cryostat. Temperature was controlled with an Oxford ITC503. The number of spins was estimated by comparing the signal intensity obtained by double integration of the first derivative signal with that of the ESR signal of Cr^{3+} in ruby comounted with the sample. The g-value was determined by using the signal of the single substitutional nitrogen ($S = 1/2$, $I = 1$, $g = 2.0024$) as internal standard.

3 Results and discussion

3.1 ESR signals of defects

In the ESR spectrum of the phosphorus-doped (111)-homoepitaxial CVD diamond film taken with the external magnetic field along the [100] axis ($\boldsymbol{B}_0$//[100]) at 80 K, a signal from defects has been observed (Fig. 1). From the number of spins determined from the signal intensity, the concentration is estimated to be ~1×10^{17} cm^{-3} if a uniform distribution is assumed. Both the g-value ($g = 2.0027 \pm 0.0001$) and the line width (ΔB_{pp} = 0.23 mT) is similar to those ($g = 2.0028 \pm 0.0001$, ΔB_{pp} = ~0.3 mT) of the H1 center ($S = 1/2$) in polycrystalline CVD diamond. The g-value did not depend on the orientation.

If the H1 center as a well-defined defect is formed in the bulk of the homoepitaxial film, the anisotropy of the hyperfine interaction ($A_{//}$ = 0.98 mT, $A_{\perp}$ = –0.20 mT) of the unique hydrogen neighbor 0.2 nm away from the unpaired electron should give a splitting of lines or at least should exhibit an angular dependence of the linewidth, the satellites intensity, and the satellite separation, unless obscured by a large residual linewidth. The anisotropy depends on the symmetry of H1which determines the number of orientations in the crystal lattice. The residual linewidth at a magnetic field orientation denotes the linewidth that each of the unique hydrogen hyperfine components of each symmetry-related site should

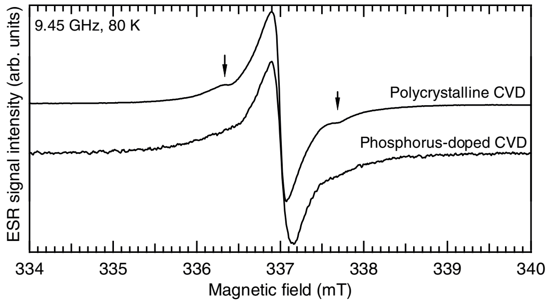

Fig. 1 ESR spectrum of phosphorus-doped homoepitaxial CVD diamond film ($\boldsymbol{B}_0$//[100], 80 K). The spectrum of polycrystalline CVD diamond (supplied by Kobe Steel) taken at room temperature is included. The arrows indicate the line positions of the hydrogen spin-flip satellites of the H1 center.

have. In monocrystalline CVD films grown on Iridium substrates, ^{1}H hyperfine parameters ($A_{//} = 0.52$ mT, $A_\perp = -0.26$ mT) were obtained from the anisotropy of the linewidth and the satellite intensity [16]. The linewidth ΔB_{pp} (0.46 mT and 0.60 mT for $\boldsymbol{B}_0$//[100] and $\boldsymbol{B}_0$//[111], respectively) is significantly larger than that of our sample. In Fig. 2, the ESR spectra of three orientations, $\boldsymbol{B}_0$//[100], $\boldsymbol{B}_0$//[111] and $\boldsymbol{B}_0$//[011] are shown for room temperature and 60 K, respectively. For both temperatures, only a slight change in the lineshape among different orientations is noticed mostly in the low field side of the signal. This anisotropy is different from one expected for the case of the H1 center which has an isotropic g-tensor and the anisotropy of the ^{1}H hyperfine interaction significantly larger than the linewidth of our sample. Thus, the ESR spectrum observed is unlikely to be arising from the H1 center well-oriented in the bulk lattice of the epitaxially grown monocrystalline film.

In the phosphorus-doped CVD homoepitaxial diamond film shown in Fig. 1, the nuclear spin-flip satellites which are the characteristic features of the H1 center are not distinctly observed. Since the formally forbidden nuclear spin-flip transitions ($\Delta M_S = \pm 1$, $\Delta m_I = \pm 1$) are less easily saturated to the microwave power, it is expected that the satellites should be easily noticeable at a microwave power where the increase of the peak height of the primary line with the increase of the microwave power is flattened. With the increase of the microwave power from 0.2 mW to 5 mW, the peak height of the signal increased by 1.5 times comparing to 5.0 times expected for the case of no power saturation (Fig. 3). At 5 mW, a broadening with a significant increase of the signal height was observed in the whole region of the wing-part while satellite peaks did not become apparent. Thus, the ESR spectrum observed is likely to be arising neither from the H1 center oriented in the bulk lattice nor from that randomly-oriented in some disordered region(s).

The H1 center is proposed to be a pair of an unpaired electron in carbon dangling bond and C–H as a relaxed structure of a hydrogen atom in a stretched C–C bond [14]. The defect observed in our phosphorus doped homoepitaxial diamond film is likely to be an unpaired electron in carbon dangling bond, however, without being accompanied by a hydrogen atom at unique close distance. In polycrystalline CVD diamond, in addition to H1, the presence of other ESR signal of $g = 2.0028$, for which it could not be determined whether the hydrogen spin-flip satellites was accompanied or not, was reported [15]. We could not determine whether the center coexisting with H1 in polycrystaline CVD diamond is the same as the defects in the phosphorus-doped CVD homoepitaxial diamond film or not.

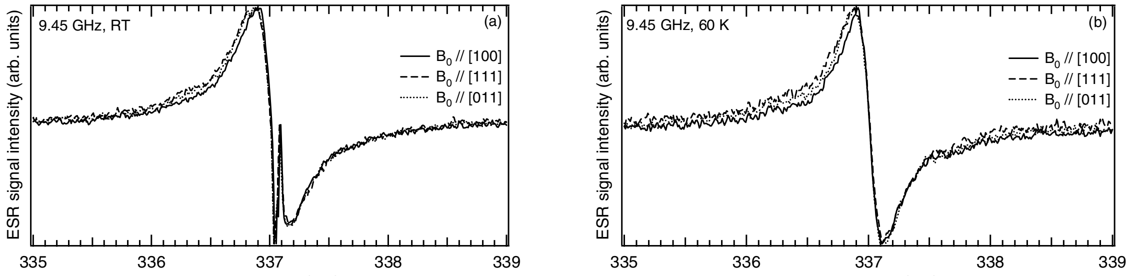

Fig. 2 Orientation dependence of the lineshape of the ESR spectra arising from defects. (a) Room temperature, (b) 60 K. The scale of the signal intensity is adjusted so that the peak heights taken at three different orientations agree.

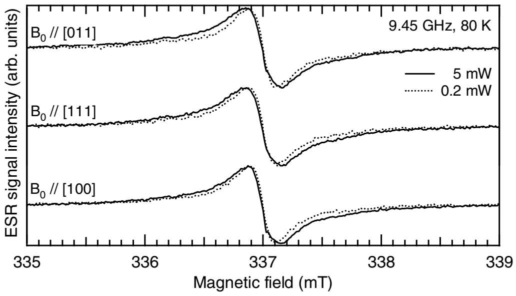

Fig. 3 Microwave power dependence of the lineshape of the ESR spectra arising from defects (80 K). The signal intensity of the spectra taken at 5 mW is scaled down so that the peak heights taken at two different powers agree.

The linewidth (ΔB_{pp} = 0.23 mT) of the signal observed in our phosphorus doped homoepitaxial diamond film is extraordinarily large compared to those of EPR spectra of typical defects in bulk diamond crystals. In the H1 spectrum, the broadening is determined not by the distribution of the g-value, since the linewidth does not depend on the microwave frequency, but dominantly by the anisotropy of the ^{1}H hyperfine interaction of the unique nearby hydrogen. In polycrystalline sample of random orientation, the linewidth is mostly determined by $A_\perp$ of the unique hydrogen and the residual linewidth to which hyperfine interactions with hydrogen in the environment (matrix nuclei) do contribute. In our sample, the defects are unlikely to be accompanied by a hydrogen atom at a distance as close as the unique hydrogen of the H1 center. The broadening is likely to be caused by site-to-site variation in the local fields, arising from hyperfine interaction with hydrogen in the environment and/or dipolar interaction among unpaired electrons. Since the hydrogen spin-flip satellites were not observed clearly, we have applied pulsed ENDOR technique to extract hyperfine interaction which might be hidden underneath the line broadening. In Fig. 4, the pulsed ENDOR spectrum taken at 8 K using the Mims sequence in which an RF pulse (duration 10 μs) was inserted between the second and the third pulses of 3-pulse stimulated echo (90°–τ–90°–t–90°–τ–echo) is shown. The observation of the ^{1}H ENDOR signal with the ENDOR frequency distributed around ^{1}H NMR frequency suggests that the unpaired electron is accompanied by hydrogen atom(s) which are located at various remote distances from the unpaired electron. Thus, the defects are formed in a region where the local hydrogen concentration is sufficiently high.

The line broadening due to dipole-dipole interactions among the unpaired electrons is estimated to be $\Delta B_{pp} = 1.1 \times 10^{-3}$ mT for the concentration of $\sim 1 \times 10^{17}$ cm^{-3}. Thus, if the defects are uniformly formed, the dipolar interaction does not contribute to the line broadening with the average concentration estimated from the number of spins and the volume of the film. If the creation of the defects is confined in certain region, the local concentration might be much higher than the average concentration. When an ESR signal is inhomogeneously broadened, consisting of many overlapping spin packets with different resonance fields, the linewidth of the spin packet is measured in time domain by the 2-pulse echo decay. The phase memory time measured by using a pulse sequence (90°–τ–90°–τ–echo, the duration of the 90 ° pulse of 32 ns) was 0.57 μs. The flipping angle of the second pulse was chosen to decrease an effect of instantaneous diffusion [17]. This relatively short phase memory time suggests a high local concentration in which fluctuation of dipolar fields due to electron spin flips and/or electron spin flip-flops might be a dominant source of the phase relaxation.

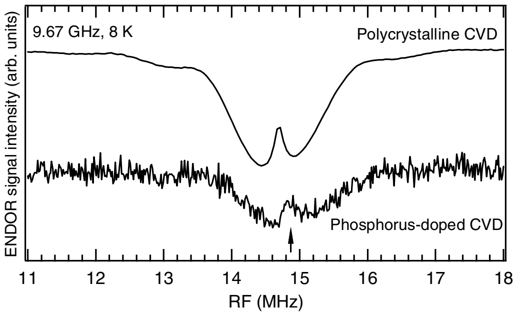

Fig. 4 Pulsed ENDOR spectrum of defects in phosphorus-doped homoepitaxial CVD diamond film ($\boldsymbol{B}_0$//[111], 8 K). The spectrum of polycrystalline CVD diamond (supplied by Kobe Steel) is included. The arrows indicate the frequency of ^{1}H NMR.

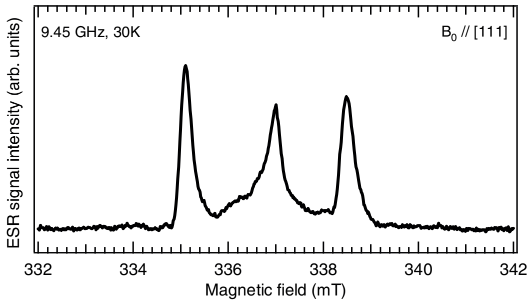

Fig. 5 ESR spectrum of phosphorus related centers in phosphorus-doped homoepitaxial CVD diamond film (***B***$_0$//[111], 30 K).

A secondary ion mass spectroscopy (SIMS) analysis of phosphorus-doped (111) homoepitaxial diamond films revealed that hydrogen is accumulated in the region near the substrate/epilayer interface and that the hydrogen concentration in the bulk is lower than phosphorus concentration by ~100 times [18]. In the phosphorus doping level of ~1×10^{18} cm^{-3}, the hydrogen concentration was below ~1×10^{17} cm^{-3} and above ~1×10^{18} cm^{-3} for the bulk and near the interface, respectively [18]. Since the defects are formed in a region where the concentration of hydrogen is relatively high and are formed with a high local concentration, it is likely that the defects are mostly formed in the region close to the substrate/epilayer interface. The H1 center in the polycrystalline CVD diamond is considered to be located at grain boundaries since the ^{1}H matrix ENDOR indicates that distant hydrogen atoms 0.2–1.0 nm away are accompanied in addition to the unique hydrogen neighbor and correlation between the H1 concentration and the total C–H stretch infrared absorption is observed [15]. In undoped (100)-homoepitaxial CVD diamond films, the ESR signal ($g = 2.0028$, $\Delta B_{pp} = 0.3$ mT) accompanying hydrogen spin-flip satellites were observed with the average concentration of ~1×10^{18} cm^{-3} [19]. The anisotropy in the linewidth, the satellites intensity, and the satellite separation was not detected. Since the average concentration increased with the film thickness, it is suggested that the defects are formed in the bulk. The distribution of defects and the local hydrogen concentration in the vicinity of the defects might be different between (100)- and (111)-homoepitaxial growth and/or between undoping and phosphorus-doping.

3.2 Phosphorus related signals

In Fig. 5, the ESR spectrum of ***B***$_0$//[111] at 30 K taken with the in-phase second harmonic detection is shown. In addition to the signal from the defects, a pair of lines is observed. The second harmonic detection with respect to the magnetic field modulation is convenient to attain a sufficient S/N for those signals which are easily saturated to the microwave power. The symmetry of defect is determined from the number of lines observed at a high symmetry directions and the number of distinguishable sites upon rotation. There are two magnetically distinguishable sites both in ***B***$_0$//[100] and in ***B***$_0$//[011], and one in ***B***$_0$//[111].Upon rotation of crystal around $[0\bar{1}1]$, each line of the pair splits into at most two lines. From the angular dependence of the line positions, it is confirmed that the two-line structure is hyperfine structure of ^{31}P and the symmetry of the phosphorus center is determined to be tetragonal. The concentration of the phosphorus center is estimated to be ~1×10^{17} cm^{-3} by using a spectrum taken with the normal in-phase detection. The ESR parameters obtained and the structure model will be presented elsewhere.

4 Conclusions

In the phosphorus-doped (111)–homoepitaxial CVD diamond film, an ESR signal from defects which are likely to be carbon dangling bonds similar to the H1 center in polycrystalline CVD diamond, however, without being accompanied by hydrogen atom at a unique close distance has been observed. The defects are likely to be formed preferentially in the region near epilayer/substrate interface, since the line broadening is ascribed to both unresolved hyperfine interactions of environmental hydrogen and dipole–

dipole interactions among the unpaired electrons. A new ESR spectrum exhibiting hyperfine interaction with a ^{31}P nucleus and having a tetragonal symmetry has been found.

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