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Hydrogen-related defects in single crystalline CVD homoepitaxial diamond film studied by EPR

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Abstract

Single crystalline chemical vapour deposition (CVD) homoepitaxial diamond films have been studied by means of electron paramagnetic resonance (EPR). Hydrogen-related defects similar to the H1 center which is accompanied by nearby hydrogen have been observed at $g=2.0028\pm0.0002$. From the thickness dependence of the signal intensity, it has been revealed that the hydrogen-related defects distribute uniformly along the depth direction in diamond films. From the non-epitaxial crystallites (NC) density dependence of the signal intensity, it has been indicated that the hydrogen-related defects do not originate from the NC. As for the thermal stability of the centers, the signal intensity does not change after annealing up to 1300 °C. These results are consistent with the hydrogen-related defects being distributed over the bulk of diamond film.

Keywords: Plasma CVD diamond film; Hydrogen; Defect; Electron paramagnetic resonance

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1. Introduction

It is well known that both electrical and optical properties of diamond are strongly influenced by hydrogen and related defects. Therefore, elucidation of the role of hydrogen in diamond is interest for both scientific and practical reasons. In electron paramagnetic resonance (EPR), the hydrogen-related defects labeled H1 and H2 were observed at $g=2.0028$ [1,2]. However, the location and distribution of them is still not clear. In polycrystalline chemical vapor deposition (CVD) diamond, it was suggested that those are located at grain boundary or other extended misfit regions rather than in bulk diamond [1,2]. To the contrary, in measurements of H1 centers in the crystalline CVD diamond deposited on Ir substrates, it was suggested that the H1 center exists in the bulk diamond [3]. In homoepitaxial diamond, secondary ion mass spectroscopy (SIMS) analysis suggested the incorporation of hydrogen in the subsurface region (approx. 20 nm from the surface) [4]. In (111) homoepitaxial phosphorus-doped diamond films grown by using CH_4/D_2 mixture, the accumulations of deuterium were detected at the substrate/epilayer interface [5].

In this paper, the first observation of an EPR spectrum originating from hydrogen-related defects similar to the H1 center which is considered to be a well defined defect with a unique hydrogen atom 0.19 nm away from the unpaired electron [1,2] in the single crystalline CVD homoepitaxial diamond film has been reported. Important information about the spatial distribution is obtained.

2. Experiment

The diamond films used in the study were deposited epitaxially on high-pressure and high-temperature (HPHT) synthetic IIa diamond (100) substrates with dimensions of 2.5 ×2.5×0.5 mm. Diamond films were grown by a step-flow mode in a microwave plasma-enhanced CVD reactor using 0.5% CH_4 diluted with H_2 [6]. The total gas pressure, total gas flow rate and input microwave power were maintained constant at 25 Torr, 400 sccm and 750 W, respectively. The substrate

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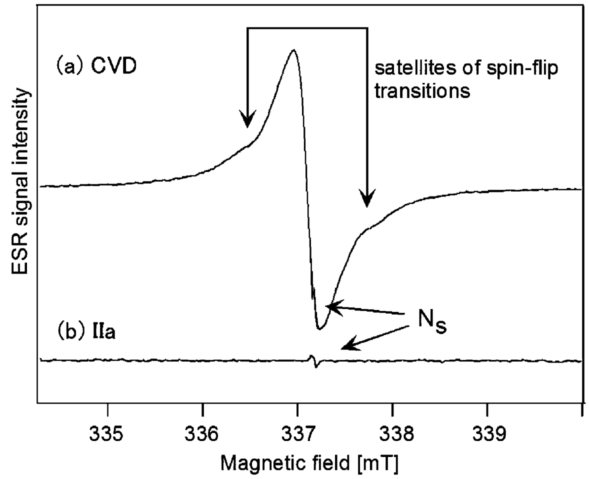

Fig. 1. The EPR spectra of (a) single crystalline CVD diamond film on IIa substrate and (b) only IIa substrate with the magnetic field along the [100] axis at room temperature. The microwave frequency is 9.45 GHz. The microwave power and the amplitude of 100 kHz field modulation were (a) 0.2 mW and 0.05 mT (b) 0.02 mW and 0.01 mT, respectively. N_S is the central hyperfine line of substitutional nitrogen ($I=1$). The assignment of the arrowed weak satellites is described in the text.

temperature was 800 °C, which was controlled independently of the input microwave power. The deposition durations of samples labeled I, II, III and V were 6 h resulting in the thicknesses of approximately 2 μm. The deposition durations of other samples labeled IV and VI were 36 h and 1 h resulting in the thicknesses of approximately 12 and 0.3 μm, respectively.

EPR spectra were measured on a Bruker ELEXSYS X-band spectrometer. EPR signal of Cr^{3+} in a single crystal of ruby was used as a reference of the spin concentration. The signal intensity was estimated by double integration of the first derivative signal.

To study the thermal stability, the samples were annealed for 30 min at temperatures between 400 and 1300 °C in vacuo. The furnace (ULVAC, MR39H/D) was evacuated down to 1×10^{-6} Torr with a turbo molecular pump. The samples were cleaned after annealing in H_2SO_4 and HNO_3 solution at 200 °C for 30 min.

3. Results and discussion

3.1. Observation of hydrogen-related defects

In Fig. 1a, the EPR spectrum of the single crystalline CVD homoepitaxial diamond film on a IIa substrate taken with a magnetic field along the [100] axis at room temperature is shown. For the comparison, the EPR spectrum of a IIa substrate taken with a magnetic field along the [100] axis at room temperature is shown in Fig. 1b. The small signal at the central part of the magnetic field in Fig. 1a and b is central hyperfine line of substitutional nitrogen (N_S, $S=1/2$, $I=1$).

In the CVD homoepitaxial diamond films, the EPR signals are observed at $g=2.0028\pm0.0002$ which agrees with the reported g-value of the hydrogen-related defects labeled H1 and H2 in polycrystalline CVD diamond [1,2]. The concentrations in different samples are listed in Table 1. As indicated in Fig. 1a, a pair of partly-resolved satellite lines are observed with the splitting (1.25 ± 0.15) mT similar to that of the X-band EPR spectrum of the H1 center [2]. The splitting is close to $2h\nu_n/g_e\beta_e$ (1.04 mT) where ν_n is the proton NMR frequency at the magnetic field strength used. The satellites were less easily saturated to the microwave power than the central line. The satellites, which arise from normally forbidden electron-nuclear spin flip ($\Delta M_S=\pm1$, $\Delta m_I=\pm1$) transitions due to dipole–dipole interaction between the unpaired electron and hydrogen, reveal that the unpaired electron is accompanied by nearby hydrogen. Thus, the observed EPR spectrum is arising from a type of hydrogen-related defects similar to the H1 center.

Upon the rotation of the crystal around $[01\bar{1}]$, no angular dependence of the lineshape (i.e. the linewidth of the central line, the intensity ratio between the satellite and the central line and the spacing of the satellites) of the EPR spectrum was detected. In polycrystalline samples, the hyperfine parameters of H1 were obtained from the microwave frequency dependence of the lineshape [1,2]. It is proposed that the H1 center is $[H-V]^0$ in which, among four carbon dangling bonds around the vacancy, one bonding to hydrogen and two bonding together leave one dangling bond where the unpaired

Table 1
Sample studied, with the estimated NC density, the thickness of epilayer, and the total spin concentration

Sample	NC density/cm^2	Thickness of epilayer/μm	Total spin concentration/cm^3
I	$(6.7\pm0.9)\times10^4$	2	$(6\pm3)\times10^{18}$
II	$(1.2\pm0.3)\times10^5$	2	$(5\pm3)\times10^{18}$
III	$(1.2\pm0.5)\times10^4$	2	$(5\pm3)\times10^{18}$
IV	$(1.1\pm0.2)\times10^5$	12	$(7\pm3)\times10^{18}$
V	$(7.4\pm0.7)\times10^4$	2	$(8\pm3)\times10^{18}$
VI	$(1.3\pm0.2)\times10^5$	0.33	$(7\pm3)\times10^{18}$

electron localizes [1]. While the H1 center in polycrystalline CVD diamond films is randomly oriented, a paramagnetic defect in the bulk of homoepitaxial CVD diamond film is likely to be oriented in the crystalline lattice with the number of orientations determined by its symmetry. A simulation of the angular dependence using the EPR parameters of H1 ($g=2.0028$, $\mathrm{A}_{\parallel}=27.5$ MHz, $A_{\perp}=-5.5$ MHz, monoclinic-I symmetry, the linewidth of 0.3 mT) has been carried out. The absence of the anisotropy of the lineshape could not be obtained from the EPR parameters of H1, unless the orientation is disordered and/or the hyperfine parameters have a considerable distribution due to site-to-site variation of the structure. Thus, the structure of the hydrogen-related defects in homoepitaxial CVD diamond film might be different from that described by the reported EPR parameters of H1 [1].

It should be noted that the linewidth ($\Delta B_{\mathrm{pp}} \sim 0.3$ mT) which is similar to that of the EPR spectra of polycrystalline diamond is unusually large compared to those of EPR spectra of typical defects in bulk diamond crystals. It is suggested that the large linewidth may be attributed to extra unresolved hyperfine structure due to interaction with remote hydrogen at random site, or may be ascribed to strain [3]. In polycrystalline diamond, it is reported that the H1 center is accompanied by another unidentified center at the same g-value [2]. The EPR spectrum in the homoepitaxial CVD films might be also consisted of two (or more than two) different species with the difference arising from different location of nearby hydrogen (including possibility of one without accompanying nearby hydrogen).

3.2. Distribution in the film

The spectra of the samples with thicknesses of 12, 2 and 0.3 μm are shown in Fig. 2. In all samples, the signals of the hydrogen-related defects are observed. The signal intensities are proportional to thickness, in other words the concentration is independent of thickness as shown in Table 1. From the results, it was revealed that the hydrogen-related defects do not exist only in the surface region and the interface region where the incorporation of hydrogen has been suggested [4,5]. This indicated that hydrogen-related defects distribute uniformly along the depth direction in diamond films.

It is well known that as-deposited CVD diamond films have a hydrogen-related conductivity layer (p-type semiconducting layer) near the surface, which can be removed by oxidation of the surface using acid solutions such as $H_2SO_4+HNO_3$. To confirm whether the observed defects reside only in the surface region or not, we compared the EPR signal intensity between as-grown film and the film after surface oxidation. The sample was oxidized by H_2SO_4 and HNO_3 solution at 200 °C for 30 min. Within the experimental error, the signal intensity did not change after the oxidation. This result confirmed that the observed defects do not exist only in the sub-surface region.

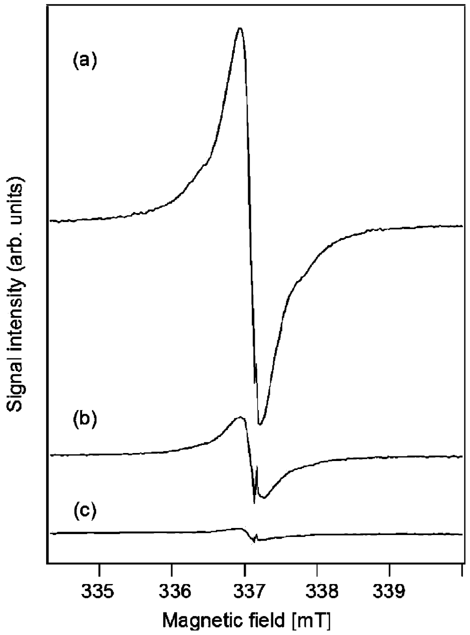

Fig. 2. The EPR spectra of the samples (a) IV, (b) V and (c) VI, respectively, with the magnetic field along the [100] axis at room temperature (microwave frequency 9.45 GHz, microwave power 0.2 mW, amplitude of 100 kHz field modulation 0.05 mT).

3.3. Dependence on NC density

In CVD diamond films, non-epitaxial crystallites (NC) are observed. It was suggested that the grain boundaries and/or dislocations localize inside of the NC sites [7]. From the ion channeling measurements, it was suggested that hydrogen is predominantly incorporated at structural defect sites such as dislocation lines in CVD films with quite high dislocation densities and high hydrogen concentrations [8]. We investigated concentration dependence of the hydrogen-related defects on the NC density. The NC density was estimated by the differential interference contrast microscope. The estimated density ranged from $1.2\times10^{4}/\mathrm{cm}^{2}$ to $1.1\times10^{5}/\mathrm{cm}^{2}$ as shown in the Table 1. As seen from the Table 1, the concentration of the hydrogen-related defects does not correlate to the NC density. This result indicated that the hydrogen-related defects do not originate from the NC. If we assume that the hydrogen-related defects should be confined in NC, the local spin concentration is estimated to be 5×10^{20}–$5\times10^{21}/\mathrm{cm}^{3}$ for the 2-μm thickness samples listed in Table 1, where we used the size of one NC of 10^{-7} cm^{2} observed by the differential interference contrast microscope. For such a large spin concentration cases, line-broadening

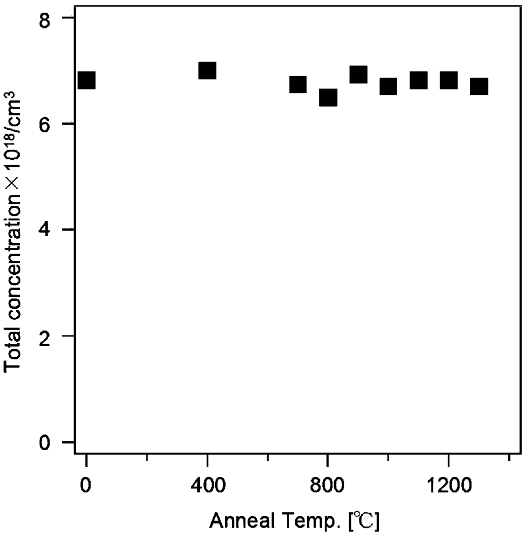

Fig. 3. The annealing temperature dependence of signal intensity of the hydrogen-related defects.

effect should give a large linewidth of ~3 mT due to electron dipole–dipole interaction [9].

3.4. Thermal annealing effect on the concentration of hydrogen-related defects

Thermal annealing effect on the concentration of the hydrogen-related defects were investigated. Both the signal intensity (Fig. 3) and the lineshape of the EPR spectrum did not change after annealing up to 1300 °C. Our result is consistent with the previous work in polycrystalline diamond, where it was reported that the concentration of H1 and H2 centers is insensitive to annealing temperature below 1227 °C (1500 K) [10]. The present result indicated that the hydrogen-related defects are stable than strongly bound hydrogen at surface, which is lost on annealing to 900–1000 °C [11].

4. Summary

EPR signals at $g=2.0028\pm0.0002$ have been observed in single-crystalline CVD homoepitaxial diamond films. They were assigned to hydrogen-related defects similar to H1 centers in which hydrogen exits near unpaired electron in carbon dangling bond. From the thickness dependence of the signal intensity, it has been revealed that the hydrogen-related defects do not exist only in the surface region and the substrate/epilayer interface region where the incorporation of hydrogen has been suggested in CVD homoepitaxial diamond films. From the non-epitaxial crystallites (NC) density dependence of the signal intensity, it has been indicated that the hydrogen-related defects do not originate from NC. In thermal annealing experiments, the hydrogen-related defects were revealed to be thermally more stable than hydrogen at surface, which is lost on annealing to 900–1000 °C. From these results, it has been suggested that the hydrogen-related defects distribute in a spatially homogeneous manner in diamond films.

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