Isotope effects between hydrogen and deuterium microwave plasmas on chemical vapor deposition homoepitaxial diamond growth

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This article shows that replacing hydrogen with deuterium improves the quality of microwave plasma-assisted chemical vapor deposition homoepitaxial diamond. Suppression of point defects in the bulk of diamond and increasing of free-exciton emission intensity were revealed by electron paramagnetic resonance, optical microscopy, and cathodoluminescence, respectively. The isotope effects on the etching rate of diamond by deuterium are also revealed. The isotope effects are discussed from the viewpoint of etching effects. © 2007 American Institute of Physics. [DOI: 10.1063/1.2727380]

I. INTRODUCTION

Diamond has attracted significant interest as material for optical devices in the ultraviolet light emission regime and for high-power and high-frequency devices because of its superior physical and electrical properties. Recently, high-quality diamond films with high Hall mobility and high growth rate are synthesized in microwave plasma-assisted chemical vapor deposition (MPCVD). Further improvements require the suppression of residual impurities and defects such as nonisolated crystallites (NC) and carbon dangling bond defects accompanying hydrogen atom (H1), because these defects extensively influence diamond’s electrical and optical properties.

In CVD techniques, diamond is grown by hydrocarbon species predominantly composed of hydrogen (H2). In plasma, electron impact with H2 produces atomic hydrogen (H). It is well known that H plays important roles in the growth of high-quality diamond. One of them is etching. It was previously reported that H selectively etches non-diamond-bonded material and graphite. A theoretical study reports that H preferentially removes CH2 moiety from the terrace of the (001) surface, promoting growth at steps (or kinks) and deposition of a smooth surface. Promoting these effects is expected to improve quality.

Replacing H2 with deuterium (D2) reportedly increases the plasma etching rate in crystalline Si, reduces light-induced degradation in amorphous Si, and increases resistance of Si-D bond breaking above that of Si-H bonds at the Si surface and the Si/SiO2 interface. MPCVD diamond films have been grown using D2 to investigate the spatial distribution of D in the bulk of diamond or to assign vibrational frequency of C-H bonds. However, isotope effects on MPCVD diamond growth have not been studied so these effects are the theme of this study.

II. EXPERIMENT

Diamond films were deposited epitaxially on high-pressure and high-temperature (HPHT) IIA and HPHT Ib single crystalline diamond (001) substrates with dimensions of 2.5 × 2.5 × 0.5 mm3 and 3.0 × 3.0 × 0.5 mm3, respectively (Sumitomo Electric Industries Ltd.). Their misorientation angles from (100) axis are shown in Table I. One benefit of a IIA substrate is that it prevents an overlap of strong electron paramagnetic resonance (EPR) signals of nitrogen. The films were grown in a MPCVD reactor using CH4 or CD4 diluted with H2 (or D2) purified to more than 99.999 999 9% by a diffusion purifier (Japan Pionics Co. Ltd.). The substrate temperature was controlled by high-frequency heater independently of the input microwave (MW) power and kept at 1073 K as measured by a thermocouple attached to the backside of a susceptor. The total gas pressure, total gas flow rate, and deposition rate were controlled by mass flow controllers.

<table>
<thead>
<tr>
<th>Film</th>
<th>Gas</th>
<th>Type</th>
<th>θoff</th>
<th>Growth rate</th>
<th>NC density</th>
<th>CΗ1/cm3</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-I</td>
<td>CD4/D2</td>
<td>IIA</td>
<td>4±1°</td>
<td>&lt;10¹⁰/cm²</td>
<td>10¹⁰/cm²</td>
<td>10¹⁰/cm²</td>
</tr>
<tr>
<td>D-II</td>
<td>CD4/D2</td>
<td>IIA</td>
<td>4±1°</td>
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<td>10¹⁰/cm²</td>
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<tr>
<td>D-III</td>
<td>CH4/D2</td>
<td>IIA</td>
<td>4±1°</td>
<td>&lt;10¹⁰/cm²</td>
<td>10¹⁰/cm²</td>
<td>10¹⁰/cm²</td>
</tr>
<tr>
<td>D-IV</td>
<td>CD4/D2</td>
<td>Ib</td>
<td>&lt;1°</td>
<td>0.12 µm/h</td>
<td>&lt;10¹⁰/cm²</td>
<td>&lt;10¹⁰/cm²</td>
</tr>
<tr>
<td>D-V</td>
<td>CH4/D2</td>
<td>Ib</td>
<td>&lt;1°</td>
<td>0.13 µm/h</td>
<td>&lt;10¹⁰/cm²</td>
<td>&lt;10¹⁰/cm²</td>
</tr>
<tr>
<td>H-VI</td>
<td>CH4/H2</td>
<td>IIA</td>
<td>4±1°</td>
<td>10²–10⁹/cm²</td>
<td>(4±2) x 10¹⁸</td>
<td>10¹⁰/cm²</td>
</tr>
<tr>
<td>H-VII</td>
<td>CH4/H2</td>
<td>IIA</td>
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<td>10¹⁰/cm²</td>
</tr>
</tbody>
</table>

Ωoff is misorientation angle from (001) axis.

The experimental error of the estimation is less than 10%.

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The NC densities are summarized in Table I, which shows CH4 /D2, and CH4 /H2. Figure 1 shows OM images of films. 

The thicknesses of films labeled D-IV, D-V, H-VIII were estimated by secondary ion mass spectroscopy (SIMS) or the step height between the substrate regions with and without a diamond mask. The thicknesses of films labeled D-I–III, H-VI–VII were simply estimated by deposition durations using the thickness data of films D-IV, D-V, H-VIII.

EPR spectra were measured by a Bruker ELEXSYS X-band spectrometer with a He cryostat. The CL measurements were performed at 200 K and acceleration voltages of 7 and 10 keV, which correspond to electron penetration depths of about 0.5 and 0.9 μm, respectively. The details of the EPR and CL measurements are described elsewhere. 

Optical emission spectra (OES) were obtained by using a charge-coupled device (CCD) detector. The emission light from the plasma was focused by a lens which is fixed to the MPCVD reactor. The focused light was transmitted by optical fiber with resolution of 2.1 nm to the CCD detector. 

For estimation of etching rates, HPHT Ib single crystal diamond was etched by inductively coupled plasma (ICP) (ULVAC Inc.). The power, bias voltage, pressure, and etching duration were 1 kW, 0 V, 4 Pa, and 4.5 h, respectively. As a mask of diamond etching, Au layers of 0.2 μm thickness were deposited by electron beam evaporation method. Au layers were removed by acid treatment after the etching. The etching rates were estimated by measuring a bump height between the Au covered surface and etched surface by stylus profiler (Dektak 8, Veeco Instruments).

### III. RESULTS AND DISCUSSION

Using optical microscopy (OM) and EPR, we investigated NC and H1’ respectively, in films grown by CD4/D2, CH3/D2, and CH3/H2. Figure 1 shows OM images of films. The NC densities are summarized in Table I, which shows that replacing H2 with D2 reduced the NC density by more than one order of magnitude.

The solid lines in Figs. 2(a) and 2(b) are EPR spectra of films grown by CH4/H2 (H-VI) and CD4/D2 (D-II), respectively. The g-values were estimated at 2.0026±0.0001. In H-VI, H1’ was clearly observed. An EPR line shape with a pair of partly resolved satellite lines with splitting of 1.25 mT, caused by the forbidden transitions of nearby H, is a characteristic of H1’ centers. In the previously reported films19 grown with the same condition of H-VI, the concentrations of H1’ (C_{H1'}) [(3–8)×10^{16}/cm^{3}] are almost the same as that of H-VI. It was clearly revealed that the defect concentration decreased more than 10 times by replacing H2 with D2 as shown in Fig. 2 and Table I.

In Fig. 2(a), the normalized spectrum of D-II grown by CD4/D2 is represented by a dotted line for comparison with the EPR line shapes. The g-value and the isotropic character of the spectra of D-I–III are identical to those of H1’. Figure 2(a) does not show the characteristic shoulder of H1’, which is reasonable where H is replaced with D. The splitting of the forbidden transition is approximately represented as 2\left( g_n \mu_n / g_e \mu_B \right) h \nu, \text{ where } g_n \text{ and } g_e \text{ are the nuclear and electronic } g \text{-values, respectively, } \mu_n \text{ and } \mu_B \text{ are corresponding Bohr magnetons, respectively, and } h \text{ and } \nu \text{ are Planck’s constant and } M W \text{ resonant frequency of EPR, respectively. When } H \text{ (} g_n = 5.5857 \text{) in H1’ is replaced by D (} g_n = 0.8574 \text{), the splitting is calculated as about } 0.2 \text{ mT, which can be hidden in the main peak. The SIMS measurement estimates the concentration of D in the film as } 5.6(\pm 5) \times 10^{16}/cm^{3}, \text{ almost identical to the spin concentration estimated from EPR. This suggests that the observed EPR signals in D-I–III mainly consists of that of H1’, where H is replaced with D, and that almost all H or D incorporated in our CVD diamond creates EPR active H1’ centers, whereas negative charged states of H-vacancy complex are observed in N-doped CVD diamond grown under high growth conditions.} \text{ }

Figure 3(a) shows the CL spectra of films D-I and H-VI. The spectra are attributed to free-exciton emission associated with a transverse optical phonon (235 nm) and its replica (242 nm). Figure 3(b) shows the free-exciton signal intensities (I_{ex}) of D-I–III and H-VI–VIII at λ=235 nm, indicating that I_{ex} of D-I–III using D2 is about 5 times larger than I_{ex} of H-VI–VIII using H2 on average. Their ratios were almost the same between acceleration voltages of 7 and 10 keV.

The growth rates of films D-IV, D-V, H-VIII are shown...
spectratically. They were measured consecutively from the Balmer lines between H and D are less than 0.2 nm, which at 486 nm were observed. The wavelength differences of the typical for this synthesis condition. These results indicate the decrease of one order of CH1/H20849. The concentration of D in the plasma will probably be larger than that of H, which can promote the etching effect. We found that the growth rate using D2 is almost half of that using H2. It was reported that CH1/H20850 decreases and I ex increases as the growth rate decreases. In those results, when the growth rate is halved by the decrease of the CH1/H2 ratio, it can be extrapolated that CH1/H2 decreases by half and about 80% of I ex increases. If these quantities are subtracted from the total amounts of differences by replacing H2 with D2, the substantial improvements by the isotope effects are estimated to be the decrease of one order of CH1/H2, and the approximately 3 times increase of I ex on average. Within our systematic experiments, this difference of CL intensity is beyond the experimental errors.

Diamond synthesis is always a competition between deposition and etching. The slower growth rate using D2 can be assumed to be due to the higher etching effects of D compared with H as discussed in the following.

Isotope effects of electron-H2 collision processes such as excitation and dissociation have been reported. One theoretical study focused on the isotope effects on the dissociation process of D2 and H2 through the ground state (A2Σu+g) to the first excited state (B3Σu−g) including vibrational levels. Their calculations revealed a larger cross section of D2 than that of H2, because the density of the states of the dissociation channel differs between H2 and D2 due to the energy difference of their vibrational levels. Through this process, the concentration of D in the plasma will probably be larger than that of H, which can promote the etching effect. We investigated the plasmas under our growth conditions by OES: a powerful technique for in situ diagnosis of plasma. Figure 4 shows the OES spectra of H2 and D2 plasmas with the same growth condition parameters without methane. The compositions of gases in each plasma are (a) 100% H2; (b) 50% H2 and 50% D2; (c) 100% D2; and (d) 100% H2, respectively. They were measured consecutively from (a) to (d) only changing H2 and D2 without switching off the plasma. The Balmer lines labeled as Hα (Dα) at 656 nm and Hβ (Dβ) at 486 nm were observed. The wavelength differences of the Balmer lines between H and D are less than 0.2 nm, which was less than our resolution of 2.1 nm. As Fig. 4 shows, the signal intensities significantly increased more than 4 times after H2 was replaced by D2. Replacing D2 by H2 returned the signal intensities to (a). Because the emission processes of D2 can be assumed to be the same as those of H2 in the present condition, the increase of the signal intensity suggests a higher concentration of D than that of H.

Other studies have reported a larger cross section of the rotational excitation (ρR) of D2 than that of H2. Furthermore, ρR of J=0→2 is reportedly larger than ρR of J=1→3, where J is rotational quantum number. From nuclear statistics, the ratio of ortho-H2 (o-H2) to para-H2 (p-H2) is 3:1, while the ratio of o-D2 to p-D2 is 1:2. From the quantum-mechanical requirements, o-H2 (D2) can only exist in odd-J (J=1,3,...) state and p-H2 (D2) can only exist in even-J (0,2,...) state. Based on these effects, D2 is expected to gain higher energy than H2 in plasma, which can cause the energy of D to be higher than that with H. During syntheses, the substrate temperature was controlled by high-frequency heater equipment, which is independent of the microwave power sustaining plasma, and kept at 1073 K. In the syntheses by using D2, 15% decrease of the power of the high-frequency heating for substrate was observed. This presumably shows higher energy of D compared with H, which may further promote the etching effect.

It should be noted that a heat capacity (Cp) of D2 at 298 K is 29.19 J/mol K which is the same with that of H2. Furthermore, Cp of atomic D is 20.8 J/mol K which is also the same as that of atomic H.

The thermal conductivities (k) of H2 and D2 at 300 K are 4.529 × 10⁻⁴ cal cm⁻¹ s⁻¹ K⁻¹ and 3.405 × 10⁻⁴ cal cm⁻¹ s⁻¹ K⁻¹, respectively. This indicates that the ability to transfer heat by H2 is slightly higher than that of D2. On the other hand, it is indicated that larger heat is transferred to the sample in the D2 synthesis compared with
of the OES signal intensity between H and D in the ICP etching was smaller than that of the MPCVD synthesis. It may be considered that the effects from the different dissociation processes with the calculated process through the ground state ($\chi^1\Sigma_g^+$) to the first excited state ($b^3\Sigma_u^+$) (Ref. 24) may be changed. If the etching rate can be assumed to be simply proportional to the relative OES signal intensity of H and D, the ratio of the etching rate by D to the etching rate by H in the MPCVD synthesis is considered to be larger than in the ICP etching.

As for the etching by D, it must have a different quality compared to the etching by H because the reduction in growth rate alone is apparently not sufficient to explain the data in this study. It can be supposed that the etching by D may promote the H etching effects for high-quality growth.11,12,23

It should be noted that the difference of bond dissociation energies between H$_2$ and D$_2$ is small. Their values of H$_2$ and D$_2$ are 435.990 and 443.533 kJ/mol, respectively.32 Similarly, the differences of it between C-H and that of C-D are small, w 338.4 and 341.4 kJ/mol, respectively. It should be noted that, as for the isotope effect on increase of the resistance of Si-D bond breaking at Si surface and Si/SiO$_2$ interface, it is interpreted that the coupling of the Si-D bonding mode to the Si bulk phonons results in an efficient channel for deexcitation.15,23 In diamond, as far as we know, such a correspondence of phonon frequencies is not reported. Therefore, the stability for C-D bond breaking at the surface can be considered to be almost the same as C-H in diamond.

IV. SUMMARY

The CVD homoepitaxial diamond films grown by D$_2$ plasma were investigated by OM, EPR, and CL, revealing suppression of the defect density and the increase of $I_{\text{ex}}$ by replacing H$_2$ with D$_2$. In the plasma of the present growth condition, higher concentration and higher energy of D compared with those of H are suggested, which can be considered to be the main sources of the isotope effect. From the ICP etching, the higher etching rate by D compared with that of H was demonstrated.