¹³C-NMR Study of CVD Diamonds

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Chemical vapor deposition (CVD) diamond films were deposited by direct current methane-hydrogen-argon plasma jet on a molybdenum plate. The ¹³C nuclear magnetic resonance (NMR) spectra were measured either by static or magic angle spinning (MAS) procedure on CVD diamond, natural diamond, and high pressure-high temperature synthetic diamond. Two narrow peaks were observed on the CVD and the natural diamonds similarly in static NMR and were scarcely affected by magic angle spinning. On the other hand, only one broad peak was observed in high pressure-high temperature synthetic diamond, the broadening being ascribed to the lattice distortion. Spin-lattice relaxation time, T_1 , was extremely long in natural diamond and rather short in high pressure-high temperature synthetic diamond. The CVD diamond showed an intermediate T_1 . It was found from ¹³C NMR spectroscopy that CVD diamond well resembled the natural diamond.

1 INTRODUCTION

Thin film of the CVD diamond has drawn much attention as a new electronic material because diamond is a good electric insulator with a high thermal conductivity in addition to its chemical stability and mechanical hardness. It can also act as a neutral semi-conductor material at elevated temperature.

The CVD diamonds have been prepared by various procedures. Among them, the plasma CVD process operated under reduced pressure using non-transfer type plasma arc is considered to be an excellent procedure to prepare thick films with sufficiently high growth rate. Characterization of such CVD diamond films seems important if the practical applications were imagined.

Thus various experimental approaches have been carried out, i.e. scanning electron microscope (SEM) observation, hardness, infra-red (IR) spectra, electron spin resonance (ESR), etc. Recently laser-Raman spectra¹⁻³⁾ and solid state NMR measurements have been carried out on CVD diamonds. Such novel characterizations are of great importance if CVD diamonds were to be practically applied.

Solid state ¹³C NMR studies on some diamonds have already been reported⁴⁻⁷⁾. However, previous studies were not better than survey and more detailed NMR studies are required. This study deals with solid state ¹³C and ¹H NMR spectra including the MAS technique on various CVD samples. The data was compared with those of a natural diamond and a synthetic diamond among five samples.

2 EXPERIMENTAL

Direct current plasma jet under reduced pressure was used for the present study. The schematic view of the plasma furnace is shown in Fig. 1. A molybdenum plate of 1.0 x 25 x 25 (in mm) was polished with #3,000 SiC emery paper, rinsed with ethanol, and served for the base plate. The

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plate was mounted in the plasma furnace and cooled with tap water which was passed behind the sample holder. The temperature of the plate was monitored by a PR-thermocouple which was mounted behind the molybdenum plate. (The temperature of the molybdenum surface which was exposed to the plasma flame was estimated to be about 300 deg. higher than that measured by the thermocouple.) After evacuating the reaction furnace, the pressure of the furnace was maintained at 3×10^{-4} Pa under desired gas flow rates. The plasma discharge was carried out using [Ar (40 dm³/min)] or [Ar (40 dm³/min) + H₂ (8 dm³/min) mixture] plasma gas (See definition in Fig. 1) under a discharge power of around 16 kW. The reaction gas was supplied from the side nozzle into the discharging flame as shown in Fig. 1, the supply velocity being varied from (1) methane: 0.5 dm³/min to 1.0 dm³/min, and hydrogen: 0 to 10 dm³/min. CH₄/H₂ ratio was calculated from the resultant mixture of the plasma and reaction gases. The temperature of the base plate was varied from 400 to 850 °C. The discharge was maintained from 5 to 120 min. The optimum deposition

condition was found around 650 °C as shown below. The CVD diamond film prepared on a molybdenum plate for 120 min had a thickness of about 100 μm. The film was stripped off the base plate and served for various measurements.

The deposited film was first characterized by an X-ray powder diffractometer (RIGAKU, RINT 1400 diffractometer) with monochromized Cu-Kα radiation by a graphite single crystal and was confirmed the formation of the diamond film. The sample was also monitored by SEM observation (scanning electron microscope: AKASHI ISI-DS130).

A 270 MHz FT-NMR spectrometer (JEOL GSX-270) with a 500 W high power amplifier and a high frequency AD-converter (2MHz) was used for ¹H and ¹³C NMR measurements. The reference for the ¹H spectrum was free water, and for the ¹³C spectrum the cubic diamond peak that was referred to adamantane in advance. The chemical shift was similar to that reported in the previous literature⁷⁾. Static spin echo technique (single pulse) with a 90-degree pulse of 1 μs for ¹H and 2 μs for ¹³C was used.

Fig. 1 Schematic illustration of non-transfer type plasma furnace operating under reduced pressure.

Fig. 2 Sample numbers prepared under various experimental conditions (temperature and reaction gas composition) and observed crystal phases.

MAS (magic angle spinning) technique for ^{13}C with a spinning rate of 4.5 kHz was used to suppress the effect of dipole-dipole interaction without any decoupling pulse. Data for the CVD diamonds were compared to those of natural diamond (broken sample from single crystal and powdered samples supplied from De-Beer) and high pressure-high temperature synthetic diamond (HP/HT diamond: the results for a sample supplied from TOMEI were selected as a representative among five kinds of HP/HT's). Laser-Raman spectra were measured using argon laser (Coherent, INNOVA-70; JASCO NR-1100) to assist the NMR results.

3 RESULTS AND DISCUSSION

As reported previously¹⁾, the quality of the CVD films considerably depended on the type of the base metal. The molybdenum metal was found to give better results than any other materials among tested in the case of the

Fig. 3 Temperature (base plate) dependence of growth rate of CVD diamond film. Plasma gas: $[\text{Ar}(40) + \text{H}_2(8)]$ in dm^3/min mixture. Reaction gas: CH_4 , $0.5 \text{ dm}^3/\text{min}$ and $10 \text{ dm}^3/\text{min}$. Pressure: 1.3×10^4 Pa. Reaction time: 10 min.

present procedure (non-transfer type plasma furnace under a reduced pressure). The growth rate of the diamond film for the present procedure is shown in Fig. 3. The corresponding X-ray diffraction patterns are shown in Fig. 4. The CVD films prepared under such conditions were attributable to the cubic diamond and little peaks attributable to graphite were observed. Since the purpose of the present investigation was not to prepare better diamond films but to characterize the deposited diamond film, the experimental conditions were expanded either in the temperature range or in the gas composition. The experimental points (sample number) which were selected in the present investigation are shown in the temperature/reaction gas composition (H_2/CH_4 ratio) diagram (Fig. 2).

Fig. 4 Temperature (base plate) dependence of X-ray diffraction patterns for CVD films. (●) (111) reflection for cubic diamond. (Peaks except for those of cubic diamond were all attributable to those for either Mo-metal or Mo_2C .) Samples are corresponding to those in Fig. 3.

3.1 Outline of diamond formation through SEM and X-ray observations

SEM photographs of the surface of the deposits for the typical experimental points, 3, 4, 5, 7, 8, cross section of the deposit for sample 3, and the corresponding X-ray diffraction patterns are shown in Figs.5 and 6. Comparing SEM photographs and X-ray

diffraction patterns for sample 3, 4, and 7 (prepared under a similar reaction gas composition), the optimum temperature for the base metal was found to lie around 650 °C as stated above (The temperature of the surface would be about 300 deg. higher than the temperature.) The growth of the excellent crystal was observed vividly in the cross

Fig. 5 SEM photographs for the surface of CVD films (#3, #4, #5, #7, #8). Sample numbers should be referred to Fig. 2. 3' shows the cross section view of sample #3.

section view at above region of the deposits. If the temperature was lowered, the crystallinity became poor, and the formation of graphite became significant at 850 °C. Even if the temperature became lower, *e.g.* at 400 °C, the formation of graphite also became significant when the content of hydrogen in the reaction gas was lowered. In the following, the CVD diamond prepared under such optimum conditions (sample number 3: *i.e.* at 650 °C and at a reaction gas composition of $[\text{CH}_4(0.5 \text{ dm}^3/\text{l}) + \text{H}_2(18 \text{ dm}^3/\text{min})]$ mixture) will be mainly discussed.

3.2 Laser-Raman spectra

Laser-Raman spectra for a natural diamond, synthetic HP/HT diamond (TOMEI), and a CVD diamond (sample 3) were measured to examine the crystallinity of these samples. Laser-Raman spectra for the CVD diamond is shown in Fig. 7. A very narrow peak at 1333 cm^{-1} which is characteristic of the rigid diamond lattice was observed

Fig. 6 X-ray diffraction patterns for CVD films. Sample numbers should be referred to Fig. 2. (●): (111) reflection for cubic diamond, and (▲): (002) reflection for graphite. (Peaks except for those of cubic diamond were all attributable to those for either Mo-metal or Mo_2C .)

similarly in each sample. The CVD diamond shows somewhat wider (about 8 cm^{-1}) spectrum than that of natural (5 cm^{-1}) and HP/HT (6 cm^{-1}) diamonds. The peak position was almost similar to each other.

Broad and very weak peak around 1550 cm^{-1} was observed in CVD diamond and indicated that the graphite-like carbon (8) was deposited at the surface or grain boundaries between each diamond particle. In fact, the polished sample which was cut out from the CVD film of 1 mm thickness was almost transparent (without fear of containing impurity graphite, see cross section view in Fig. 5-3') and no Raman peak for graphite was detected, and the peak at 1333 cm^{-1} also became narrower than that observed for as-grown sample (Fig. 7) and indistinguishable from the natural diamond.

3.3 ^1H NMR spectrum

^1H NMR spectrum was measured for CVD diamond because $[\text{H}_2 + \text{CH}_4]$ gas was used in the synthesis of CVD diamond and C-H bonds might be formed at the defect in sp^3 array of cubic diamond. The observed spectrum of CVD diamond as well as those of

Fig. 7. Laser-Raman spectrum of CVD film (#3). (Ar laser)

Fig. 8 MAS effect for ^{13}C NMR for natural (Top), CVD (Middle), and HP/HT (Bottom) diamonds. Left: MAS spectra, Right: Static spectra. Peak (a) was attributed to the cubic diamond and (b) hexagonal diamond (See text.). Wide peak at +7 kHz (c) was attributed to background spectrum of sample tube.

natural and HP/HT diamonds was similar to the background spectrum, and any sign for the formation of C-H bonds was not detected in ^1H NMR spectra except for one synthetic diamond sample (3 μm diameter, WEBER), where a significant and narrow ^1H spectrum was observed. Since the sensitivity of ^1H NMR spectrum was very high in the NMR spectrometer used and even water molecules that were adsorbed on NMR sample tube were detectable with a sufficient sensitivity, the hydrogen content in the present sample was expected to be low enough.

3.4 ^{13}C NMR spectra

3.4.1 MAS effect MAS (Magic Angle Spinning) effect was examined first. The crystallinity can be revealed from the MAS effect because the main effects to broaden the NMR spectra are the dipole-dipole coupling between the neighboring nuclei with magnetic moments and the unsymmetrical potential gradient caused by the lattice defects,

and such effects should be suppressed by the "Magic Angle Spinning". MAS and static ^{13}C NMR spectra of three different diamonds are shown in Fig. 8. Very narrow two peaks ((a) and (b)) were found to be separated well enough even in the static spectrum for natural and CVD diamonds. The MAS-NMR spectra for the natural diamond and the CVD diamond were not so different much from those of static NMR spectra indicating that the CVD diamond as well as the natural

diamond had an excellent symmetry and dipole-dipole interactions induced by lattice distortion was extremely low.

On the other hand, HP/HT diamond showed a poor resolution in the static spectrum which extended from +2 kHz to -2 kHz. The peak (overlapped by peaks (a) and (b)) became doublet in the MAS spectrum though peak (b) was too weak to detect. Wide peak at +7 kHz (peak (c)) was attributed to the background spectrum either of the sample tube or the MAS probe.

The broadness and the resulting MAS effect (narrowing) revealed that the irregular carbon array in the diamond lattice occurred in HP/HT diamond. The MAS effect on HP/HT diamond was accountable as follows. T_1 for HP/HT diamond was short enough (less than 100 s) as seen in Fig. 9, and the hexagonal peak at -2kHz was not detectable in Fig. 8 (right, bottom). However, the static ^{13}C NMR spectrum for HP/HT diamond extended to the position of hexagonal diamond (b) (see below). Thus the irregularity in HP/HT must

be caused by the cubic-hexagonal random array (or short range hexagonal array) and/or lattice defect of sp^3 carbon atoms.

According to this simple study, it was found that CVD diamond had far better symmetry in crystal lattice than the HP/HT diamonds.

3.4.2 Relaxation time To prove the good crystallinity, another study was carried out. It is well known that the diamond has an extremely long relaxation time due to the hardness and high crystallinity. In the case of FT-NMR, the intensity of the spectrum is to be suppressed if the pulse interval (PD) is set shorter than the longitudinal relaxation time (T_1). Thus T_1 for the diamond can be estimated from the PD dependence of the spectrum intensity. Figure 9 shows the pulse interval (PD) dependence of ^{13}C NMR intensity (peak (a)) for various diamonds. Each curve was normalized to the value at PD = 400 s. The intensity for the HP/HT diamond reached a steady value at above 100 - 250 s. On the other hand, the intensity in the natural diamond was still increasing monotonously

Fig. 9 Pulse interval (PD) dependence of intensity of peak (a) for various diamonds. ○: HT diamond, ▲: CVD diamond, □: Natural diamond. Each curve was normalized to intensity at PD = 400 s.

even at PD = 400 s indicating the extremely long relaxation time T_1 for the well crystallized natural diamond, extending the order of "hour". The result for CVD diamond was intermediate and still increasing even at PD = 400 s showing a very long T_1 though it was shorter than that of the natural diamond. The PD (T_1) study also indicated that the CVD diamond had better symmetry than the HP/HT diamond.

3.4.3 Origin of peak (b) Several properties of peak (a) stated above indicate that the nature of the carbon atoms which lie in rigid and symmetrical lattice, and indicate the characteristics of cubic diamond. However, the origin of the peak (b) was somewhat ambiguous. The peak had a similar nature to peak (a) though the intensity was far smaller than (a). The intensity ratio of the peak (a) to peak (b) increased with increasing the pulse interval (PD). Spectrum (b) almost disappeared at PD = 400 s. This fact indicated that the spin-lattice relaxation time, T_1 , of spectrum (a) was longer than that of spectrum (b) as will be shown in Fig. 9 (5). Thus the true abundance ratio of the species (b) to (a) must be smaller in comparison with the apparent intensity ratio of (b) to (a) shown in Fig. 8, in which spectrum (a) was suppressed considerably due to its long T_1 . The true abundance may be seen in ^{13}C spectrum for HP/HT MAS spectrum in Fig. 8. The abundance of species (b) was estimated to be less than presumably 1/100 - 1/10000 according to the result shown in Fig. 9. Peak (b) may be ascribed to neighboring spin of ^{13}C (^{12}C had no nuclear magnetic moment). However, the intensity ratio of the peaks, (b)/(a), was estimated to be about 4/100 (4 means coordination number) and also peak (b) must be one of the doublet, the center of the peak being peak (a). However such a peak which should be located at +2kHz was not observed. The spectrum (b) was, temporary or for convenience, ascribed to the "hexagonal diamond" if the narrow line width in the static NMR spectrum, little MAS effect and small

Fig. 10 ^{13}C MAS NMR spectra of various CVD films. Sample number should be referred to Fig. 2. Peak (a):cubic diamond, (b): hexagonal diamond (See text.), (c): background spectrum of sample tube.

NMR spectrum, little MAS effect and small abundance were taken into account (9). Such assumption for "hexagonal diamond" will be proved further below, especially in Fig. 10.

Figures 10 shows the ^{13}C MAS NMR spectra for various CVD diamond films prepared here. The nature of peak (a) and (b), line width in static NMR and MAS effect, seems similar with each other. Samples 7 and 8 indicate only peak (b).

In the case of X-ray diffraction as seen in Fig. 6, they contained detectable diamond with considerably wide X-ray diffraction peaks, although these samples mainly consist of graphite. In addition, The ^{13}C NMR peak for graphite is to be undetectable in this frequency region because of their very wide spectrum due to the magnetic moment of the conducting electrons. These facts suggest that the peak can be attributed neither to the cubic diamond nor to graphite.

According to the above consideration, peak (b) should be attributed to some kind of diamond which differ from peak (a), *i.e.* cubic diamond and was ascribed to the hexagonal or hexagonal/ cubic diamond array of carbon atoms.

To examine the nature of hexagonal diamond, the ^{13}C NMR was measured in HP/HT diamond (Du Pont EI) in which hexagonal diamond was detected to some extent. However any significant difference from other HP/HT diamond was not detected. Since

decisive comparison between cubic and hexagonal diamonds could not be carried out, peak (b) was named as "residual" hexagonal diamond for convenience because it must be somewhat different from the bulk hexagonal diamond, and may suggests the presence of cubic/hexagonal mixed array.

4 CONCLUSION

It was found from ^1H NMR study that CVD diamond contained few hydrogen atoms even if H_2 or CH_4 gases were used in CVD synthesis. The ^{13}C NMR spectra of the CVD diamond which were prepared under optimum conditions resembled that of the natural diamond and the lattice contained few irregular arrays. In addition, the presence of hexagonal or cubic/hexagonal arrays was detectable due to the extremely long T_1 for the cubic array and rather short T_1 for the

hexagonal array. The hexagonal array that was almost undetectable by other procedures was revealed by the ^{13}C NMR spectroscopy.

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