Isotopic enrichment of diamond using microwave plasma chemical vapor deposition with high carbon conversion efficiency

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Abstract

Controllability of the carbon isotopic ratio of diamond was investigated. Diamond crystals were grown using microwave plasma-assisted chemical vapor deposition. First, the highest carbon isotopic enrichment and their controllability were examined. Although the highest ¹²C enrichment of 99.998% was achieved using methane with an isotopic ratio of 99.999%, the memory effect of unintended carbon isotope was found to be considerable when the carbon isotopic ratio of feeding methane was tuned for isotopic multilayer formation. A unique gas feeding sequence was proposed for increasing the carbon conversion efficiency from methane to diamond. Increasing the conversion efficiency is done by finding a suitable balance between the methane feeding rate and the carbon consumption rate for diamond growth. High conversion efficiency of 70% was obtained for polycrystalline diamond with a high ¹²C isotopic ratio of 99.997%.

Key words: diamond; chemical vapor deposition; isotopic enrichment; conversion efficiency

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1. Introduction

Carbon isotopic (CI) enrichment is an effective means to improve diamond physical properties. A representative example is the marked improvement of thermal conductivity of diamond using carbon-12 (^{12}C) isotopic enrichment [1]. From the viewpoint of the functionalization of diamond crystals, CI control of diamond is as important as impurity-doping for electrical conductivity control. The CI control techniques are not limited to the property improvement of diamond crystals. Evaluation of ion mixing effects that occur during profile characterization of impurities can be done using **secondary ion mass spectrometry (SIMS)**. The results are not negligible when the impurity profile is of nanometer scale, which is one example. Here, the degree of an ion mixing effect can be extracted from the CI profile synchronized with an impurity profile [2]. Thereby, the depth resolution of an impurity doping profile can reach the scale of a few nanometers.

Relative to the CI control of diamond, the establishment of a high CI enrichment technique with precise control is a key issue. Because the natural isotopic abundance (NA) of carbon is 98.9% for ^{12}C and 1.1% for ^{13}C , higher enrichment is more readily achievable for ^{12}C diamond than for ^{13}C diamond. The highest value of ^{12}C isotopic ratio reported to date is 99.97% [3]. These diamond crystals were grown using high-pressure and high-temperature (HPHT) method. In this case, the ^{12}C enrichment might be limited by the ^{13}C contamination emitted from the high-pressure cell used for the diamond synthesis. Another possible cause when using the HPHT method is the ^{13}C contained in carbon heaters.

These problems are obviated when using microwave plasma-assisted chemical vapor deposition (MPCVD). The highest CI enrichment is expected to be obtained using highly CI enriched methane for diamond MPCVD. In addition, the CI ratio of the diamond film can be modulated intentionally in the growth direction by changing the CI ratio of the feeding methane. Watanabe *et al.* demonstrated the $^{12}\text{C}/^{13}\text{C}$ diamond multilayer growth in this manner [4]. They controlled the ^{12}CI ratio up to 99.8% using ^{12}CI enriched (>99.9%) methane and ^{13}CI ratio up to 94% using ^{13}CI enriched (>98.7%) methane.

The highest ^{12}CI enrichment for the MPCVD has not been clarified. Instead of ^{12}CI enrichment diamond, ^{12}CI enrichment pyrolytic carbon powder was used as a source material for the growth of HPHT diamond showing a ^{12}CI ratio of 99.97%. Anthony *et al.* grew ^{12}CI enriched HPHT diamond crystals using enriched polycrystalline diamond as a source material [5]. Because the obtained highest ^{12}CI ratio for the HPHT crystals was reported as 99.951%, the ^{12}CI ratio for the source polycrystalline diamond is regarded as higher than this value and possibly the highest among the values reported for the ^{12}CI -enriched CVD-grown diamond, although the value of ^{12}CI ratio of this polycrystalline diamond is not described in this report.

To date, CI enrichment of diamond has not been studied widely. The reason partially derives from the high cost of CI-enriched methane. Typically, the price of the enriched methane is several orders of magnitude higher than that of highly purified NA methane. Moreover, it depends strongly on the CI ratio. This fact engenders a difficulty of highly

CI-enriched diamond crystal growth with thickness, such as a self-standing plate because a large amount of the highly CI-enriched methane is consumed for their growth.

Under the conventional diamond MPCVD condition, the conversion efficiency η of carbon from gas-phase methane to the solid-phase diamond is as low as $\leq 1\%$ [6]. Here, the carbon conversion efficiency η in the case of MPCVD is defined as the ratio of the total carbon molar number in diamond to the total carbon molar number injected into the reactor. Therefore, more than 99% methane is emitted to the atmosphere without being used for diamond growth. Although higher η of approx. 10% has been reported [6], the problem clarified in this study is a lowering of diamond crystalline quality with η increase. High η growth with better crystalline quality is therefore an indispensable technique for diamond growth with CI enrichment.

This study will provide guidelines for obtaining high CI enriched diamond growth based on MPCVD. Here, the CI ratio attained in different diamond layer construction will be discussed. A growth technique that offers high η of $>50\%$ is proposed. Finally, the proposed high η growth method is applied for the highest ^{12}CI -enriched diamond.

2. Experiments

^{12}CI -enriched diamond films were grown using the MPCVD system developed at the National Institute for Materials Science. Details of the MPCVD system are described elsewhere [7]. One important function of the system is that a diamond growth reactor was designed based on an ultra-high vacuum (UHV) compatible chamber. A load-lock chamber was also used to

suppress external gas leakage. The carrier gas was hydrogen that had been purified using a palladium purifier (impurity level <0.1 ppb). Four kinds of methane with different CI ratio were used for this study: (a) ^{12}C -enriched methane that was specified to 99.999% enrichment, (b) ^{12}C -enriched methane that was specified to 99.96% enrichment, (c) natural abundance isotopic (^{12}C : 98.9%, ^{13}C : 1.1%) methane, and (d) ^{13}C -enriched methane that was specified to 99% enrichment.

To satisfy both a higher growth rate and better crystalline quality, diamond film growth under the high microwave power density condition is preferred [8]. Diamond growth parameters for the homoepitaxial diamond growth were the following: reaction pressure of 16.0 kPa, microwave power of 1.2 kW, methane concentration ratio of 1%, total gas flow of 200 sccm, and substrate temperature of 920–970°C. HPHT Ib(100) single crystals were used for the substrates. A microwave power density under the conditions presented above was as high as 50 W cm⁻³. One sample, S1, was grown with identical CI ratio methane, whereas another sample named S2 was grown with changing of the CI ratio for multilayer formation. The growth time for S1 was 2.5 h. The gas flow sequence for methane applied for S2 growth is shown in Table I. Plasma was turned off every time when the carbon isotopic ratio in methane was changed from one to the other.

For the growth of polycrystalline diamond named S3, we applied a special gas flow sequence to increase the carbon conversion efficiency. A circular Mo plate of 30 mm diameter and 5 mm thickness was used as a substrate. Growth parameters applied for the polycrystalline

diamond are listed below: the reaction pressure was 18.7 kPa, microwave power was 1.7 kW, and substrate temperature was 870–910°C. The microwave power density under these conditions was 70 W cm⁻³.

The CI ratio of diamond was estimated using SIMS measurements (IMS 7f; Cameca SAS). Primary ions used for this study were either 15.0 keV Cs⁺ or 10.0 keV O₂⁺. Normally, the sputtering rate is calculated by dividing the total depth by the sputtering time in the case of single crystal analysis. However, the single-crystal diamond sample S2 comprises a different carbon isotopic ratio in the sputtering direction. The sputtering rate is inversely proportional to the mass of target element [9,10]. This mass difference between ¹²C and ¹³C gives rise to an 8% error in the sputtering rate. For this study, the depth scale was calculated considering the carbon isotopic ratio at each depth.

The surface morphology of the diamond films was characterized using an optical microscope equipped with Nomarski-mode filters and a laser microscope equipped with a laser wavelength of 408 nm. To clarify the quality of the polycrystalline diamond plate, Raman spectra were recorded using a laser Raman microprobe with confocal collection optics having a spatial resolution of approximately 1 μm. The single-mode 514.5-nm line of an Ar⁺ ion laser was used for excitation. Low laser power of 7 mW was used on the sample surface so that no appreciable peak shift or peak broadening resulted from the irradiation heating. A liquid-nitrogen-cooled charge-coupled device (CCD) was used for the photon detection. The

weight increment and the film thickness were measured respectively using a microbalance and micrometer.

3. Results and Discussion

3.1 High ^{12}C carbon isotopic enrichment in diamond growth

Both homoepitaxial diamond samples S1 and S2 were macroscopically flat in optical microscope images. The calculated average roughness Ra of both sample surfaces was less than 5 nm. Figure 1(a) presents the CI depth profile for sample S1. Figure 1(b) shows a depth profile of ^{12}C and ^{13}C ratio of sample S1 obtained using SIMS measurements. Inset is the magnified profile at the boundary between the ^{12}C isotopic enriched layer and the substrate with natural isotopic abundance. The dashed line is the expected ^{13}C ratio from the feeding gas sequence. Since the thickness of ^{12}C -enriched MPCVD layer was $1.25\mu\text{m}$ and the growth time was 2.5 h, the growth rate was estimated as $0.5\pm0.1\ \mu\text{m h}^{-1}$. The minimum ^{13}C ratio of sample S1 was 0.002%, which is an almost identical value the ^{12}C methane to that used for this growth. This isotopic purity is the highest among the reports to date on the ^{12}C -enriched diamond including both HPHT and CVD methods. Results also showed that the transit depth range of CI ratio from NA to ^{12}C enriched layer was approximately 70 nm. Before starting the growth of sample S1, the reactor was devoted for the ^{12}C enriched (99.999%) diamond film growth and ^{13}C ratio in the diamond films were less than 0.003%. Therefore, ^{13}C contamination occurring at the interface is thought to derive from the plasma etching of Ib substrate in the initial stage of

diamond growth. The nitrogen concentration was below the detection limit of SIMS measurements of $2 \times 10^{16} \text{ cm}^{-3}$.

Then, to evaluate the controllable range of CI enrichment, the ^{12}CI (or ^{13}CI) ratio of the feeding gas to the MPCVD reactor was modulated intentionally at each layer's growth. Figure 2(a) presents a stacking sequence of CI modulated multilayer within a [homoepitaxial](#) film. The layer growth duration is presented in Table I. This diamond sample was designated as S2. After each layer's growth, plasma was quenched and the reactor was evacuated to minimize the memory effect of residual CI gas. The modulation range of CI ratio was 0.001%–99% for the ^{13}CI and from 1%–99.999% for the ^{12}CI . In all, nine layers were stacked on the Ib(100) substrate. The stacking order was selected to evaluate the memory effect of unintended isotopic carbon adequately. Here, ^{13}C is the unintended isotopic carbon for ^{12}CI -enriched layer growth, and vice versa.

Figure 2(b) presents the CI depth profile of sample S2 as estimated from SIMS measurements. The dashed line represents the depth profile of the ^{13}C concentration expected from the gas feeding sequence. Unlike the identical CI layer of the S1 sample, the S2 sample clearly comprises layers with different CI ratios. A discrepancy was apparent in the CI ratio between the feeding gas and diamond when the CI enrichment was higher than three orders of magnitude. The minimum ^{13}CI ratio of sample 2 was attained in the region of the layer A, which was the first layer grown on the substrate using the highest ^{12}CI enriched (99.999%)

methane. Although the ^{13}C ratio in feeding methane is 0.001%, the ^{13}C ratio in the layer A was higher than 0.02%.

A slow decrease of the ^{13}C ratio in the growth initial stage resembles the result obtained for sample S1. As described above, ^{13}C contamination is thought to occur as a result of hydrogen etching of a diamond substrate in the initial stage of diamond growth where there is a temporal difference between hydrogen plasma ignition and methane flow. In other words, diamond growth of more than 100 nm is necessary to obtain a high ^{12}C ratio on the order of 5N grade (99.999%).

In fact, CI in layer B was comparable to that in the feeding methane, which was 0.04% as ^{13}C ratio. After the growth of layer C being composed of NA carbon, the ^{12}C enriched layer D was over grown using the ^{12}C enriched (99.96%) methane. Although the ^{13}C ratio in the layer D was decreased from that of the former NA layer, the value was found to be comparable to or slightly higher than that in layer B, which was grown using the same ^{12}C enriched (99.96%) methane. Moreover, the highest ^{12}C enriched (99.999%) methane was used in the following growth step sequence, the ^{13}C ratio continued to increase in the layer E in the diamond growth direction. The gradual increase of ^{13}C background level might originate from desorption of ^{13}C from the MPCVD reactor which was adsorbed in the former growth sequence. The reactor is heated during growth, giving rise to desorption of the adsorbed ^{13}C . A continuous ^{13}C increase in film thickness or in growth time suggests that ^{13}C background level is approx. 0.1 atomic percent. Cleaning of the reactor inner wall is necessary to obtain higher CI enrichment.

The ^{13}C enriched layer F was deposited immediately after diamond growth using the highest ^{12}C enriched methane. The ^{13}C ratio in this layer F corresponds well to the value that is anticipated from the source ^{13}C enriched (99%) methane. Then the layer G was grown using the highest ^{12}C enriched (99.999%) methane. Although the ^{13}C isotopic ratio decreased from the former layer F, the ^{13}C ratio was 0.1%. This value is about two orders of magnitude higher than the value expected from the CI ratio of methane. In addition, ^{13}C ratio was not identical within layer G.

The interface between two adjacent layers being composed of different CI ratio had a sharpness of 20–40 nm. Because the ion mixing effect occurred during the SIMS measurement under the similar condition is approx. 10 nm [2, 11], the interface broadening does not mainly arise from SIMS measurements. Broadening of the CI profiles at each layer is inferred to be attributable to the memory effect of counter-isotopic carbon adsorbed in the reactor.

The highest ^{12}C enrichment being controlled in the CI multilayer is as high as approx. 99.9% (3N). Finally, using ^{13}C enriched methane containing ^{12}C of 1.0% and NA methane containing ^{13}C of 1.1%, a complementary carbon isotopic profile was realized, as demonstrated in layers H and I in Fig. 2(b). The isotopic control is highly reproducible within the CI ratio range of 1–99%.

3.2 High conversion efficiency of ^{12}C carbon

This subsection presents discussion of an attempt to increase the carbon conversion efficiency η in diamond growth. The gas flow path of methane in the MPCVD system under the conventional diamond growth condition is presented in Fig. 3(a). The arrow length corresponds to the total flow amount of gas consumed for each process. Under the normal diamond growth condition, the total flow rate of feeding gas is set as higher for the precise control of methane concentration in the reactor and for the suppression of the impurity incorporation in diamond crystals because of an external gas leakage. Typically, the total gas flow rate is 400–1000 sccm. The methane concentration is 0.1–10% of the total gas flow. Normally, the values of methane concentration and total gas flow rate are constant during diamond growth. Because of the higher total gas flow rate, the residence time of the methane in the reactor is short. A large volume of the methane is emitted to the atmosphere, without conversion to diamond. Results show that the carbon amount emitted from the pumping port is comparable to the carbon amount injected from the gas inlet port.

Figure 3(b) shows the gas flow path under the high η growth condition. For this study, we applied this growth condition with unique flow procedure for increasing η . The flow-rate sequence used in this study is the following [12]. First, the hydrogen gas was injected to the reactor at a normal flow rate for diamond MPCVD (step 1). The reaction pressure in the reactor was finally regulated at a value that was slightly smaller than the target value for diamond growth, to realize suitable methane concentration after methane injection in the subsequent step. Plasma ignition was also done in this step. Then, the feed gas was switched from pure

hydrogen to pure methane. At the same time, the total gas flow rate decreased to less than one-tenth (step 2). No gas evacuation was conducted during this step. Once both the reaction pressure and methane concentration in the reactor became target values, the total gas flow rate decreased to a very small value (step 3). Over time, the methane concentration changed gradually to a value that was determined by the balance between the total gas flow rate and the diamond growth rate. During the diamond growth, the reaction gas was evacuated continuously to maintain constant pressure. Although the amount of carbon emitted to the atmosphere was not zero, the value was negligibly small compared to the case of the conventional growth condition.

In the simple estimation assuming $\eta=1$ and diamond growth area of 7 cm^2 (a 3 cm diameter circular shape), the diamond growth rate of $1.3\text{ }\mu\text{m h}^{-1}$ is expected at the methane flow rate of 0.1 sccm. This is a suitable growth rate range to grow diamond crystals with better crystalline quality using the high microwave power density condition [8]. In this study, the polycrystalline diamond plate was grown using this gas flow procedure. The average methane flow rate was 0.18 sccm. The highest ^{12}C enriched (99.999%) methane was used for this growth. From the gas monitoring system, the methane concentration was found to be 4% initially. It decreased gradually to 1% during growth. The concentration was finally stabilized with the balance between the gas flow rate and the diamond growth rate.

The number of carbon atoms composing the polycrystalline diamond S3 was estimated from the weight gain of diamond: 1413 mg. However, the total amount of carbon injected in the

reactor was counted from the product of methane flow rate of 0.18 sccm and feeding time of 336 hr. Because the total input methane amount was 3716 cc, the weight increment is expected to be 1991 mg when all the methane is used for the diamond growth. By comparing these values, the carbon conversion efficiency η of sample S3 was estimated as 71%. This result suggests that carbon atoms injected in the reactor were converted to diamond effectively using the proposed gas flow procedure.

The carbon conversion efficiency η of 70% obtained in this study is quite a high value compared to those obtained in previous work. Although the mechanism of high efficiency is still not clarified, a possible understanding is the following. Because the plasma generation region being the heating parts for the reaction is localized in the center of the reactor, carbon radicals that were created in plasma can return to stable gas phase such as methane, when they come to the cold part in the reactor. As a result, formation of solid carbon film on the cold part is inferred to be negligibly small. On the other hand, because the substrate holder is located just under the plasma, carbon radicals coming to the sample holder become diamond in a short time. In this way, the carbon source can have a long residence time in the reactor until they contribute to a diamond growth. Because the reaction chamber and sample holder stage of the MPCVD system were water-cooled to keep a lower temperature in this study, the total carbon deposition in the reactor is inferred to be insignificant.

Figure 4(a) shows a photograph of polycrystalline diamond grown on the whole area of the Mo substrate. After the MPCVD growth, the diamond plate was removed spontaneously from

the Mo substrate because of the difference of thermal expansion coefficient. The edge of the diamond plate was laser cut to realize a regular circular shape of 29 mm diameter with 470 μm thickness. The average growth rate in this condition was estimated as 1.4 $\mu\text{m h}^{-1}$. The average grain size of the polycrystalline diamond was 50 μm .

Figure 4(b) shows a Raman spectrum of sample S3. As a reference, Raman analysis was conducted also for a commercialized optical-grade polycrystalline diamond plate from Element Six Ltd. and a high-quality IIa (100) diamond single crystal grown using the HPHT method. A signal reflecting *sp*² phases appearing at around 1600 cm^{-1} was negligibly small for sample S3, suggesting that the quality of the polycrystalline diamond is rather higher. No remarkable difference was found among these crystals in the Raman peak position. Raman peak width of sample S3, 2.6 cm^{-1} , is slightly larger than that of a single crystal, 2.3 cm^{-1} , and is equivalent to that of the high-quality polycrystalline diamond.

The isotope enrichment of sample S3 was evaluated using SIMS measurement. Results prove that the ¹²CI ratio is 99.997%, which is comparable to that of sample S1 grown using the conventional gas flow procedure even though the high η growth method was applied for sample S3 growth. The water-cooled reactor wall used for this study was made mainly of stainless steel and molybdenum. No graphite component was used for the specific purpose such as substrate holder heating. This reactor configuration is thought to provide effective suppression of unintentional ¹³C incorporation. Nitrogen, boron, and hydrogen concentrations were below the detection limit of SIMS measurement of $2 \times 10^{16} \text{ cm}^{-3}$, $3 \times 10^{17} \text{ cm}^{-3}$, and $1 \times 10^{14} \text{ cm}^{-3}$. The

superior purity of sample S3 is attributed to the low external leakage of UHV-compatible reactor.

4. Conclusion

The carbon isotopic ratio of diamond was controlled with good reproducibility up to 99.9% for ^{12}C and 99% for ^{13}C using microwave-assisted chemical vapor deposition. Higher carbon isotopic enrichment was suppressed by the memory effect of unintended isotopic carbon that is adsorbed onto the reactor. In the case of diamond growth with an identical ^{12}C isotopic enrichment, the highest ^{12}C isotopic ratio of 99.998% was achieved by growing a diamond using a highly ^{12}C (99.999%) enriched methane. A high carbon conversion efficiency of approx. 70% from methane to diamond was achieved under high microwave power density conditions of 70 W cm^{-3} . ^{12}C -enriched polycrystalline diamond plate showed high isotopic enrichment of 99.997%. A sharp Raman peak indicated better crystalline quality of the grown diamond plate.

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Layer	Isotopic ratio in methane [%]		Growth time [min]
	^{12}C	^{13}C	
Substrate	98.900	1.100	
A	99.999	0.001	10
B	99.990	0.010	42
C	98.900	1.100	42
D	99.990	0.010	31
E	99.999	0.001	31
F	1.000	99.000	30
G	99.999	0.001	30
H	1.000	99.000	30
I	98.900	1.100	30

Table I Isotopic ratio and growth duration for each layer of sample S2.

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Figure captions

Fig. 1. (a) Schematic showing the stacking sequence of a homoepitaxial diamond layer with identical carbon isotopic ratio, ^{13}C : 0.001%. (b) Depth profile of ^{12}C (red line) and ^{13}C (blue line) isotopic ratio of the sample S1 that was homoepitaxial film grown with a constant $^{12}\text{C}/^{13}\text{C}$ ratio during growth. The dashed line is the ^{13}C isotopic ratio expected from the gas feeding sequence. Inset is the magnified profile at the boundary between the ^{12}C isotopic enriched layer and the substrate with natural isotopic abundance.

Fig. 2. (a) Schematic showing the stacking sequence of homoepitaxial diamond layers with various carbon isotopic ratios. The range of ^{13}C isotopic ratio is from 0.001% to 99%. (b) The depth profile of ^{12}C (red line) and ^{13}C (blue line) isotopic ratio of sample S2 that was homoepitaxial film grown with changing the $^{12}\text{C}/^{13}\text{C}$ ratio during growth. The dashed line is the ^{13}C concentration expected from the gas feeding sequence.

Fig. 3. Schematic views of the total amount of gas flow under (a) conventional growth condition and (b) a high carbon conversion condition.

Fig. 4. (a) Free-standing ^{12}C diamond polycrystalline plate S3 grown under the high carbon conversion condition. The diameter was 29 mm with thickness of 470 μm . The ^{12}C isotopic ratio

was 99.997%. (b) Raman spectra of the polycrystalline diamond S3, a commercialized optical-grade polycrystalline diamond plate from Element Six Ltd. and a high-quality IIa (100) diamond single crystal grown using HPHT.

(a)

(b)

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I: ^{13}C : 1.1%
H: ^{13}C : 99%
G: ^{13}C : 0.001%
F: ^{13}C : 99%
E: ^{13}C : 0.001%
D: ^{13}C : 0.04%
C: ^{13}C : 1.1%
B: ^{13}C : 0.04%
A: ^{13}C : 0.001%
Substrate Diamond Ib; N.A ^{13}C : 1.1%

(a)

(b)

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Fig. 3 T. Teraji et al.

(a)

(b)

Fig. 4 T. Teraji et al.