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

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ABSTRACT

Isotopically-controlled 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 ^{12}C isotopic ratio of 99.998% was achieved using methane with an isotopic ratio of 99.999%, the memory effect of an unintended carbon isotope was found to be considerable when the carbon isotopic ratio of feeding methane was tuned for isotopic multilayer formation. Secondly, 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. A high conversion efficiency of 70% was obtained for a polycrystalline diamond with a high ^{12}C isotopic ratio of 99.997%.

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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 by secondary ion mass spectrometry (SIMS) is one example. The ion mixing effects are not negligible when the impurity profile is of nanometer scale. 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 a high-pressure and high-temperature (HPHT) method. In this case, the ^{12}CI 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 $^{12}C/^{13}C$ 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 the ^{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. For the growth of HPHT diamond showing the highest ^{12}CI ratio of 99.97%, instead of ^{12}CI enrichment diamond, ^{12}CI enrichment pyrolytic carbon powder was used as a source material [3]. Anthony et al. grew ^{12}CI enriched HPHT diamond crystals using enriched polycrystalline diamond as a source material [5]. Because the highest ^{12}CI ratio obtained 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 the ^{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, price rate of methane depends strongly on the CI ratio. This fact engenders a difficulty of highly CI-enriched and thick diamond crystal growth, such as a self-standing ^{12}CI-enriched diamond 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, under the conventional condition, more than 99% methane is emitted to the atmosphere without being used for diamond growth. Although a higher η of approx. 10% has been reported [6], the problem clarified in this report 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. Then, a growth technique that offers a 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 ratios were used for this study: (a) [12]CI-enriched methane that was specified to 99.999% enrichment, (b) [12]CI-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]CI-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, which is a flow rate ratio of methane to the total process gas, 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 an identical CI ratio of methane, whereas another sample named S2 was grown by changing 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 1. In order to minimize the memory effect of residual CI gas, plasma was turned off and process gas was evacuated from the growth reactor every time when the carbon isotopic ratio in methane was changed from one to the other.

For the growth of a 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 O$_2^+$. Normally, the sputtering rate of SIMS measurement 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 a target element [9,10]. This mass difference between ^{12}C and ^{13}C 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. A 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. Fig. 1(a) presents a stacking sequence of a homoepitaxial diamond layer of sample S1. Fig. 1(b) shows a depth profile of the isotopic ratio of ^{12}C and ^{13}C for 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]CI ratio from the feeding gas sequence. Since the thickness of the [12]CI-enriched MPCVD layer was 1.25 μm and the growth time was 2.5 h, the growth rate was estimated as 0.5 ± 0.1 μm h^{-1}. The minimum [13]CI ratio of sample S1 was 0.002%, which is an almost identical value to the [13]CI ratio of methane used for this growth. This isotopic purity is the highest among the reports to date on the [12]CI-enriched diamond including both HPHT and CVD methods. Results also showed that the transit depth range of CI ratio from NA to the [12]CI enriched layer was approximately 70 nm. Before starting the growth of sample S1, the reactor was devoted for the [12]CI enriched (99.999%) diamond film growth and [13]CI 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 the Ib substrate in the initial stage of diamond growth. The nitrogen concentration of the homoepitaxial film was below the detection limit of SIMS measurements of 4×10^{15} cm^{-3}.

Then, to evaluate the controllable range of CI enrichment, the [12]CI (or [13]CI) ratio of the feeding methane gas to the MPCVD reactor was modulated intentionally at each layer's growth. Fig. 2(a) presents a stacking sequence of the CI modulated multilayer within a homoepitaxial film. The layer growth time is presented in Table 1. This diamond sample was designated as S2. The modulation range of the CI ratio was 0.001%–99% for the [13]CI and 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.

Table 1
Isotopic ratio and growth time for each layer of sample S2.

Layer	Isotopic ratio in methane [%]		Growth time [min]
	[12]C	[13]C	
Substrate	98.9	1.1	10
A	99.999	0.001	42
B	99.96	0.04	42
C	98.9	1.1	31
D	99.96	0.04	31
E	99.999	0.001	30
F	1	99	30
G	99.999	0.001	30
H	1	99	30
I	98.9	1.1	30