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Nucleation Enhancement of Nanocrystalline Diamond Growth at Low Substrate Temperatures by Adamantane Seeding

K. Tsugawa,* M. Ishihara, J. Kim, Y. Koga, and M. Hasegawa*

Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST) Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Continuous nanocrystalline diamond films have been grown on Si and glass substrates at substrate temperatures of around 150 °C by the microwave plasma chemical vapor deposition technique. We have observed the nucleation enhancement of diamond crystals from adamantane ($C_{10}H_{16}$) seeding for the first time, which is effective for the formation of high-density nanocrystalline diamond films at low substrate temperatures. X-ray diffraction analyses indicate that the deposited films comprise diamond nanocrystals with an average size of 14 nm. UV Raman spectra of the films clearly exhibit the diamond signature at 1333 cm^{-1}.

Introduction

Diamond films, in general, are grown by using the chemical vapor deposition (CVD) technique. Diamond grows from carbon source gas diluted with H_2 gas during the CVD process. CH_4 gas is employed as a carbon source in most cases. The substrate temperature reaches 800−1000 °C in the usual diamond CVD processes, or above 400 °C for nanocrystalline diamond (NCD) films. High deposition temperatures limit the substrate of diamond deposition, such as a Si wafer, restricting applications of diamond. Thus, low-temperature growth gives a wide substrate selection, such as glass, metals, and plastics. Hence, it will open new application fields of diamond. From this point of view, many efforts have been made to lower the process temperature.[1−3]

Ong et al.[1] have developed a low-temperature diamond-deposition process using the microwave plasma CVD (MWPCVD) method in a pulsed mode. They reported diamond deposition on quartz substrates at around 400−600 °C. Muranaka et al.[2] have reported diamond synthesis on Si substrates at 130 °C using microwave plasma. Hiraki[3] has utilized the magnetoactive MWPCVD technique for low-temperature diamond deposition at 200−600 °C. Recently, Piazza and Morell[4] have reported NCD growth on polyimide films at substrate temperatures of around 250 °C using sulfur-assisted hot-filament CVD. Despite these attempts, however, conclusive evidence that a diamond film grows at a substrate temperature as low as 100 °C has not been reported so far. Establishing technologies for low-temperature synthesis of diamond, such as below 200 °C, will lead to the next generation of diamond applications.

In this study, in an attempt to lower the substrate temperature in a MWPCVD process, we have succeeded in the synthesis of continuous NCD films at substrate temperatures around 150 °C. To reduce the substrate temperature, we have adopted 1 or 2 orders of magnitude lower pressure of the reaction gas mixture than conventional MWPCVD methods and microwave surface-wave plasma with low electron temperatures (1−2 eV). The main topic in this work is its special substrate pretreatment to increase the nucleation density of diamond at such low temperatures, where adamantane ($C_{10}H_{16}$) is used for a seeding material of diamond.

In diamond CVD processes, where diamond powders of approximately micrometer in size are used for the substrate seeding before the CVD treatment; in general, the nucleation density decreases with lowering substrate temperatures. In this case, nanocrystal seeding by using NCD powder suspensions for the substrate pretreatment is effective to increase nucleation density.[5] This fact implies that the nucleation density is expected to increase with decreasing dimensions of seeding materials. On the basis of this concept, we have selected adamantane as the seeding material.

Adamantane is the lowest dimensional *diamondoid*[6] that has the same carbon atomic geometry as diamond. In other words, it exists at the smallest end in continuous structural series formed by hydrogen-terminated diamonds and nanometer-sized diamondoid hydrocarbons, namely, the smallest diamond molecule. It has been suggested to be responsible for nucleating diamond films.[7]

Experimental Methods

Si(001) wafers and borosilicate glass wafers with a diameter of 100 mm were used as substrates for the low-temperature diamond deposition. The substrates were sonicated in adamantane−hexane or adamantane−ethanol solution for 15 min for the adamantane seeding. In comparison with this pretreatment, graphite-cluster diamond (GCD) particles were used as the seeding material, which consist of nanosized (∼5 nm) diamond crystals and graphite, synthesized by shock compression. In this case, the substrates were sonicated in GCD ethanol suspension for 15 min and washed in ethanol by sonication. After drying, the substrates were set into the reaction chamber. This GCD seeding has been used for large area NCD depositions by the same MWPCVD system as this work, where high-quality transparent NCD films have been grown over a 30 × 30 cm^2 area at substrate temperatures of 400−500 °C.[8] The details of the MWPCVD system are described elsewhere.[8] The MWPCVD system generates a microwave surface-wave plasma with a low electron temperature of below 2 eV in the CVD region, which is an advantage for the low-temperature growth of diamond.[8]

* To whom correspondence should be addressed. E-mail: k.tsugawa@aist.go.jp (K.T.), hasegawa.masataka@aist.go.jp (M.H.).

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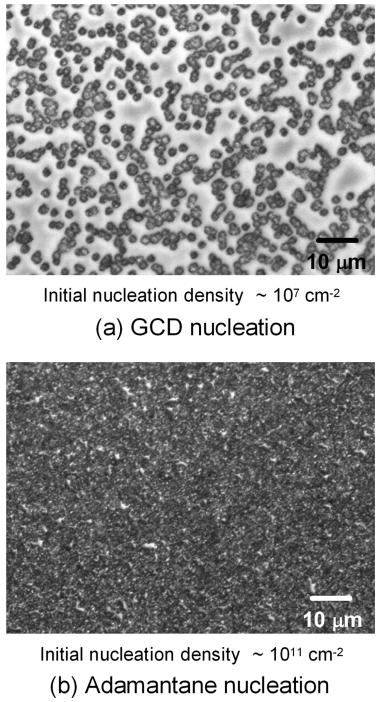

Figure 1. Optical micrographs of diamond films grown at around 150 °C on borosilicate glass substrates. (a) A diamond film nucleated by GCD seeding. (b) A diamond film nucleated by adamantane seeding.

Lower reaction gas pressures in the range of 2.0×10^1 to 1.0×10^2 Pa than conventional diamond CVD processes (10^3 to 10^4 Pa) were used for the low-temperature growth. A microwave power of 10−20 kW at 2.45 GHz was applied to produce a surface-wave plasma over a 30×30 cm^2 area with H_2 (90−98%)/CH_4 (1−5%)/CO_2 (1−5%). By using an advanced gas-buffer substrate-cooling system and a water-cooled substrate holder, the substrate was maintained at a temperature of around 150 °C (150 ± 20 °C). The substrate temperature was monitored by a radiation pyrometer and a K-type thermocouple in contact with the substrate.

After the CVD treatment by the surface-wave plasma, the deposited films were characterized using optical micrography, UV Raman scattering spectroscopy (excitation wavelength = 244 nm), and X-ray diffraction spectrometry.

Results and Discussion

Figure 1 shows optical micrographs of diamond films deposited at substrate temperatures of around 150 °C (150 ± 20 °C). Figure 1a displays a film grown on the borosilicate glass substrate using the GCD seeding. The film is not continuous but discrete particles. The initial nucleation density of diamond on the substrate is around 10^7 cm^{-2}, which is estimated from the particle area density in the picture. On the other hand, using the adamantane seeding, the films deposited at the same substrate temperatures are continuous, as demonstrated in Figure 1b. The estimated initial nucleation density is around 10^{11} cm^{-2}. The difference between the nucleation densities is clearly observed in the pictures.

Figure 2 indicates a typical X-ray diffraction pattern with Cu Kα of a continuous diamond film grown on a Si substrate using the adamantane seeding. The deposition duration is 8 h, and the film thickness is around 500 nm. In the pattern, the peak of reflection from diamond (111) planes is clearly observed at $2\theta = 43.9°$. In addition, the (220) and (311) peaks of diamond

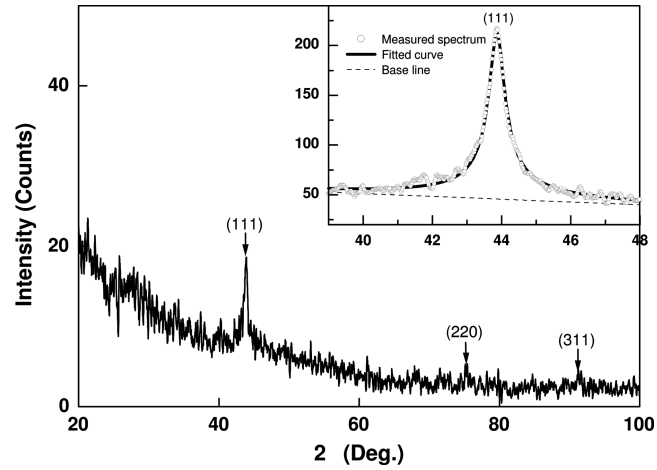

Figure 2. Typical X-ray diffraction pattern by Cu Kα of a nanocrystalline diamond film grown at around 150 °C on a Si substrate using the adamantane seeding.

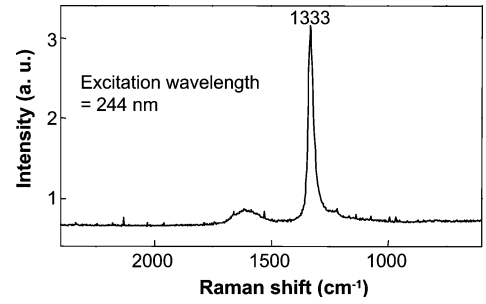

Figure 3. Typical UV Raman scattering spectrum of a nanocrystalline diamond film grown at around 150 °C on a Si substrate. The excitation wavelength is 244 nm.

are also seen in the pattern. Assuming the absence of mechanical stress in the film, the average crystallite size of the diamond film is estimated from the broadening of the diffraction peak by using the following Scherrer equation[9]

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Here, D_{hkl} is the mean crystallite size perpendicular to the direction of *hkl*. λ and θ are the radiation wavelength (1.54 Å for Cu Kα) and Bragg angle, respectively. The shape factor K is 0.89 when the full width at half-maximum (fwhm) in radians of a peak is used as the peak broadening β. By employing the fwhm of the (111) line in the inset of Figure 2, which is fitted by the Pearson VII function,[10] the average crystallite size of the film is estimated at 14 nm. Hence, the film is found to be a NCD film composed of nanosized diamond crystals.

Figure 3 exhibits a typical Raman scattering spectrum of a diamond film deposited on the Si substrate using the adamantane seeding, where the Raman scattering is excited by 244 nm UV light. In the spectrum, a broad peak at around 1580 cm^{-1} attributed to an sp^2 bonded carbon component (graphite) is also seen. The sp^2 peak, however, is much lower than the peak of diamond at 1333 cm^{-1}, as compared with those of NCD films deposited by other CVD techniques in the literature[11] evaluated by UV Raman spectra with the same excitation wavelength. This indicates that the NCD film in the present work exhibits good crystalline quality with small sp^2 components.

On the basis of the suggestion of adamantane as possible diamond-forming precursors by Matsumoto and Matui,[7] there

have been several attempts to synthesize diamond films from adamantane seeding in MWPCVD[12] and in combustion CVD.[13] In both cases, however, no evidence to enhance the diamond nucleation has been obtained. Those results are probably caused by their high substrate temperatures around 900 °C because adamantane is not stable above about 500 °C.[7] In our case, however, this problem does not emerge due to the substrate temperatures below 200 °C. This leads to that the adamantane seeding clearly exhibits the effect to increase the nucleation density of diamond, as demonstrated in Figure 1.

After the pretreatment procedures of the GCD seeding, the substrates are expected to be homogeneously covered with residual GCD particles, as observed in other NCD seeding.[14] On the other hand, after the adamantane seeding, we presume that the precipitated adamantane molecules adsorb on the substrate to cover the surface homogeneously. Because the adamantane molecule is much smaller than the GCD particles, it should exhibit much larger particle (molecule) density on the substrate surface. That may exceed 10^{14} molecules/cm^2,[15] while the GCD adlayer probably indicates less than 10^{12} particles/cm^2.[14] In addtion, the adamantane adlayer is macroscopic in this work, in contrast to the microscopic GCD adlayer that is invisible. The thick adamantane adlayer forms a high-carbon-density layer near the surface in the hydrogen plasma during the initial stage of the CVD process. The high-carbon-density layer accelerates diamond nucleation and protects the diamond nuclei on the substrate from the etching by the hydrogen plasma. Thereby, the high nucleation density is likely yielded under the low nucleation-rate condition due to a low substrate temperature.

Conclusions

Low substrate temperatures around 150 °C have been realized in NCD synthesis with the MWPCVD method by using a low-pressure surface-wave plasma. Using this plasma, high-quality continuous NCD films have been successfully deposited at substrate temperatures of around 150 °C by using adamantane as seeding material. The adamantane-enhanced nucleation at a low substrate temperature is confirmed for the first time. From the analysis of the X-ray diffraction pattern, the diamond film grown in this work is found to be NCD with an average crystallite size of 14 nm.

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