

Enhancement of Nucleation Density on Diamond Chemical Vapor Deposition

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The supersaturation of carbon source at an initial stage of deposition was investigated for the enhancement effect of nucleation density on diamond fabrication by conventional microwave plasma apparatus. Under the supersaturation conditions, carbonaceous fine particles were deposited in a high density on Si substrate. These fine particles could act as nucleation sites during successive diamond deposition step. Consequently, we achieved the enhancement of nucleation density up to $5 \times 10^6 \text{ cm}^{-2}$. Raman spectra and scanning tunneling spectra show that the carbonaceous particles might be gassy carbon.

Key words: diamond deposition, CVD, nucleation phenomena, high supersaturation, boron nitride interlayer

1. INTRODUCTION

The diamond films have been studied extensively in recent decade, due to the attractive character of diamond, i.e., the highest hardness among all the materials, wide band gap for high temperature semiconductor, widespread transparency range from ultraviolet to infrared radiation, etc. Diamond was generally deposited on substrate by chemical vapor deposition method (CVD) from a hydrocarbon as a carbon source diluted with an amount of hydrogen [1,2]. To date, however, we have faced several problems to utilize diamond films for practical applications, for example as hard coating, optical coating and electric devices. Most of all, the problem on nucleation phenomena is significantly important in order to promote the adhesion strength and the surface smoothness. The diamond nucleation in the CVD process is so much different from the case in other process of film fabrication. Note that diamond is the metastable phase under the CVD conditions. Moreover, the morphology of grown diamond films by any methods is quite unique, compared with other films. The diamond film consists of the single crystal particles of a few μm in size, which results in the rough surface and the weak adhesion. This could be due to the extremely high surface energy and the low nucleation density in CVD process.

To deposit a thermodynamically stable material using CVD, a supersaturation is universally applicable in order to promote the nucleation density. In the case of carbon deposition, sustaining the high supersaturation conditions causes the deposition of graphitic carbon, which is stable phase under these conditions. Since the diamond nuclei could be formed only at an initial stage of deposition, it is a possibility to enhance the nucleation density of diamond, as far as the high supersaturation

conditions is limited in a precisely short time after starting the diamond deposition.

Therefore, in this paper, we investigated the enhancement effect of the carbon source supersaturation at initial stage of deposition on nucleation density of diamond fabricated by conventional microwave plasma.

2. EXPERIMENTAL

The deposition process in two sequential steps was performed in the plasma generated by conventional MW plasma CVD equipment, which was described in details elsewhere [3].

The experimental conditions for the two-step deposition technique are listed in Table I. In step 1, high supersaturation plasma was generated using the high concentration methane diluted by hydrogen (50%CH₄-H₂). Consequently, the certain carbonaceous material could be deposited onto (100) Si (B doped p-type, 10 Ωcm , 15 \times 20 \times 0.4 mm³) substrate for 1 min. The substrates used here were ultrasonically pretreated in

Table I Experimental Conditions.

	step 1	step 2
source gas	CH ₄ -H ₂	CH ₄ -O ₂ -H ₂
flow rate	100.0 sccm	100.0 sccm
CH ₄	50.0 vol%	10.0 vol%
O ₂	0.0 vol%	4.0 vol%
pressure	6.0 kPa	6.0 kPa
substrate	Si (100)	
size	15 \times 20 \times 0.6 mm ³	
temperature	700 °C	900 °C
MW power supply	220 W	410 W
duration time	1 min	0 ~15 min

the acetone bath with SiC (#100) powder. The substrate temperature shown in Table I was the value at the end of step 1, since the temperature was monotonically increased during the short duration time.

In step 2, diamond was grown on the carbonaceous material deposited during step 1 in the 10%CH₄-4%O₂-H₂. The conditions in step 2 were selected to be suitable for the growth of single diamond phase.

Both the deposits after step 1 and after step 2 were observed by a field emission scanning electron microscope (FE-SEM) and an atomic force microscope (AFM). Micro Raman scattering spectroscopy (Raman) and scanning tunneling

spectroscopy (STS) characterized the crystal structure and the band structure of the obtained samples, respectively. Moreover, surface enhanced Raman spectroscopy (SERS) was also carried out for higher sensitive measurement for the fine particles less than 100 nm in size. For SERS, Ag fine particles were evaporated in vacuum on the sample surface.

3. RESULTS AND DISCUSSIONS

The nuclei fabricated in step 1 and the diamond particles grown on nuclei in step 2 was observed. Fig. 1 shows the FE-SEM micrographs of deposits after step 1 and after step, respectively. AFM images of the correspondent deposits were

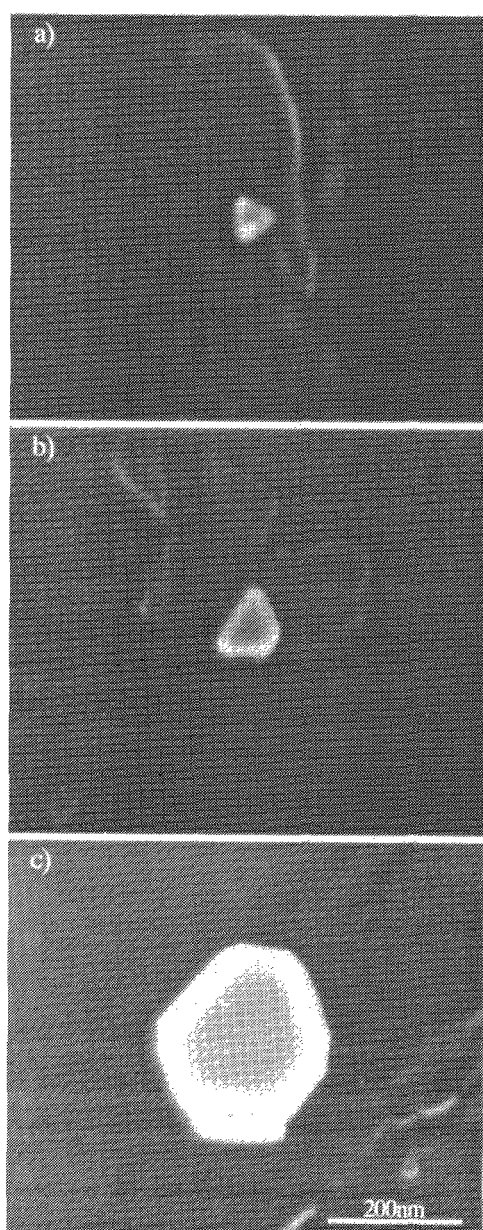


Fig. 1 Scanning electron micrographs of deposits, a) after step 1, b) after step 2 for 1 min, and c) after step 2 for 5 min.

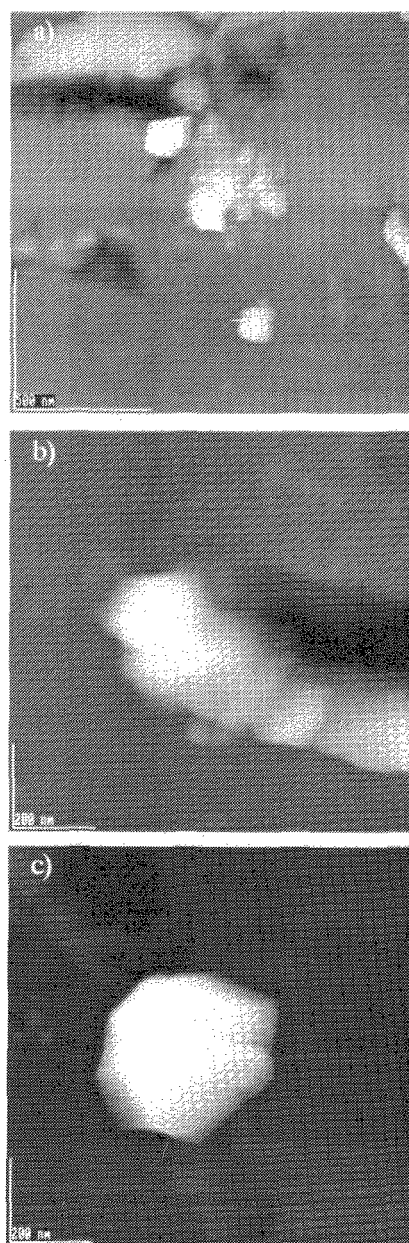


Fig. 2 Atomic force images of deposits, a) after step 1, b) after step 2 for 1 min, and c) after step 2 for 5 min.

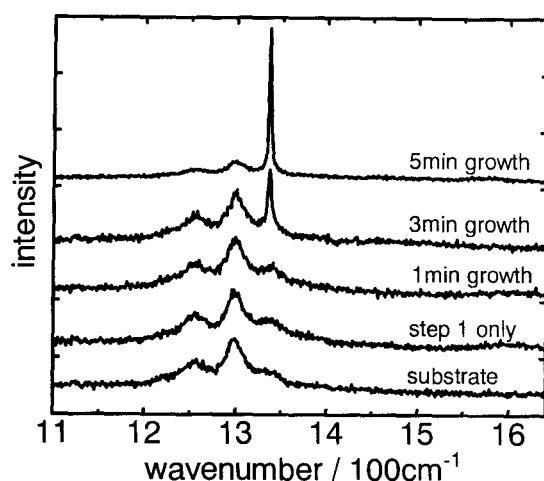


Fig. 3 Micro Raman scattering spectra of carbon deposits, as a function of deposition time.

also shown in Fig. 2. Although the observation area of each photograph in Figs. 1 and 2 were close to the center of substrate, the observed particles might be different from each other.

After step 1, the polygonal nuclei of around 50 nm in size were deposited on substrates, shown in Fig. 1 a). The number density of nuclei was estimated from SEM observation to be about $5 \times 10^6 \text{ cm}^{-2}$, which was two orders higher than without step 1. In Fig. 2 a), we can also observe not only three nuclei of 50 nm in size, but also the scratches and the hollows induced during the substrate pretreatment. It indicated that the nuclei could not be necessarily formed on the scratches or the hollows.

Fig. 1 b, c) and Fig. 2 b, c) indicate that the diamond particles were grown according to the duration time of step 2. The particle after 5 min growth, which was 400 nm in diameter, had the crystal habit clearly, shown in Fig. 1 c). During step 2, the grown particles were located at the position of nuclei deposited in step 1, which means that no nucleation might be occurred in step 2. These facts point out that the deposit in step 1 should act as nucleation site for diamond during step 2.

Raman spectra of these deposits were shown in Fig. 3. The particles grown in step 2 over 3 min could be identified to be diamond due to the sharp peak at 1333 cm^{-1} . On the other hand, the spectra of deposit for the short deposition time were identical to that of pre-treated substrate. This is due to the facts; carbon impurity was introduced into substrate surface during ultrasonic pretreatment, the small deposit for short duration time could not be detected due to insufficient Raman's sensitivity, and the samples, which was exposed to air after deposition, were evaluated in air. Therefore, in order to identify the structure of nuclei deposited in step 1, SERS and in-situ measurement in vacuum are necessary for the high sensitive measurement and the minimization of surface contamination, respectively. The long deposition (over 5 min) under the supersaturation condi-

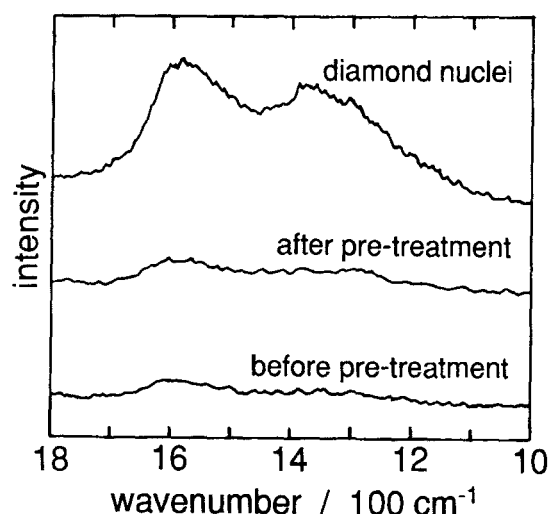


Fig. 4 Surface enhanced Raman spectra of carbon deposits after step 1, compared with those of substrate both before and after ultrasonic pre-treatment using SiC powder.

tions such as step 1, however, means that the spherical coarse particles should be deposited. These coarse particles could be identified to be glassy carbon by Raman. Hence, the nuclei deposited in step 1 might be glassy carbon, although the duration time was as short as 1 min.

SERS for the high sensitive measurements was executed for several samples with the Ag fine particles deposited by vacuum evaporation method. Fig. 4 shows the SERS spectra of deposit after step 1 and the spectra of substrates before and after the were shown for the polygonal particles deposited in step 1, ultrasonic pretreatment for the references. The distinctive peaks although normal Raman could detect no peaks. The carbonaceous materials was fabricated in step 1, which was clearly different from either the carbon contamination originally presented on the substrate or the contamination introduced during the pretreatment. The structure of deposit in step 1 was identified to be nearly glassy carbon. The long duration under the conditions of step 1 could cause the large spherical particles to be deposited, while the deposit in step 1 (short duration) yielded the fine polygonal particles. In spite of the difference of deposit morphology, both the deposits were identified to be glassy carbon. This is due to the features of SERS that can detect the signal from several atomic layers on samples. Therefore, the surface structure of polygonal fine particles with less than 100 nm in diameter was nearly glassy carbon, although the inner structure has the possibility to be different from the surface.

STS was also performed for the measurements of band structure of the deposit using scanning tunneling microscope. Fig. 5 shows several spectra of deposited particles after step 1 and after step 2. Although the measurements were lack of reproducibility at present, the fine particles deposited in step 1

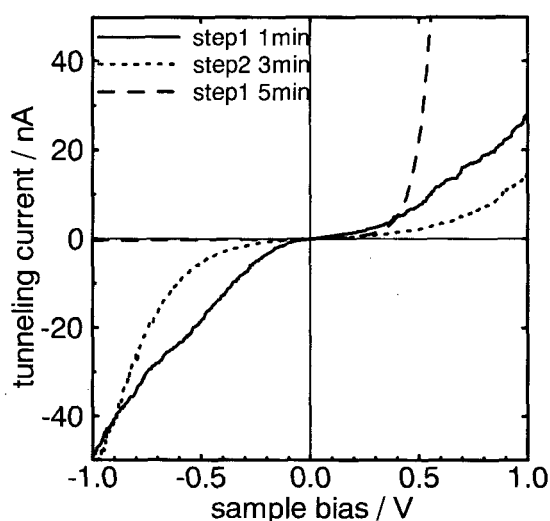


Fig. 5 Scanning tunneling spectra of carbon deposits after step1 and step2.

might have the surface layer with low electron conductivity, which was in good agreement with the results of SERS. This feature was different from that of deposit for 5min under the conditions of step 1. This fact might correspond to the difference of morphology observed by AFM and FE-SEM. The STS spectrum after step 2, however, means neither the band structure of diamond nor that of p-type conduction surface layer on H-terminated diamond surface. Contrary to this spectrum, the Raman spectra shown in Fig. 3 means that the deposits were identified to be the single phase of diamond. This unexpected

spectrum might be due to the facts that the contamination was present on the sample surface, which was introduced by the exposure of air after the preparation of fine particles, and that the surface structure was reconstructed. In the future, we must execute the in-situ measurements on the real surface structure in detail.

4. CONCLUSIONS

Under the supersaturation conditions, the carbonaceous fine particles were deposited in a high density on Si substrate. These fine particles could act as nucleation sites during successive diamond growth step. Consequently, we achieved the enhancement of nucleation density up to $5 \times 10^6 \text{cm}^{-2}$. Raman and STS results show that the structure of carbonaceous particles might be gassy carbon.

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