Journal of the Korean Chemical Society
2004, *Vol. 48, No. 6*
Printed in the Republic of Korea

단 신

다이아몬드 막 특성 향상을 위한 CH_4-H_2-O_2 플라즈마 내의 CH_4 기체 유량의 시간 의존 싸이클릭 변조 프로세스

김 성 훈*
신라대학교 나노화학소재공학과
(2004. 8. 24 접수)

Time-Dependent Cyclic Modulation Process of CH_4 Gas Flow Rate in CH_4-H_2-O_2 Plasma for the Enhancement of Diamond Film Characteristics

Sung-Hoon Kim*
Department of Nano Materials Chemistry & Engineering, Silla University, Busan 617-736, Korea
(Received August 24, 2004)

주제어: 다이아몬드 막, CH_4 기체 유량의 시간의존 변조, 산소 혼입, 마이크로파 플라즈마 화학 기상 증착 장치
Keywords: Diamond Films, Time-Dependent Modulation of CH_4 Flow Rate, Oxygen Incorporation, Microwave Plasma-Enhanced Chemical Vapor Deposition

The diverse practical application of the synthetic diamond films requires the improvement of the diamond quality and the diamond nucleation density.[1,2] For the enhancement of the diamond films quality, the incorporation of the etching gases, such as oxygen, carbon monoxide or carbon dioxide, has been well known as the promising in-situ technique.[3,4] Previously, we reported the cyclic modulation technique of atomic hydrogen concentration for the enhancement of the diamond films quality.[5] The main reason for the enhancement of the diamond quality was attributed to the superior etching capability of nondiamond components, compared with the diamond component, in the film by oxygen related molecule or the atomic hydrogen.[6] For the enhancement of the diamond nucleation density, the incorporation of the etching gas components in the source gas was known to give either the enhancing or the detrimental effect according to their amount.[7] In case of higher concentration, the oxygen or the atomic hydrogen can remove even the sub-critical size of diamond nuclei as well as the nucleation site on the silicon surface.[8] This leads to a longer incubation time for the nucleation, and as a result, the diamond nucleation density decreases. In case of lower concentration, on the other hand, the etching gas components might facilitate the suitable nucleation sites on the substrate.[9] Consequently, they can enhance the diamond nucleation density.

In this work, we suggest a new method to enhance both the diamond quality and the nucleation density than those of the oxygen incorporation process or the cyclic process. By simply combining the cyclic modulation technique of CH_4 flow and the oxygen incorporation process, we could noticeably enhance the diamond film characteristics.

EXPERIMENTAL SECTION

Diamond films were deposited on the 10.0×10.0 mm^2 pretreated (100) Si substrate in a horizontal-type MPECVD system. The substrate was merely heated by the plasma. We deposited diamond film under substrate temperature=*ca.* 850 °C, microwave power

−800 W, and total pressure−5.33 kPa condition. The pretreatment was carried out by an ultrasonic treatment for 30 minutes using diamond powders in ethanol solution. Before the deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4, H_2 and O_2 were used as source gases. Total flow rate was fixed at 100 standard cm^3 per minute (sccm). Concentrations of CH_4 and O_2 were fixed at 1.5% and 0.5%.

To elucidate the effect of the cyclic process on the enhancement of the diamond nucleation density and the diamond quality, we deposited the diamond film via two different ways, namely, the cyclic process and the normal process. For the cyclic process, we incorporated the cyclic modulation process of CH_4 flow during the initial deposition stage. The cyclic modulation was carried out through on/off control of CH_4 flow. Namely, it was started from H_2+CH_4−O_2 plasma (CH_4 flow on) and ended in H_2+O_2 plasma (CH_4 flow off). Actually, it was proceeded as H_2−CH_4+O_2 (120 s)→H_2−O_2 (120 s)→H_2+CH_4+O_2 (120 s)→H_2−O_2 (120 s), then 32 min depositing the diamond film under H_2+CH_4 plasma condition. So, the total on/off CH_4 flow modulation time was 8 min and the total reaction time was 40 minutes. For the normal process, we deposited the diamond films for 40 min without the incorporation of the CH_4 flow cyclic modulation and the oxygen incorporation. The detailed reaction flow condition for the different samples was shown in *Table* 1.

We investigated the detailed surface states, and the grain morphologies using field emission scanning electron microscopy (FESEM). The qualities of diamond grains on the pretreated glass substrate were investigated by a micro-Raman spectrometer (Renishaw 2000) with *ca.* 1 mm spot size using an Ar laser source.

RESULTS AND DISCUSSION

First of all, we investigated the surface images of as-deposited diamond films without the oxygen incorporation in the source gas. To reduce the measurement error, we set the measuring position as *ca.* 1 mm apart from the outermost edge of the substrate. *Fig.* 1a shows FESEM image of as-deposited diamond films, in case of the normal process (sample A). The diamond nucleation density on the pretreated Si substrate surfaces was counted about 1.8×10^{10} (nuclei/cm^2). *Fig.* 1b shows FESEM image of as-deposited diamond films, in case of the CH_4 flow rate on/off cyclic modulation process under CH_4+H_2 plasma condition (sample B). The number density of diamond nuclei on Si substrate was counted more than 8.5×10^{10} (nuclei/cm^2). *Figs.* 1c and d show FESEM images of as-deposited diamond grains, in case of CH_4 flow on/off cyclic

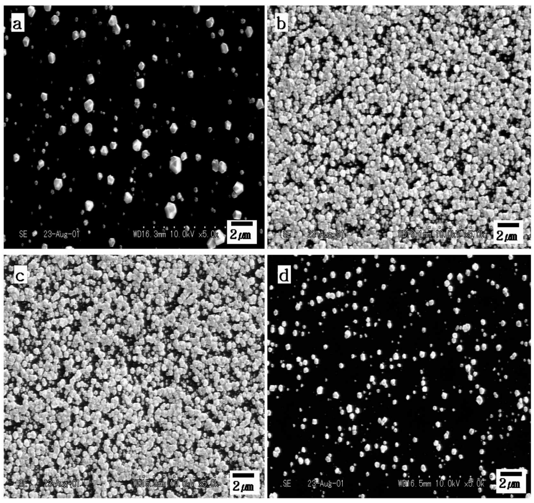

Fig. 1. FESEM images of as-deposited diamond grains of (a) sample A, (b) sample B, (c) sample C and (d) sample D.

Table 1. Reaction flow conditions for different samples

Process / Samples	H_2 flow rate (sccm)	CH_4 flow rate (sccm)	O_2 flow rate (sccm)	CH_4 flow cyclic on/off time under CH_4-H_2-O_2 plasma (min)	CH_4-H_2 plasma reaction time after cyclic process (min)
Sample A	98.5	1.5	0	0	40
Sample B	98.5	1.5	0	8	32
Sample C	98.0	1.5	0.5	8	32
Sample D	98.0	1.5	0.5	8	32
				(O_2 flow on/off cyclic time)	

modulation process (sample C) and O_2 flow on/off cyclic modulation process (sample D) under the condition of the oxygen incorporation. The number densities of nuclei on Si substrate were counted about 7.8×10^{10} (*Fig.* 1c) and 2.0×10^{10} (*Fig.* 1d) (nuclei/cm^2), respectively. Based on the results of *Fig.* 1, we suggest that the CH_4 flow on/off cyclic modulation process with or without the incorporation of oxygen can increase the diamond nucleation densities on the pretreated Si substrate. In addition it is also derived, from the comparing results of *Figs.* 1a with d, that the oxygen flow on/off cyclic modulation process doesnt give rise to the noticeable increase in the diamond nucleation density, compared with the normal process.

To investigate the enhancement of the diamond quality by the oxygen incorporation under the condition of the cyclic modulation process, we investigated the diamond grains on Si substrate using micro-Raman spectroscopy with *ca.* 1 μm spot size. *Fig.* 2 shows micro-Raman spectra of the different samples. It reveals the enhancement of the diamond quality by the cyclic modulation process of CH_4 flow rate (*Figs.* 2b and c) or O_2 flow rate (*Fig.* 2d), compared with the normal process. To analyze the extent of the diamond quality enhancement according to the different samples we measured the variation of the relative intensity ratio (I_d/I_a) of diamond (at 1,332 cm^{-1}) to amorphous carbon (around 1,500 cm^{-1}) as shown in *Table* 2.

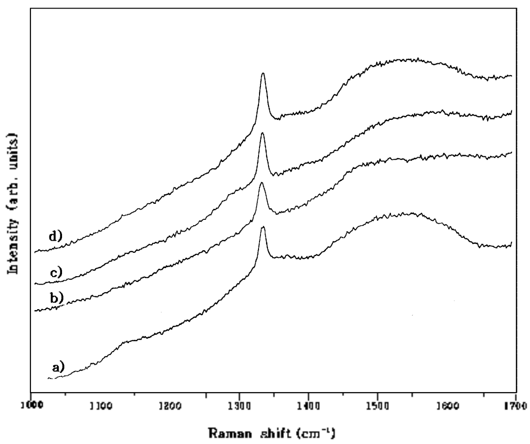

Fig. 2. Micro-Raman spectra for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

Table 2. I_d/I_a values of micro-Raman spectra for (a) sample A, (b) sample B, (c) sample C and (d) sample D

Samples	Sample A	Sample B	Sample C	Sample D
I_d/I_a	1.1±0.15	2.0±0.07	2.3±0.05	2.4±0.08

Based on the results of the I_d/I_a intensity according to the samples A through D, it is suggested that the cyclic modulation process would enhance the diamond quality with or without the incorporation of oxygen (compare samples A with B, C and D). Previously, it was reported that the cyclic modulation process could produce more atomic hydrogen during the plasma reaction.[9,10] These results reveal that the abundant amount of etching source gas, such as the atomic hydrogen and the oxygen, in the plasma during the cyclic process seems to be associated with the diamond quality enhancement, because the atomic hydrogen and oxygen can more readily etch away amorphous carbon than the diamond component in the grain.

By comparing I_d/I_a of sample B with that of sample C, we observed the increase in I_d/I_a at sample C. It reveals the relative increase of diamond component in the grain by the oxygen incorporation even under the similar process condition of the CH_4 flow on/off cyclic modulation.

In addition, the combined results of *Figs.* 1 and 2 for samples C and D indicate that the diamond nucleation density of sample C would be enhanced while the diamond quality was maintained. These results reveal the possibility to enhance not only the diamond quality but also the diamond nucleation density by the on/off cyclic modulation of CH_4 flow under CH_4-H_2-O_2 flow condition.

The decrease in the diamond nucleation density by the on/off cyclic modulation of O_2 flow (sample D) seems to be due to the removal of sub-critical size diamond nuclei as well as nucleation sites on a silicon surface by the excess etching source gases, such as atomic hydrogen and the oxygen related components.[8]

CONCLUSIONS

Both the diamond nucleation density and the diamond quality could be enhanced by the on/off cyclic modulation process of CH_4 flow under the condition of the oxygen incorporation. Regardless of the oxygen incorporation in the source gas, not only the diamond quality but also the diamond nucleation density was enhanced by the on/off cyclic modulation of CH_4 flow.

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