

단 신

다이아몬드 막 특성 향상을 위한 $\text{CH}_4\text{-H}_2\text{-O}_2$ 플라즈마 내의 CH_4 기체 유량의 시간 의존 싸이클릭 변조 프로세스

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(2004. 8. 24 접수)

Time-Dependent Cyclic Modulation Process of CH_4 Gas Flow Rate in $\text{CH}_4\text{-H}_2\text{-O}_2$ Plasma for the Enhancement of Diamond Film Characteristics

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(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 $10.0 \times 10.0 \text{ mm}^2$ 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 H₂ plasma for a few minutes. CH₄, H₂ and O₂ were used as source gases. Total flow rate was fixed at 100 standard cm³ per minute (sccm). Concentrations of CH₄ and O₂ 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 CH₄ flow during the initial deposition stage. The cyclic modulation was carried out through on/off control of CH₄ flow. Namely, it was started from H₂+CH₄+O₂ plasma (CH₄ flow on) and ended in H₂+O₂ plasma (CH₄ flow off). Actually, it was proceeded as H₂+CH₄+O₂ (120 s)→H₂+O₂ (120 s)→H₂+CH₄+O₂ (120 s)→H₂+O₂ (120 s), then 32 min depositing the diamond film under H₂+CH₄ plasma condition. So, the total on/off CH₄ 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 CH₄ 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/cm²). Fig. 1b shows FESEM image of as-deposited diamond films, in case of the CH₄ flow rate on/off cyclic modulation process under CH₄+H₂ plasma condition (sample B). The number density of diamond nuclei on Si substrate was counted more than 8.5×10^{10} (nuclei/cm²). Figs. 1c and d show FESEM images of as-deposited diamond grains, in case of CH₄ flow on/off cyclic

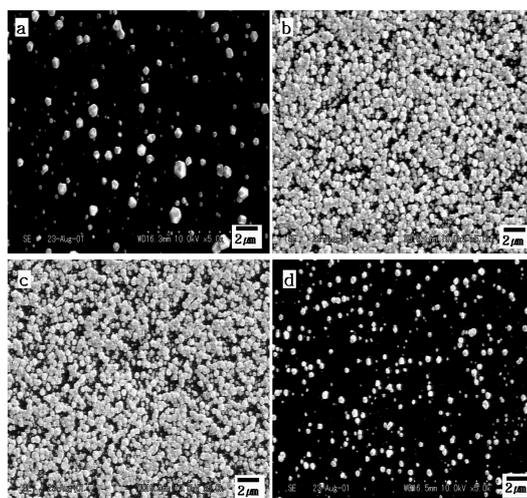


Fig. 1. FESEM images of as-deposited diamond grains of (a) sample A, (b) sample B, (c) sample C and (d) sample D.

Table 1. Reaction flow conditions for different samples

Samples	Process	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

(O₂ flow on/off cyclic time)

modulation process (sample C) and O₂ 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/cm²), respectively. Based on the results of Fig. 1, we suggest that the CH₄ flow on/off cyclic modulation process with or without the incorporation of oxygen can increase the diamond nucleation densities on the pre-treated 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 doesn't 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 CH₄ flow rate (Figs. 2b and c) or O₂ 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.

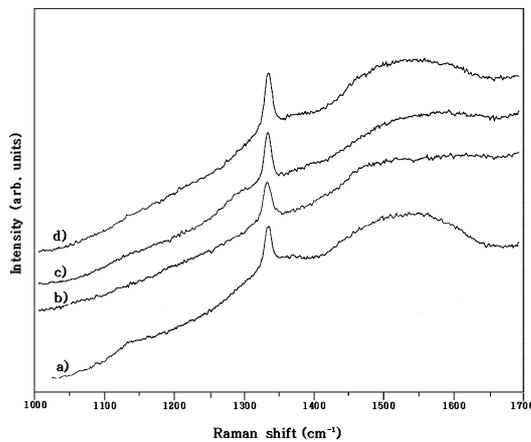


Fig. 2. Micro-Raman spectra for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

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 CH₄ 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 CH₄ flow under CH₄-H₂-O₂ flow condition.

The decrease in the diamond nucleation density by the on/off cyclic modulation of O₂ 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 CH₄ 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 CH₄ flow.

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