Time-Dependent Cyclic Modulation Process of CH<sub>4</sub> Gas Flow Rate in CH<sub>4</sub>-H<sub>2</sub>-O<sub>2</sub> Plasma for the Enhancement of Diamond Film Characteristics

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The diverse practical application of the synthetic diamond films requires the improvement of the diamond quality and the diamond nucleation density. 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. Previously, we reported the cyclic modulation technique of atomic hydrogen concentration for the enhancement of the diamond films quality. The main reason for the enhancement of the diamond quality was attributed to the superior etching capability of non-diamond components, compared with the diamond component, in the film by oxygen related molecule or the atomic hydrogen. 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. 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. 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. 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<sub>4</sub>, flow and the oxygen incorporation process, we could noticeably enhance the diamond film characteristics.

EXPERIMENTAL SECTION

Diamond films were deposited on the 100×100 mm<sup>2</sup> 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℃, microwave power...
-800 W, and total pressure=5.23 kPa condition. The pretreatment was carried out by an ultrasonic treatment for 30 minutes using diamond powders in ethyl alcohol solution. Before the deposition reaction, we cleaned the substrate with H\textsubscript{2} plasma for a few minutes. CH\textsubscript{4}, H\textsubscript{2}, and O\textsubscript{2} were used as source gases. Total flow rate was fixed at 100 standard cm\textsuperscript{3} per minute (sccm). Concentrations of CH\textsubscript{4} and O\textsubscript{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\textsubscript{4} flow during the initial deposition stage. The cyclic modulation was carried out through on/off control of CH\textsubscript{4} flow. Namely, it was started from H\textsubscript{2}−CH\textsubscript{4}−O\textsubscript{2} plasma (CH\textsubscript{4} flow on) and ended in H\textsubscript{2}+O\textsubscript{2} plasma (CH\textsubscript{4} flow off). Actually, it was proceeded as H\textsubscript{2}−CH\textsubscript{4}+O\textsubscript{2} (120 s)→H\textsubscript{2}−O\textsubscript{2} (120 s)→H\textsubscript{2}+CH\textsubscript{4}+O\textsubscript{2} (120 s)→H\textsubscript{2}+O\textsubscript{2} (120 s), then 32 min depositing the diamond film under H\textsubscript{2}+CH\textsubscript{4} plasma condition. So, the total on/off CH\textsubscript{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\textsubscript{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.

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<th>Table 1. Reaction flow conditions for different samples</th>
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<td>Sample D</td>
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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\textsuperscript{9} (nuclei/cm\textsuperscript{2}). Fig. 1b shows FESEM image of as-deposited diamond films, in case of the CH\textsubscript{4} flow rate on/off cyclic modulation process under CH\textsubscript{4}+H\textsubscript{2} plasma condition (sample B). The number density of diamond nuclei on Si substrate was counted more than 8.5×10\textsuperscript{9} (nuclei/cm\textsuperscript{2}). Figs. 1c and d show FESEM images of as-deposited diamond grains, in case of CH\textsubscript{4} flow on/off cyclic modulation processes. The grain sizes and qualities of diamond grains were increased due to the oxygen incorporation. Therefore, it was concluded that the oxygen incorporation plays an important role in the diamond nucleation process.
modulation process (sample C) and O, 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 $7.8 \times 10^4$ (Fig. 1c) and $2.0 \times 10^5$ (Fig. 1d) (nuclei/cm$^2$), respectively. Based on the results of Figs. 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 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 does not 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 ($I_d$/$I_s$) of diamond (at 1332 cm$^{-1}$) to amorphous carbon (around 1500 cm$^{-1}$) as shown in Table 2.

![Graph](image-url)

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

<table>
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<tr>
<th>Samples</th>
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<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
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<tr>
<td>$I_d$/$I_s$</td>
<td>1.1±0.15</td>
<td>2.0±0.07</td>
<td>2.3±0.08</td>
<td>2.4±0.08</td>
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Based on the results of the $I_d$/$I_s$ 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. These results reveal that the abundant amount of etching source gas, such as the atomic hydrogen and 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 $I_d$/$I_s$, of sample B with that of sample C, we observed the increase in $I_d$/$I_s$ 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, 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.

**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.

REFERENCES