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다이아몬드 박막의 저온 선택 증착 향상

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Enhancement of Low Temperature Selective Deposition of Diamond Film

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For the practical application of diamond films to electronic devices, especially field emission displays (FEDs), the achievement of low temperature deposition of diamond film, namely, the diamond film deposition on indium tin oxide (ITO) glass substrate is preferential[1-3]. Furthermore, the enhancement of the diamond nucleation densities is essential to increase the efficiency of field emission characteristics, such as low operating voltage, high emission current, emission uniformity, and so forth. From the manufacturing point of view, the patterning of the diamond films to be suitable for the field emitter is also indispensable. However, unfortunately, the patterning of the diamond films has been regarded as the most difficult barrier because of the hardness and chemical inertness of diamond[4]. Recently, we were able to achieve the patterning of the diamond film via the enhancement of the selective deposition of diamond film on glass substrate by the cyclic process[5]. The cyclic process is the in-situ process that has the advantage for the further enhancement of the diamond nucleation densities, consequently increasing the efficiency of diamond field emission characteristics. For the cyclic process, we incorporated the cyclic modulation of CH_4 flow rate during the initial deposition stage. The cyclic modulation was carried out through the on-off control of CH_4 flow. Namely, it was started from $H_2 + CH_4$ plasma (CH_4 flow on) and ended in H_2 plasma (CH_4 flow off)[6].

This work presents the method to obtain an enhanced selective deposition of diamond film having high nucleation densities on pretreated glass substrate under the relative low temperature (about 450 °C) deposition condition. In detail, we deposited the diamond film by changing the cyclic modulation time interval during the cyclic process. We investigated the variation of the diamond nucleation densities including the grain sizes as a function of the cyclic modulation time interval. Based on these results, we discussed the cause for the enhancement of the selective deposition of diamond film on glass substrate as a function of the cyclic modulation time interval.

EXPERIMENTAL SECTION

We deposited diamond films on the 1.0 × 1.0 mm^2 patterned glass substrate in a vertical-type MPECVD system. The pattern could be achieved by unidirectional scratching on the selected area of glass substrate using *ca.* 3 μm size diamond powders. Actually, unidirectional scratching was achieved by manual for 3 times with patch incorporating diamond powders and acetone. Before patterning, we exposed the selected area for the scratch via covering the residual glass substrate surface using tape. In this way, we made both the pretreated and the untreated areas on glass substrate, consequently obtaining the patterned glass substrate. The low temperature (*ca.* 450 °C) diamond deposition in this work could

be achieved by keeping the substrate distance (*ca.* 3 cm) from the plasma under the relative low microwave power (400 W) and total pressure (1.73 kPa) condition.[7]

Before the deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. H_2 flow rate and CH_4 flow rate were fixed as 200 sccm (standard cm^3 per minute) and 4 sccm, respectively.

To elucidate the effect of the cyclic process on the enhancement of the selectivity of the diamond film deposition and the diamond nucleation density, 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 of CH_4 flow rate during the initial deposition stage. The cyclic modulation was carried out through on/off control of CH_4 flow. Namely, it was started from $H_2 + CH_4$ plasma (CH_4 flow on) and ended in H_2 plasma (CH_4 flow off). The total on/off CH_4 flow modulation time was fixed as 12 min. After the cyclic modulation, we deposited the diamond film for 5 h and 48 min. So, the total reaction time was 6 hours. For the normal process, we deposited the diamond film for 6 h without the incorporation of the cyclic modulation during the initial deposition stage.

The detailed surface states and the grain sizes were investigated by using scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

After 6 h deposition reaction, we first investigated the surface images of as-deposited diamond films, especially around boundary areas between the pretreated surface and the untreated surface on glass substrate. *Figs.* 1a – d show SEM images around boundary areas of as-deposited diamond films in the normal process (*Fig.* 1a) and in the cyclic process having the CH_4 flow on – off – 30/30 sec (*Fig.* 1b), 60/60 sec (*Fig.* 1c), and 90/90 sec (*Fig.* 1d), respectively. As shown in these figures, on the untreated area of glass substrate, we could not observe any distinct difference of the diamond nucleation densities between the cyclic process and the normal process. On the pretreated area of glass substrate, however, we could observe the enhancement of the diamond nucleation densities.[5] The number densities of nuclei on the pretreated glass substrate were counted as *ca.* 8.0×10^6 (normal process), *ca.* 1.1×10^7 (30/30 sec cyclic process), *ca.* 1.3×10^7 (60/60 sec cyclic process), and *ca.* 1.9×10^7 (90/90 sec cyclic process), respectively. From these results, we can undoubtedly confirm the enhancement of the diamond nucleation densities by the cyclic process, as previous report.[5] In addition, by comparing the results according to the cyclic modulation time interval, we can suggest that the diamond nucleation densities would be much more enhanced under 90/90 sec, namely, under the longer cyclic modulation time interval condition (compare *Figs.* 1b, c with d). Indeed, we can obtain the highest diamond nucleation densities on the pretreated area, with little change of the diamond nucleation densities on the untreated area, by using the cyclic process having the longer cyclic modulation time interval. Therefore, we suggest that the cyclic process having longer cyclic modulation time interval may be the optimal condition for the enhancement of the selectivity of diamond film deposition on glass substrate.

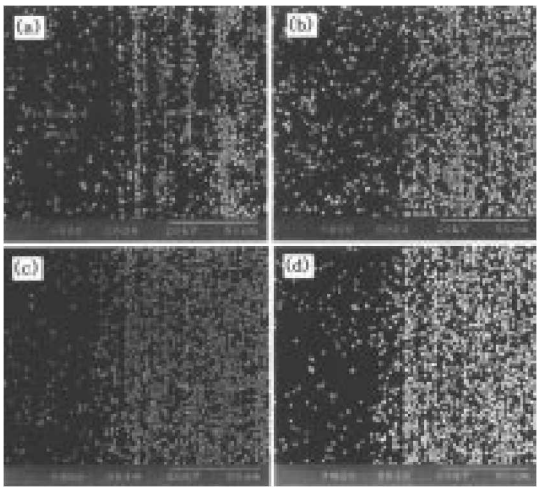

Fig. 1. SEM images of as-deposited diamond films around the boundary areas between the pretreated surface and the untreated surface under (a) the normal process, (b) 30/30 sec cyclic process, (c) 60/60 sec cyclic process, and (d) 90/90 sec cyclic process, respectively.

To closely measure the grain sizes, we investigated the surface states of the pretreated surfaces by a high-magnified image of SEM (see *Figs.* 2a–d). The average grain sizes of the diamond nuclei were measured as *ca.* 0.42 μm (normal process), *ca.* 0.45 μm (30/30 sc cyclic process), and *ca.* 0.45 μm (60/60 sec cyclic process), and

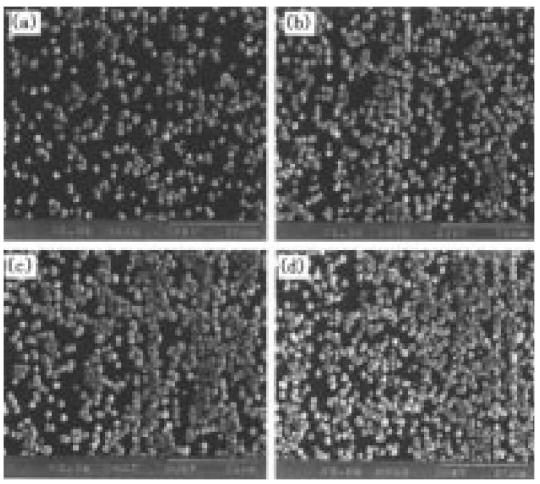

Fig. 2. High-magnified SEM images of the films deposited on the pretreated glass substrate under (a) the normal process, (b) 30/30 sec cyclic process, (c) 60/60 sec cyclic process, and (d) 90/90 sec cyclic process, respectively.

ca. 0.47 μm (90/90 sec cyclic process) in diameter. These results also indicate a little increase in the average grain size of the diamond nuclei by the cyclic process,[5] especially under the condition of the longer cyclic modulation time interval condition.

The cause for the enhancement of the diamond nucleation densities on the pretreated glass substrate by the cyclic process may be attributed to the cyclic modulation of the H_2/CH_4 concentration ratio in the source gas. As previous reports,[7] the pretreated area has rough surfaces. The rough surface can enhance the suitable diamond nucleation sites by the cyclic process having more atomic hydrogen concentration than the normal process. In the case of the untreated area, however, the relatively smooth surface states seem to be insufficient for readily diamond nucleation by the cyclic process. Consequently, in case of glass substrate, the cyclic process can enhance the selective deposition of diamond film via the relative increase in the nucleation densities on the pretreated area than on the untreated area. In addition, the enhancement of the selectivity of diamond film deposition under the longer cyclic modulation time interval condition may be related to the concentration of the atomic hydrogen. As previous report[8], we understand the gradual increase of atomic hydrogen concentration during CH_4 flow off time and the abrupt decrease of atomic hydrogen concentration during CH_4 flow on time. Therefore, the longer cyclic modulation time interval (90/90 sec) condition may impose more atomic hydrogen concentration, compared with the shorter cyclic modulation time interval condition (30/30 sec) in the cyclic process. Consequently, 90/90 sec cyclic process would be the optimal condition for the enhancement of the selectivity of diamond film deposition via the atomic hydrogen interaction with the pretreated glass substrate.

CONCLUSIONS

The diamond nucleation densities on the pretreated glass substrate would be much more enhanced under the condition of the longer cyclic modulation time interval in the cyclic process. Consequently, the cyclic process having longer cyclic modulation time interval may be the optimal condition for the enhancement of the selectivity of diamond film deposition on glass substrate via the relative increase in the nucleation densities on the pretreated area, compared with the untreated area. The cause for this may be attributed to the increase in the amount of atomic hydrogen concentration during the cyclic process with increasing the cyclic modulation time interval.

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