Journal of Korean Vacuum Science & Technology; JKVST
Vol. 4, No. 1, March 2000, pp. 18~22

Enhancement of the nucleation density for diamond film on the pretreated glass substrate by the application of cyclic modulation of the source-gas flow rate

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(Received January 31, 2000)

For the enhancement of the nucleation density of the diamond film, we introduced the cyclic process. The cyclic process was carried out by the on/off control of CH_4 flow rate for a relatively short time (10 min), compared with the total reaction time (6 h). Prior to depositing the diamond film, we made the pretreated glass substrate via the unidirectional scratch using ~1 μm size diamond powders. Diamond films were deposited on the pretreated glass substrate in a microwave plasma enhanced chemical vapor deposition (MPECVD) system. We observed the enhancement of the nucleation density of the diamond films caused by the cyclic process. Detailed surface morphologies of the substrate were investigated after the cyclic process. Based on these results, we discussed the cause for the enhancement of the nucleation density on the pretreated glass substrate by the cyclic process.

I. Introduction

Owing to the several specific properties of diamond, such as the highest thermal conductivity and low thermal expansion coefficient at room temperature, high band gap energy, and highest hardness among the materials [1,2], diamond film is considered to be suitable for the high performance electronic devices. Considering the practical application of diamond films to electronic devices, both the heteroepitaxial growth of the diamond film, namely, the {100}-oriented texture growth of diamond film on (100) Si substrate, and the patterning of diamond film have been regarded as the most urgent step to be considered.

It is known that {100}-oriented diamond grains produce a very smooth surface suitable for electronic devices [3,4]. The bias enhanced (BEN) method, which was previously developed for diamond nucleation on a non-treated Si substrate [5], has been applied to the {100}-oriented texture growth of diamond film on (100) Si substrate [3,5]. Although the BEN method enables {100}-oriented texture growth. Further refinement of the process is necessary to improve film characteristics, such as diamond quality and large area deposition. Among the many techniques for improving film properties, the cyclic process is the choice for increasing the film growth rate as well as diamond quality [6,7].

One of the most difficult barriers for the application of synthetic diamond films to electronic devices lies in the patterning of the diamond. The conventional technique for fabricating the patterns of semiconductor materials is the etching technique, which is difficult to carry out due to the hardness and chemical inertness of diamond. Therefore, the selective deposition of diamond film has been regarded as a promising method to replace the etching technique. For the selective growth, the conventional method is the pretreatment techniques of substrates with the masking process [8]. This process may use the favorable nucleation of diamonds on the pretreated area of the substrate. For the practical application, therefore, it is important to enhance the nucleation density on the pretreated area of the substrate.

This work presents the enhancement of the nucle-

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ation density on the pretreated glass substrate by using the cyclic process in a MPECVD system. After the cyclic process, detailed studies on the surface morphologies and microstructures have been carried out. Based on these results, we discuss the cause of the enhancement of the nucleation density on the pretreated glass substrate.

II. Experimental

Diamond films were deposited on the pretreated glass substrate in a conventional-type MPECVD system. 1×1 cm^2 squared slide glass (thickness = ~2 mm) was used as a substrate. The temperature of the substrate was measured by a backside-touching K-type chromel-alumel thermocouple, as ~450°C. CH_4 and H_2 were used as source gases. The gas flow rate and the total pressure in the reaction chamber was precisely controlled by a mass flow controller (MFC; Tylan FC 260) and an automatic pressure controller (MKS 253A), respectively. H_2 flow rate was fixed as 200 sccm. CH_4 flow rates were varied as 2, 4, 6, and 8 sccm according to the reaction processes. Total pressure in the reaction chamber and the microwave power were set as 13 Torr and 400 W, respectively.

We investigated the morphologies of the film surfaces and the nucleation densities using the scanning electron microscopy (SEM).

III. Results & Discussion

The pretreatment was carried out by unidirectional scratch using 1 μm size diamond powders. Before pretreatment, we exposed the specified area for the scratch by covering the residual glass substrate surface using tape. In this way, we made both the pretreated and the untreated areas on the glass substrate. The substrate, placed on the Mo substrate holder, was cleaned with H_2 plasma for 10 minutes at the initial stage of the process. It was merely heated by the plasma. We can lower the substrate temperature as ~450°C by separating the substrate from the plasma. The cyclic modulation of the source gas flow rate was carried out by on/off control of CH_4 flow rate. Namely, it was started from H_2 + CH_4 plasma (CH_4 flow on) and ended in H_2 plasma (CH_4 flow off): H_2 + CH_4 (150 sec) → H_2 (180 sec) → H_2 + CH_4 (150 sec) → H_2 (120 sec). Total on/off CH_4 flow modulation time was fixed as 10 min.

To elucidate the effect of the cyclic modulation on the nucleation density, we deposited the diamond films in two different ways, namely, the normal process and the cyclic process. After depositing the diamond films, we compared the results with each other. For the normal process, we deposited the diamond films for 6 h without the incorporation of the cyclic modulation. For the cyclic deposition process, we incorporate the cyclic modulation for 10 min during the deposition process. In this case, the deposition time was 5 h and 50 min. Therefore the total reaction time was 6 h.

After 6 h reaction, we investigated the surface images of as-deposited diamond films on the pretreated glass substrate. Figs. 1~3 show SEM images, in the case of the normal process, of as-deposited diamond films on the pretreated glass substrate under 2, 4, and 6 CH_4 flow rate conditions. We can observe the well-developed grains on the pretreated glass substrate. By the micro-Raman spectroscopy, we investigated the components of the grain. We

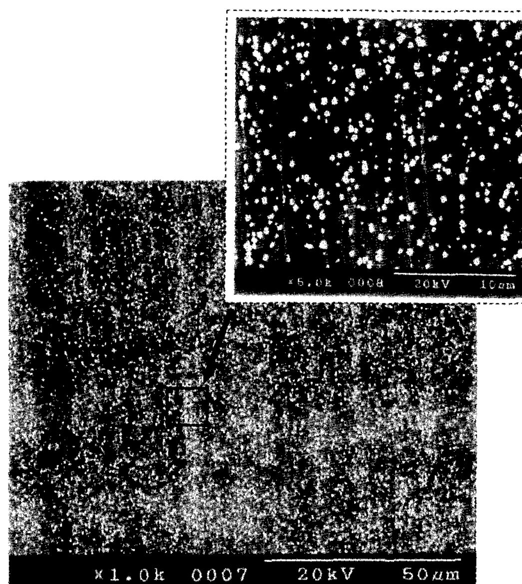

Fig. 1. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the normal process, under 2 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

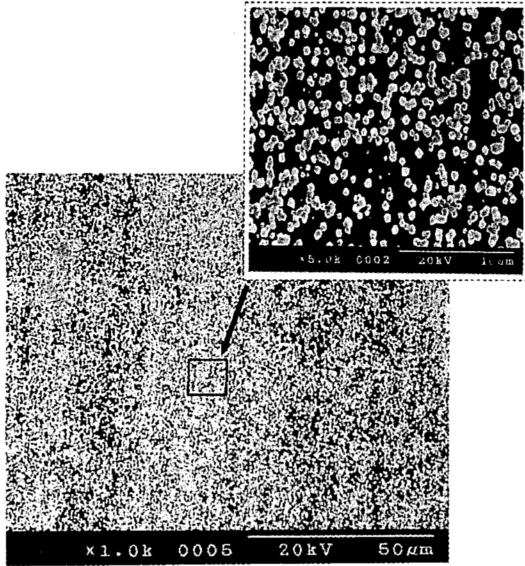

Fig. 2. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the normal process, under 4 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

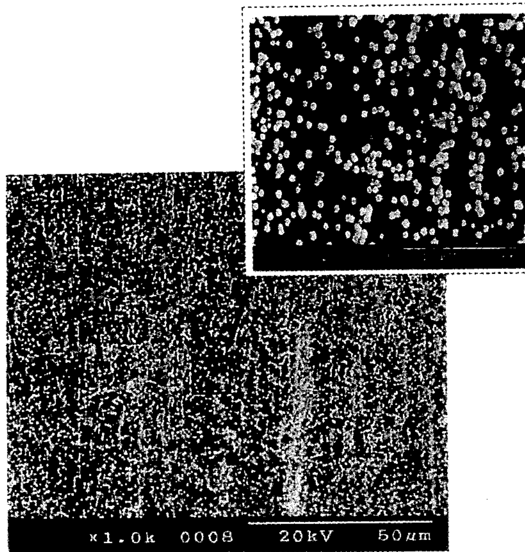

Fig. 3. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the normal process, under 6 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

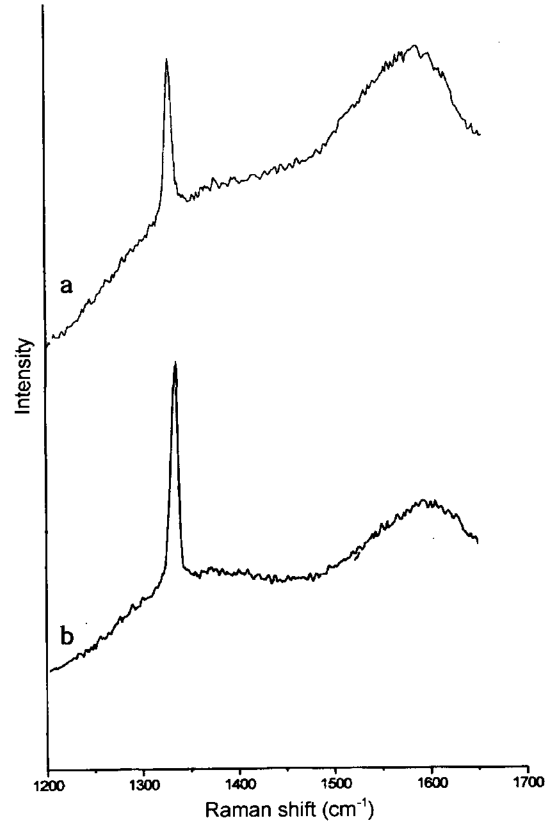

Fig. 4. Raman spectra of the films deposited on the pretreated glass substrate in (a) the normal process and (b) the cyclic process under 2 sccm CH_4 flow rate condition.

could find the peaks of the diamond (at 1332 cm^{-1}) and the amorphous carbon (around 1500 cm^{-1}), as shown in Fig. 4a. Obviously, it indicates the existence of diamond components in the grain. To measure the nucleation density, we investigated the detailed surface states of the pretreated surfaces by the high magnified images (see the insets of Figs. 1 ~3) of SEM. In the case of 2, 4, and 6 sccm CH_4 flow rates, the number density of the nuclei on the pretreated surfaces was counted as about 1.1×10^{10} (Fig. 1), 1.3×10^{10} (Fig. 2), and 1.1×10^{10} (Fig. 3) (nuclei/cm^2), respectively.

In the case of the cyclic process, we also investigated the surface images of as-deposited diamond films as a function of CH_4 flow rate (see Figs. 5-7). By comparing the surface images (Figs. 5-7) of the cyclic process with those (Figs. 1-3) of the normal process, we can obviously see the enhancement of the nucleation density on the pretreated glass substrate by the cyclic process. It is noted that we can

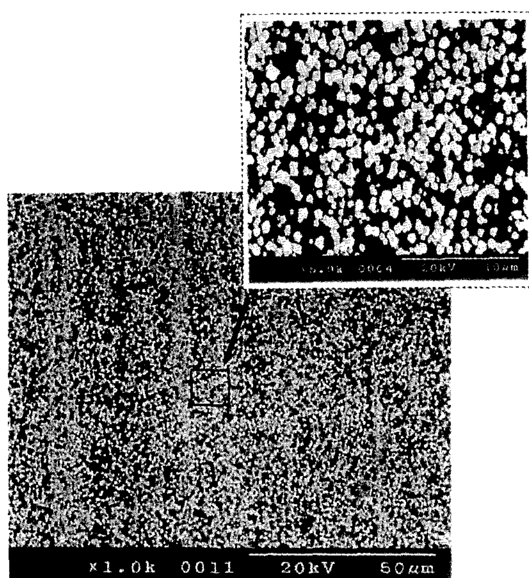

Fig. 5. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the cyclic process, under 2 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

enhance the nucleation density on the pretreated glass substrate, merely by the application of the on/off control of CH_4 flow rate for a relatively short time (10 min), compared with the total reaction time (6 h). In this case, we could also confirm that the main component of the grain was the diamond, as shown in Fig. 4b.

Using the high magnified SEM images (see the insets of Figs. 5-7), we measured the number density of the nuclei as a function of CH_4 flow rates. On the pretreated surfaces, the number density was measured as about 1.7×10^{10} (the inset of Fig. 5), 2.3×10^{10} (the inset of Fig. 6), and 1.8×10^{10} (the inset of Fig. 7) at 2, 4, and 6 sccm CH_4 flow rates, respectively. These values are ~1.7 times higher than those of the normal process. Clearly these results reveal the increase in the nucleation density on the pretreated surfaces by the cyclic process.

The cause for the increase in the nucleation density by the application of the cyclic process may attribute to the cyclic modulation of the H_2/CH_4 concentration ratio in the source gas. Previously, we reported that the pretreated glass substrate has rough surfaces and that residual diamond particles are on

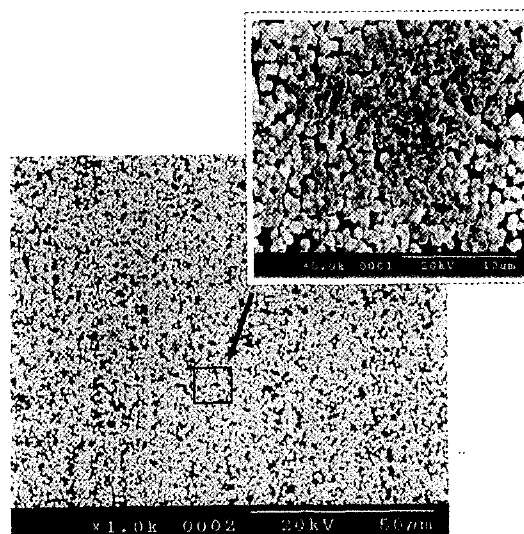

Fig. 6. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the cyclic process, under 4 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

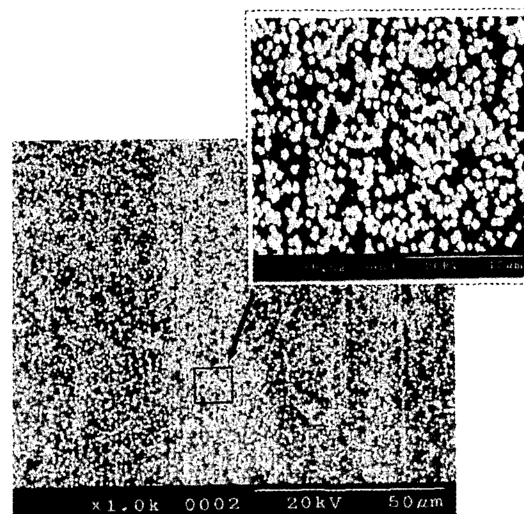

Fig. 7. SEM image of as-deposited diamond film surface on the pretreated glass substrate, in the case of the normal process, under 6 sccm CH_4 flow rate condition. Inset is the high magnified SEM image of the indicated area by arrow.

the substrate (9). The cyclic modulation of the H_2/CH_4 concentration in the source gas may enhance the suitable nucleation sites on the residual diamond

grains as well as on the roughened glass substrate. Consequently, the cyclic process can enhance the number density of the nuclei on the pretreated glass substrate by the cyclic process. We may suggest that the abundant amount of atomic hydrogen during the cyclic process seems to be the main cause for the increase in the number density of the nuclei, because atomic hydrogen can readily etch the surface of the pretreated glass substrate. Consequently, it may produce the more suitable sites for the diamond nucleation.

IV. Conclusions

We can achieve the cyclic process by the on/off control of CH_4 flow rate for 10 min during the initial reaction process. Using the cyclic process, we can improve the nucleation density of the diamond grain. The cause for this result may be attribute to the cyclic modulation of the H_2/CH_4 concentration ratio in the source gas during the initial deposition stage.

Acknowledgement

This research was supported by the 1999 research fund from Silla University.

References

[1] J. C. Angus and C. C. Hayman, Science, **241**, 913 (1988).
[2] K. E. Spear, *J. Am. Ceram. Soc.*, **72**, 171 (1989).
[3] K. Kobashi, N. Nishimura, Y. Kawate, and T. Horiuchi, Phys. Rev., B **38**, 4067 (1988).
[4] S. Yugo, T. Kanai, T. Kimura, and T. Muto, Appl. Phys. Lett., **58**, 103 (1991).
[5] X. Jiang, C.-P. Klages, R. Zachai, M. Hartweg, and H.-J. Fusser, Appl. Phys. Lett., **62**, 3438 (1993).
[6] B. Cline, W. Howard, H. Wang, K.E. Spear, and M. Frenklach, J. Appl. Phys., **72**, 5962 (1991).
[7] D. S. Olson, M. A. Kelly, S. Kapoor, and S. B. Hangstrom, J. Mater. Res., **9**, 1546 (1994).
[8] J. L. Davidson, C. Ellis, and R. Ramesham, J. Electron. Mater., **18**, 711 (1989).
[9] S. H. Kim, Y. S. Park, S. K. Jung, D. H. Kang, and J.-W. Lee, J. Vac. Sci. Technol. A **13**(3), 1619 (1995).