MORPHOLOGY AND GROWTH OF DIAMOND FILMS

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Diamond films were synthesized on Si substrates by microwave-plasma chemical-vapor deposition using a mixture of methane and hydrogen for the source gas. The film surfaces exhibited a class of morphologies which depended sensitively on the methane concentration. During the CVD process, the surface morphology changed periodically with time in such a way that a microcrystalline phase and a faceted phase appeared alternately. Surface morphologies of the films deposited using a mixture of methane, hydrogen and diborane for the source gas was also studied. It was found that a needle-like graphite was deposited when the B/C ratio in the reaction gas was greater than 0.8%.

1. Introduction

Diamond films synthesized by chemical-vapor deposition (CVD) using a methane-hydrogen mixed gas consist of fairly large crystalline grains and exhibit a variety of crystal habits for different methane concentrations \( c_m \) (\( c_m \) is defined by \( \text{CH}_4/(\text{CH}_4+\text{H}_2) \) in units of vol%), and this fact has attracted investigations into the surface morphology and growth of diamond films. However, no such work has been done on B-doped, p-type semiconductive diamond films which can be synthesized by adding diborane (\( \text{B}_2\text{H}_6 \)) to the source gas (the diborane concentration \( c_d \) is defined by \( \text{B}_2\text{H}_6/(\text{B}_2\text{H}_6+\text{CH}_4+\text{H}_2) \)). In this paper, our previous results on the morphology and growth of non-doped diamond films will be first described briefly, and then the new data on the morphology of B-doped films deposited on Si and non-doped diamond films will be presented.

The microwave plasma CVD method was used to synthesize diamond films. The experimental setup has been described elsewhere. For the substrate, a piece of Si, 2 cm\( \times \)1 cm in area and 0.5 mm thick, was used. Note that prior to deposition, the Si substrates were polished with a diamond paste for one hour. The substrate temperature was kept at 800°С during the synthesis. A mixture of methane and hydrogen was used for the source gas. For B doping, a small amount of diborane was mixed with the methane-hydrogen gas. The total gas flow rate was 100 cc/min and the pressure of the chamber was maintained at 30 Torr.

2. Morphology of non-doped films

Figure 1 summarizes the morphology of diamond films deposited for seven hours on Si. For

![Morphology of Diamond Films](image)

Fig. 1. Morphology of non-doped diamond films deposited on Si.

$c_m=0.3\%$, the substrate was covered with diamond grains having triangular (111) crystallographic planes. The surface morphology changed markedly at $c_m=0.4\%$, where the majority of the crystallographic planes appearing on the film surface were (100), characterized by planar square faces. Such features became more prominent as $c_m$ increased to 1.0\%. As the concentration increased beyond $c_m=1.2\%$, the density of (100) faces decreased and the square feature gradually faded, and for concentrations higher than $c=1.6\%$, the film surfaces become totally microcrystalline and no crystallographic planes of diamond were observed. It is interesting that a crossover from (111) to (100) occurred in a very narrow range at about $c_m=0.4\%$, whereas the microcrystallization of the film took place over a relatively wide concentration range above 1.2\%.

3. Growth cycle of non-doped films

For the study of the film growth, the CVD synthesis was interrupted every few hours and the specimen was observed by SEM. It was found that during the film growth, two different morphological phases appeared on the film surface periodically with deposition time; a microcrystalline phase and a faceted phase. Typical surface structures of these phases are shown in Figs. 2a and 2b for $c_m=1.2\%$. The former phase appeared as an initiation of a higher-order growth. After about 10 h, this phase was quite suddenly taken over by the latter phase, then followed by the former phase. Such a cyclic feature was also observed for $c_m$ less than 1.2\% but the changes were less clear, partly because the periods of the cycle were longer than for $c_m=1.2\%$.

![Fig. 2. Surface structures of diamond films synthesized for (a) 32.3 h and (b) 44.8 h with $c_m=1.2\%$.](image)

![Fig. 3. Morphology of bilayers: (a) Non-doped diamond film deposited on Si for 7 h with $c_m=0.5\%$. This film was used as the first layer. (b) Second layer; $c_d=1$ ppm, (c) second layer; $c_d=10$ ppm, (d) second layer; $c_d=20$ ppm and (e) a magnified view of Fig. 3(d).](image)
4. Morphology of B-doped films deposited on Si

Figures 3a-3d show SEM photographs of the films deposited directly on Si with $c_m=0.5\%$ and $c_d=0, 1, 10$ and 20 ppm for 7 h. The surface of the non-doped film (Fig. 3a) displayed triangular (111) faces, as already seen in Fig. 1. For $c_d=1$ ppm (Fig. 3b), the surface morphology was almost identical to Fig. 3a, indicating that the B-doped diamond film has good crystallinity. The grain size became smaller when $c_d=10$ ppm (Fig. 3c), and the morphology was greatly modified when $c_d=20$ ppm (Fig. 3d), where a needle-like deposit was formed (Fig. 3e). An X-ray diffraction study of the film showed an existence of graphite, but no indication of boron carbide. Thus, it was found that the addition of 20 ppm diborane in the reaction gas resulted in the liberation of graphite.

5. Morphology of B-doped films deposited on non-doped diamond films synthesized with $c_m=0.5\%$

In applying diamond films to electronic devices, p-n and p-p' junctions will be used. Thus, it is of great interest to investigate the morphology of bilayer films. To this end, the first layer was directly deposited on Si with $c_m=0.5\%$ for 7 h using the same experimental conditions as described in Section 1, and the second layer was then deposited on the first layer for 7 h with $c_m=0.5\%$ and $c_d<100$ ppm. The SEM data are presented in Figs. 4a-4d. As seen in Fig. 4a, the surface of the first layer consisted of triangular (111) faces. When $c_d=1$ ppm (Fig. 4b), the surface of the second layer had a similar triangular feature. As $c_d$ increased to 10 ppm (Fig. 4c), the grain size became smaller, and for $c_d=20$ ppm (Fig. 4d), the film surface was partially covered by the needle-like structures already seen in Section 5. It is very interesting to note that the needle-like deposit existed only on triangular (111) faces, and no deposit existed on square (100) faces. Such selective deposition may be related to the fact that (111) lattice planes of bulk diamonds can incorporate impurities more easily than any other plane.
6. Morphology of B-doped films deposited on non-doped diamond films synthesized with $c_m = 1.2\%$

Similar experiments were repeated using non-doped diamond films (synthesized for 7 h using $c_m = 1.2\%$) for the first layer and B-doped films (deposited using $c_m = 1.2\%$ and $c_d < 50$ ppm) for the second layer. As stated in Section 2, the surface of the non-doped film consisted of only (100) faces, as seen in Fig. 5a. When $c_d = 1$ ppm (Fig. 5b), the surface of the second layer consisted of triangular faces very similar to those already seen in Fig. 4b. This indicates that the morphology of the B-doped second layer was not influenced by the morphology of the first layer. When $c_d = 10$ ppm (Fig. 5c), the grain size became smaller, and when $c_d = 20$ ppm (Fig. 5d), the entire film was covered by a featureless deposit, perhaps graphite. Furthermore, when $c_d = 50$ ppm (Fig. 5e), the needle-like structures appeared on the film surface; however, this non-selectively covered the diamond faces of the first layer. In both Figs. 4d and 5e, the B/C atomic concentration ratio in the reaction gas was about 0.8, demonstrating that the B/C ratio is a key factor in determining the surface morphology of the B-doped second layers.

7. Summary

Morphology and growth of non-doped and B-doped diamond films were studied using films deposited on Si by microwave plasma CVD. For non-doped films, a morphological crossover from (111) to (100) occurred at about $c_m = 0.4\%$. A microcrystallization was found to occur for $c_m > 1.2\%$. In B-doped films directly deposited on Si, the needle-like deposit was formed when $c_d = 20$ ppm. Similar deposits were observed for B-doped films deposited on non-doped diamond films synthesized with $c_m = 0.5$ and 1.2%, when B/C = 0.8. The data obtained in the present work will be useful in the application of diamond films to multilayered semiconductive devices.

Acknowledgements. The authors wish to thank Mr. T. Nakatsu of KOBELCO Scientific Research for taking SEM photographs. They are also grateful to Prof. R. F. Davis of North Carolina State University for his continued interest in and support of the KSL-NCSU joint research.

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