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Growth of diamond films with bias during microwave plasma chemical vapor deposition

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Abstract

Diamond films on 3-inch diameter (100) silicon wafers were synthesized with bias during microwave plasma vapor deposition (MPCVD). The deposition parameters were as follows: 0.13% CH_4 in H_2, pressure at 30 torr; deposition temperature at 768–869 °C, and a deposition time of 3–3.5 h. The bias voltage applied to the substrates during diamond growth varied from 0 to −450 V. The deposited films were characterized by Raman spectroscopy and electron microscopy. The results show that the film properties are uniform across the whole 3-inch diameter area. Raman spectra show that the ratio of sp^3 to sp^2 is increased with the bias voltage up to −350 V, while further increases in voltage resulted in a decreased ratio. It was found that column-shaped grains of diamond were directly grown from the substrate surface without grain coalescence in the lateral direction during growth. The nucleation density of diamond with biased growth was of the order of 10^9 cm^{-2}.

Keywords: Diamond films; CVD; Bias; Raman spectroscopy

1. Introduction

Diamond growth by chemical vapor deposition is conventionally achieved with pre-treatments of either scratching or bias-enhanced nucleation method. Yugo et al. [1] first successfully enhanced diamond nucleation on Si (100) by using a bias enhanced nucleation (BEN) method without diamond powder pre-treatment. Jiang et al. [2] and Stoner et al. [3] prepared oriented diamond films on silicon and silicon carbide using BEN and subsequent texture growth in MPCVD. The successful deposition of oriented diamond films was established by the fact that the substrates did not suffer from disruption of crystal lattice. Since then, many works have studied the BEN process [4–7], and through such studies, the quality of oriented diamond films has gradually improved [8–14]. Most studies have used BEN methods as a pre-treatment process to obtain a higher nucleation density. However, there are few reports on the bias effect on the growth process. This work shows the influence of negative bias on the CVD diamond growth process. The characterization of the diamond film was accomplished by Raman spectroscopy, scanning electron microscopy (SEM), and cross-section transfer electron microscope (TEM).

2. Experimental

Diamond film deposition was carried in a DMS-100 diamond CVD system (Wavemat Inc.) [15]. The DMS-100 diamond CVD system was composed of the MPDR® 313 EHP plasma source, a microwave power supply, an integral substrate holder, a programmable logic controller (PLC) watchdog, and a mechanical pump. The Si substrates were polished using 0–0.25 μm synthetic diamond powders before deposition. Dry synthetic diamond powders were spread on a 3-inch diameter sacrificial silicon wafer, which was used as a lapping surface. The substrate surface was then prepared by scratching for 30 min. After the polishing operation, the substrates were ultrasonically rinsed in acetone, methanol and de-ionized water. The deposition conditions for diamond films on 3-inch diameter silicon wafer were as follows: electromagnetic field, TM_{013} mode; gas flow rate 4 sccm for CH_4 and 300 sccm for H_2; total pressure of 30 torr; power of 3.25 kW; substrate tem-

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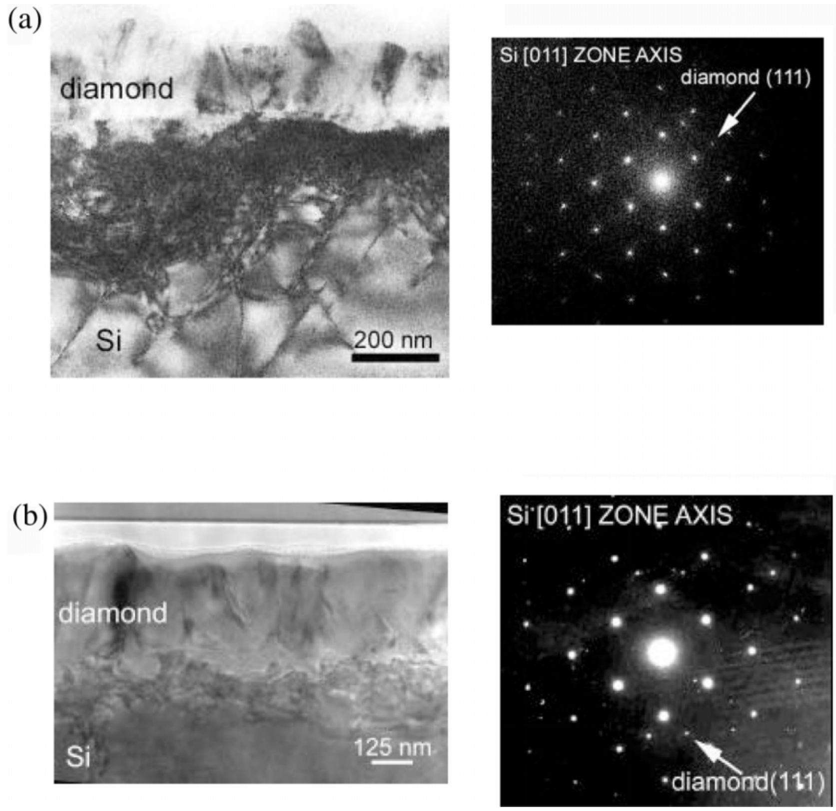

Fig. 1. Cross-sectional TEM images with selected diffraction patterns (a) −350 V and (b) −450 V.

perature range: 725–850 °C; deposition time of 3.5 h; and a negative bias voltage in the range of 0 to −450 V.

3. Results and discussion

3.1. Bias nucleation process

Fig. 1 shows typical cross-sectional TEM images obtained from samples grown with different bias volt-

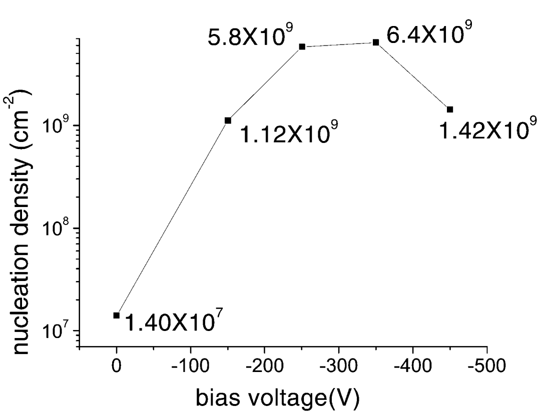

Fig. 2. The effect of bias voltage on the nucleation density of diamond.

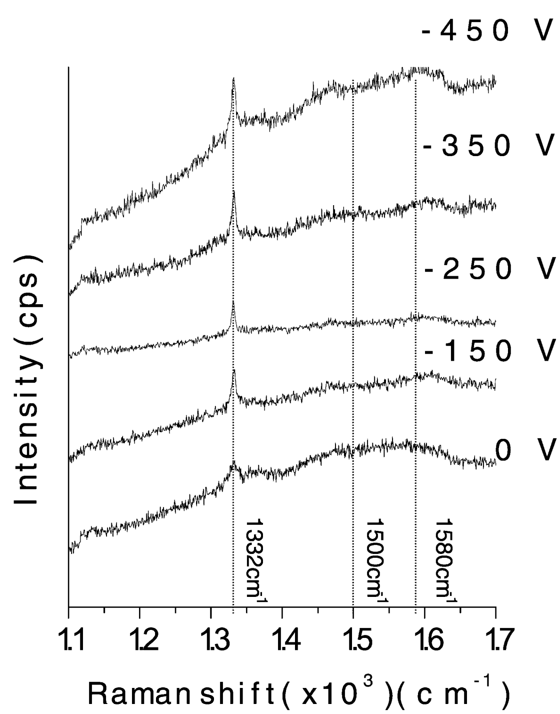

Fig. 3. Raman spectra from samples deposited with different bias voltages.

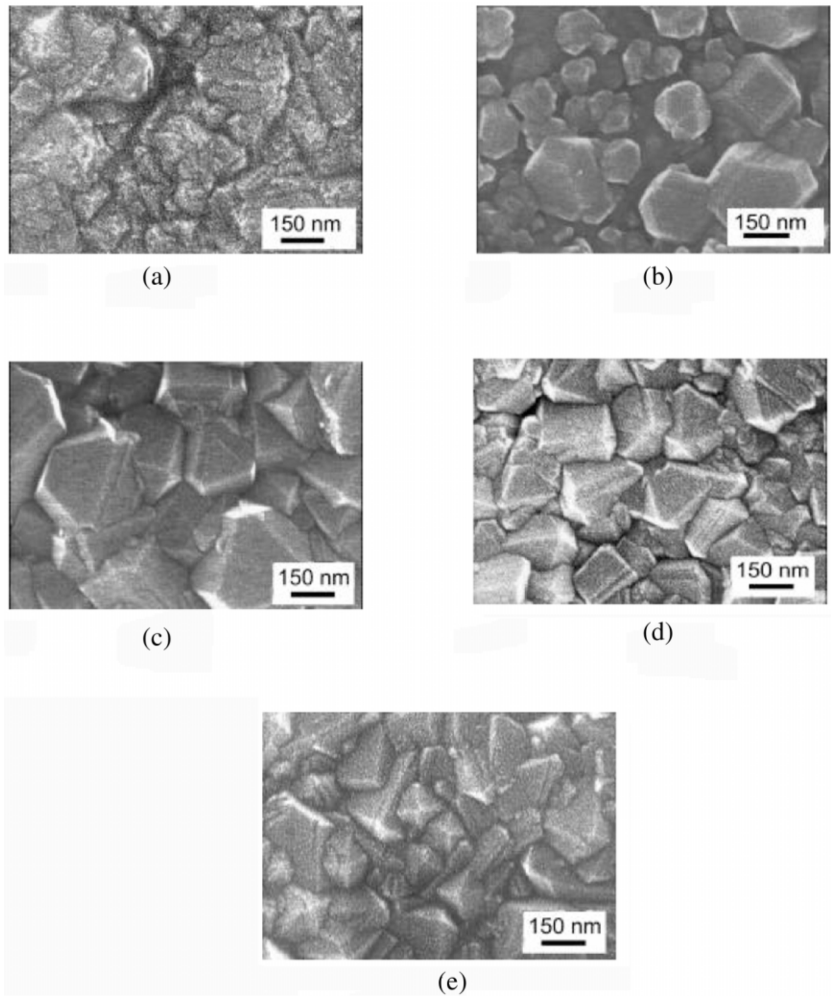

Fig. 4. SEM micrographs: (a) no bias; (b) −150 V; (c) −250 V; (d) −350 V; and (e) −450 V.

ages. The nucleation density of diamond measured from many TEM images is shown in Fig. 2. It indicates that bias treatments increase the nucleation density by two orders of magnitude to 10^9 cm^{-2}. The density slightly increases with voltage but decreases when 450 V is applied. The TEM images also reveal that Si surfaces were heavily damaged, probably due to the pre-treatment of scratch.

3.2. Bias growth process

From Raman spectra and SEM observations, it can be found that all the diamond films deposited are uniform all over the 3-inch specimens. Fig. 3 compares Raman spectra obtained from samples deposited with different negative bias voltages. It can be seen that the deposited films with bias have a better quality than those without bias. Also, the spectra show that the diamond peak is apparently increased with the magnitude of bias voltage applied. The ratio of the sp^3/sp^2 increases with the negative bias voltage up to −350 V, and decreases when the bias voltage is further increased to −450 V. From the results, this suggests that better diamond quality could be obtained with the applied voltage at −350 V. The reason for the improvement in quality with the increase of bias voltage to −350 V might be due to etching out the graphitic carbon in the films, while a further increase of voltage with a higher energy of ions impinging on the diamond surface might cause disorder in the film, which results in a band near 1500 cm^{-1} related to the disordered sp^3 carbon, as observed in Raman spectra. According to Sharda et al. [16,17], the appearance of the band was due to the increase in bias voltage.

Fig. 4 shows the surface morphology with the negative bias voltages ranging from 0 to −450 V. No preformed orientation can be seen on these films. The average size of diamond particles with no bias is 140 nm, smaller than those with bias (180–200 nm). The smaller size is mainly due to secondary nucleation. SEM also shows that without applied bias, the facet of diamond films is not well developed. Instead, well-

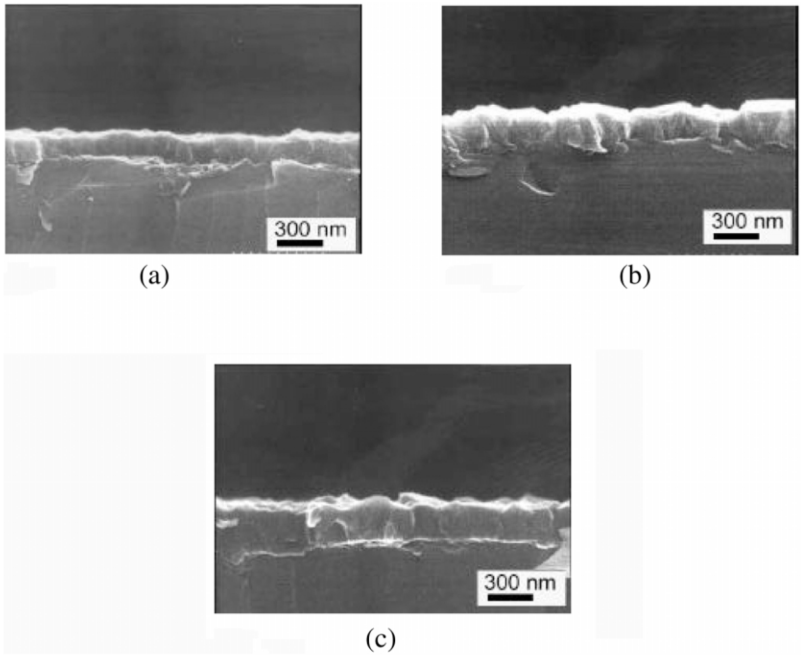

Fig. 5. SEM micrographs in cross section showing the effect of bias voltage: (a) no bias; (b) −150 V; and (c) −450 V.

defined facets of diamond were observed in conditions of biased growth. This implies that there is no strong damage even with high-energy ions continuously bombarding the diamond surface during growth. This is consistent with the results of Raman spectra in Fig. 3. Fig. 5 demonstrates the SEM images in cross section with the negative bias voltage ranged from 0 to −450 V. Grain coalescence cannot be seen in the growth stage. The lateral sizes of the diamond grains are relatively uniform along the direction normal to the film surface. This is probably due to the directionality of the ion bombardment during applied bias. Also, the bias voltage has no strong effect on diamond growth rate as the thicknesses are similar for growth with different bias.

4. Conclusion

Diamond films were synthesized with bias during microwave plasma chemical vapor deposition. The film properties are uniform across the whole 3-inch diameter area. The nucleation density slightly increases with the applied bias voltage during nucleation step. After biased growth, the quality of the films can be improved as the ratio of the sp^3/sp^2 from Raman spectra increases with the negative bias voltage up to −350 V. With biased growth, the film morphology has well developed facets. SEM also shows that diamond columnar grains have relatively uniform sizes along the growth direction.

Acknowledgments

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