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Improvement on the growth of ultrananocrystalline diamond by using pre-nucleation technique

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Abstract

Ultrananocrystalline diamond (UNCD) films, which possess very smooth surface, were synthesized using CH_4/Ar plasma. The Si-substrate was pre-nucleated using bias enhanced nucleation (BEN) technique under CH_4/H_2 plasma, so that the growth of UNCD films can be markedly enhanced. The growth rate of these UNCD films were observed to be correlated intimately with the deposition conditions, such as substrate temperature, microwave power, total pressure, CH_4 ratio. When the nucleation process was carried out under methane and hydrogen (CH_4/H_2) plasma with negative DC bias voltage, no pretreatment on substrate was required prior to the formation of diamond nuclei. The growth kinetics of BEN induced nuclei was monitored by the evolution of the bias current to ensure the full coverage of diamond nuclei on the Si-substrate. The average grain size of BEN induced diamond nuclei is about 30 nm, with the nucleation site density more than 10^{11} sites/cm^2. The growth rate of UNCD is markedly enhanced due to the application of BEN induced nuclei. Moreover, the growth rate of UNCD films was more significantly affected by the substrate temperature, but was less influenced by the microwave power. All of these UNCD films showed similar morphology, i.e., with grain size less than 10 nm and surface roughness around 20 nm. They also possess the same Raman spectra, i.e., the same crystallinity. However, the deposition rate can be increased from about 0.2 μm/hr to 1.0 μm/hr when substrate temperature increased from 400^{0}C to 600^{o}C.

Novelty:
The ultrananocrystalline diamond (UNCD) films were grown on bias-enhaned nucleation substrate to improve the of growth behavior.

Keywords: UNCD, high speed growth, BEN, MPECVD

Submission of this paper has been approved by the co-authors.

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I. Introduction

The unique combination of the physical and chemical properties of diamond film save drawn more attention among researcher to use diamond in many applications. However, the high roughness of microcrystalline diamond films made them inapplicable in specific applications. In the recent past, very smooth ultra nano-crystalline diamond (UNCD) films deposited by CH_4/Ar mixture has been established. The detail mechanism for the formation of UNCD from CH_4/Ar plasma has been reported[1, 2]. Recent application of nano-diamond films in bio-sensors[3], filed emission[4, 5] and bio-medical application[6] have shown the promising future of this nano-material. Even so, no detailed study has been performed on the growth rate and formation of nucleation sites by biased enhanced nucleation (BEN) method to grow uniform UNCD film on the silicon surface. Therefore, it is significant to understand more precisely on the deposition rate and deposition conditions influencing growth process of UNCD film.

The substrate pretreatment strongly affects the nucleation and growth process of diamond films determining the initial deposition rate, crystal quality and surface roughness. High deposition rate is primarily important to grow thick diamond films normally required for application like SAW devices[7]. Moreover, a smooth surface of diamond film is another important requirement. Thus, suitable conditions need to be established to grow ultrananocrystalline diamond grains to directly obtain a smoother film. One of the most effective methods of diamond nucleation is bias enhanced nucleation (BEN) method[8, 9]. The formation of nano-diamond phase on silicon acts as nucleation center for the growth of either nano-crystalline or microcrystalline diamond depending on the deposition parameters used.

One of the main objectives of the present work was to systematically investigate the nucleation behavior of UNCD on silicon surface using a BEN technique. As BEN method does not involve any scratching by diamond abrasives, it avoids the confusion of presence of any residual diamond particle on the substrate. Another objective of current study is to find a suitable deposition condition for the high and uniform growth of UNCD. The effect of microwave power, substrate temperature, CH_4 to Ar ratio and total pressure on the growth rate is reported in this article.

II. Experimental

The bias enhanced nucleation (BEN) diamond films were grown in a 2.45 GHz ASTeX microwave plasma enhanced chemical vapor deposition (PECVD) system on N-type mirror polished Si (100) substrates. A microwave power of 1.5 kW (ASTeX 5400), total pressure of 55 torr and 300 sccm H_2 flow rate were used during biased treatment. Different substrates were biased treated for different time intervals (0 to 15 minutes) at constant biased voltage (-125 V) and the resulted bias current – time relationship was measured. Silicon substrates after BEN process were used for the deposition of UNCD in an IPLAS MPCVD system. Table I presents the detail experimental deposition conditions used for UNCD growth. In Series - P, C, T and MW, chamber pressure, CH_4/Ar ratio, temperature and microwave power was varied respectively, keeping rest of the parameters constant.

Surface morphology of samples was examined with a field emission scanning electron microscope (JEOL 6010). Crystal quality of UNCD films was investigated by Raman Spectroscopy using 514 nm argon laser beam (Renishaw). Surface topography and roughness was measured with atomic force microscopy (PARK).

III. Results and discussion

(a) Nucleation process

The formation of nanodiamond phase for the nucleation of diamond growth during BEN is known for last few years. Therefore BEN time is crucial to create uniform nucleation center on the silicon. Figure 1 shows the nucleation of nano-diamond films deposited after different BEN time intervals. The SEM images show uniform island growth at the beginning after 5 minutes of BEN (Fig 1a) and subsequent increase of coverage in nano-diamond grains clusters on the surface after 7 minutes (Fig 1b). After 8 minutes of BEN, the whole silicon surface is covered by cluster of nano-diamond crystals. The average size of nano-diamond cluster is around 150 nm and size of each diamond grain in the clusters is ~ 20 nm (Fig 1c). A saturation of nano-diamond growth occurs after 8 minutes of BEN, covering whole area of silicon substrate. At 10 min of BEN, cluster size of nano-diamond is decreased but diamond grain of size 50 nm started to appear (Fig 1d). The surface morphology is almost same after 10 minutes BEN. This establishes the minimum time (8 minutes) required for the creation of high nucleation centers and uniform nano-diamond layer on silicon. The grain size is also found to be smallest (~20 nm) after 8 minutes of BEN. The thickness was about 250 nm.

The measurement of bias current during BEN in our study indicates direct correlation in the formation of nano-diamond phase on silicon, which is shown in fig. 2 for the trend of bias current versus time at a constant negative bias voltage of 125 V. When there is no methane flow, bias current is about -52 mA. This current starts to decrease in the first 3 minutes, which may be due to methane content increases and changes plasma condition. The subsequent increase of bias current which has been attributed to the enhancement in electron emission from the highly emissive diamond formed on silicon substrate surface and the bias current become saturated after 10 minutes indicating no more nano-diamond coverage increase in surface.

(b) Growth process

Figure 3 shows the effect of various parameters on the deposition rate of UNCD. The deposition rate of diamond film is found to depend significantly on the temperature and the ratio of CH_4 to Ar in the reactant gas compared to microwave power and total pressure. The effect of chamber pressure in the deposition rate is linearly increases from 100 torr to 150 torr. There is no much effect of pressure on the deposition rate. However, there is a striking increase in deposition rate when CH_4/Ar ratio was increased from 0.5 % to 2.0 %. The substrate temperature is another important parameter for increasing deposition rate. The deposition rate is found to increase around 4 times with increase in temperature from 400^{o}C to 600^{o}C while all other parameters were held constant. The deposition rate of UNCD increases with microwave power from 600 W to 750 W. However, deposition rate comes down and become almost constant in the microwave power range of 900 W to 1200 W. We have grown a UNCD film having highest deposition rate of ~1 μm/hr at 750 W with combination of parameters: 150 torr pressure, 600 ^{o}C temperature and 1 % methane.

Figure 4 shows typical SEM images of UNCD film. Diamond grains of size less than 10 nm have been grown under above described deposition conditions. Unlike the agglomeration observed after bias enhanced nuclation, UNCD film shows a uniform and smooth surface having numerical diamond crystallites density of as high as 10^{12} /cm^2. This high nucleation density was due to formation of high nucleation centers during BEN and the growth in CH_4/Ar plasma. The inset shows a cross-sectional image of UNCD film. The surface roughness of the diamond films is strongly affected by deposition method. AFM analysis shows that the surface roughness of the BEN film using CH_4/H_2 source gas under continuous bias (-125 V) in 8 minutes period was about 13.2 nm. This surface roughness reduces to 10 nm after deposition of UNCD using CH_4/Ar source gas. The decrease of surface roughness is well matched with decrease of diamond grain size measured by SEM. Size of diamond grains were less than 10 nm after UNCD deposition on a 20 nm diamond crystallites film formed during negative biasing.

Raman technique is one of the important non-destructive characterization techniques to study the properties of any type of carbon forms. There are four main peaks normally observed at around 1140 cm^{-1}, 1330 cm^{-1}, 1470 cm^{-1} and 1560 cm^{-1} in visible Raman spectrum of UNCD films[10, 11]. Figure 5 shows the Raman spectra of UNCD films deposited on silicon at different experimental conditions. These Raman spectra are found to be very similar to as reported in literature[10, 11]. The broad peak at 1330 cm^{-1} and 1560 cm^{-1} are commonly termed as D-band and G band respectively. The peaks at 1140 cm^{-1} and 1470 cm^{-1} are sometimes assigned to nano-crystalline diamond films[12, 13]. However, there is certain ambiguity in these two peaks. Ferrari *et. al.* [14] and Kuzmany *et. al.* [15] have assigned these two peaks at 1140 cm^{-1} and 1470 cm^{-1} to trans-polyacetylene segments present at the grain boundaries and surfaces of diamond films. However, these two peaks are most commonly observed in UNCD or NCD film[10, 11]. Since the sp^2-bonded carbon is highly sensitive to visible Raman spectroscopy than sp^3-bonded carbon, sharp peak at 1332 cm^{-1} is not observed. In our study, the peak height of 1140 cm^{-1} and 1470 cm^{-1} suggests the increase in trans-polyacetylne percentage with substrate temperature. Raman spectra of series –P, -C and -MW samples are almost same indicating not much change in crystallinity of UNCD films by varying pressure, CH_4/Ar ratio and microwave power.

IV. Conclusion

UNCD film of diamond grain less than 10 nm was grown on BEN treated silicon surface. Nucleation density of ~10^{12} grains/cm^2 was obtained in the growth process. Silicon substrate was biased for different time interval to study the formation of nucleation center. Our study has shown that a minimum 8-minute of bias enhanced nucleation was needed for uniform growth of UNCD film. Agglomeration of diamond crystallites obtained in BEN diamond growth was not observed after the growth of UNCD in a CH_4-Ar medium. AFM study depicted the improvement in smoothness of UNCD film to 6.83 nm from 10.83 nm obtained by BEN NCD film. Raman spectra have shown the peak at respective positions that normally observed in UNCD films.

V. Acknowledgment

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VI. References

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Table I: Experimental deposition conditions for UNCD growth on BEN silicon surface.

Materials	Pressure (Torr)	CH_4/Ar Ratio (%)	Temperature (^oC)	MW Power (W)
Series-P	100~150	1 %	400	1200
Series-C	150	0.5 ~ 2 %	400	1200
Series-T	150	1 %	400 ~ 600	750
Series-MW	150	1 %	600	600 ~ 1200

Figure captions

Fig 1. SEM images of diamond films grown on silicon surface after different BEN time intervals, (a) 5 min., (b) 7 min., (c) 8 min. and (d) 10 min of BEN.

Fig. 2. Bias current from the electrode to the substrate holder during the bias enhanced nucleation as a function of time.

Fig. 3. Effect of pressure, CH_4 to Ar ratio, substrate temperature and microwave power on the deposition rate of UNCD

Fig. 4. FE-SEM image of UNCD grown under deposition condition of 750 W microwave power, 150 torr total pressure, total flow of 200 sccm Ar-CH_4 (CH_4-1 %) and substrate temperature 600 ^{o}C in 3 hr deposition period. Inset shows a cross-sectional view.

Fig. 5. Visible Raman spectra UNCD films obtained under different experimental conditions.

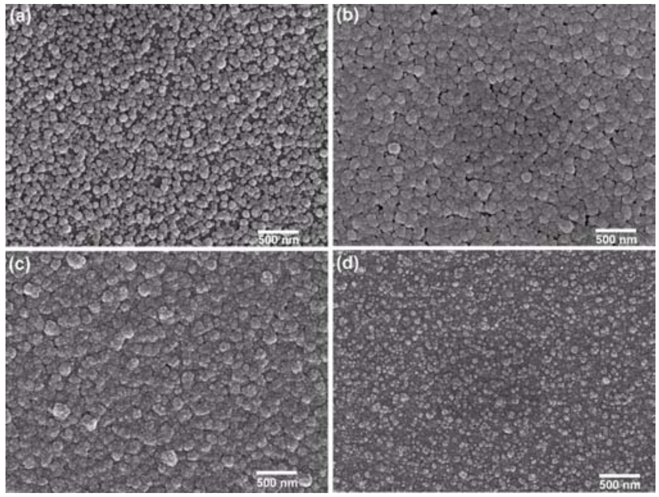

Figure 1 Y. C. Lee et. al.

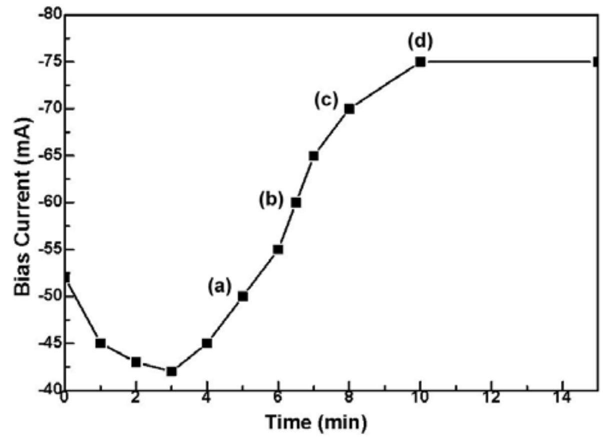

Figure 2 Y. C. Lee et. al.

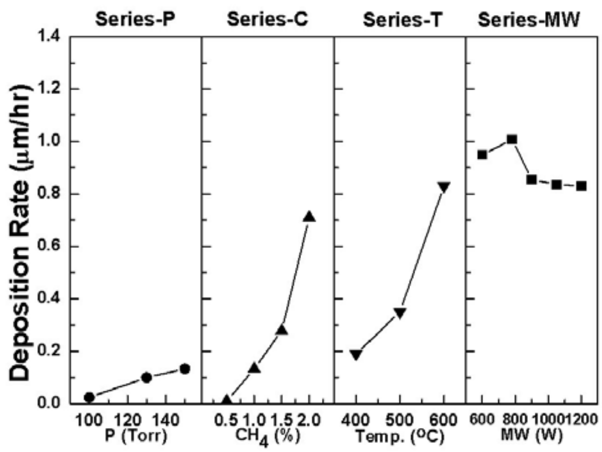

Figure 3 Y. C. Lee et. al.

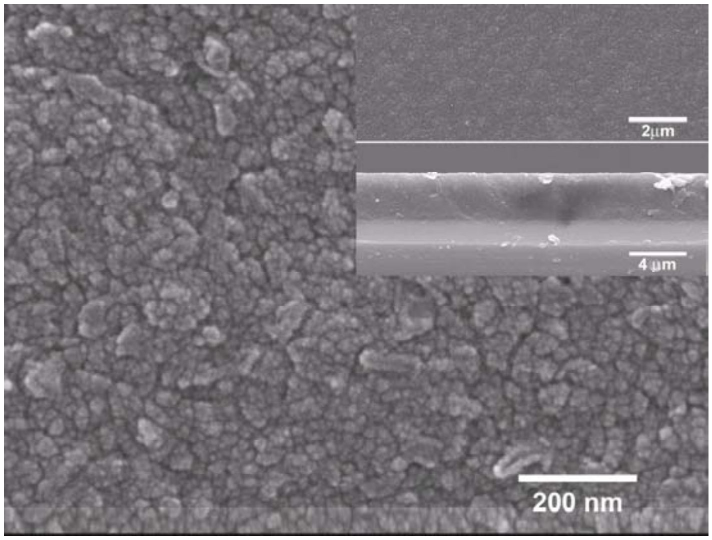

Figure 4 Y. C. Lee et. al.

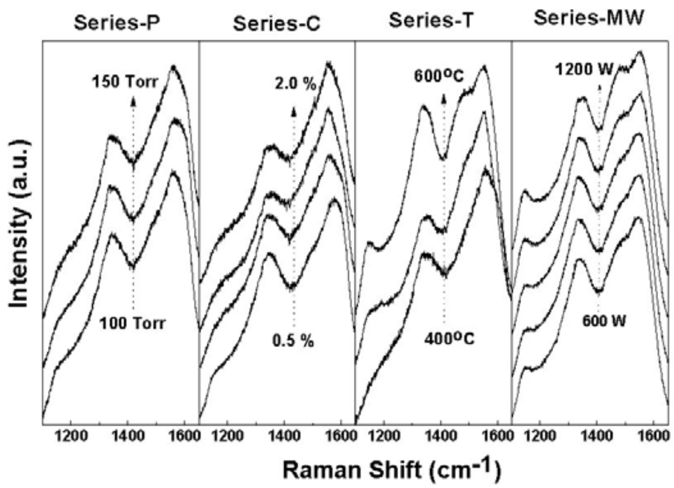

Figure 5 Y. C. Lee et. al.