Available online at www.sciencedirect.com
SCIENCE DIRECT®
Diamond & Related Materials 15 (2006) 353 – 356
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

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

Yen-Chih Lee [a], Su-Jien Lin [a], Debabrata Pradhan [b], I-Nan Lin [b,*]

[a] Department of Material Science and Engineering, National Tsing-Hua University, 300, Taiwan, R.O.C.
[b] Department of Physics, Tamkang University, 151 Yin-Chuan Rd. Tamsui, Taipei, 251, Taiwan, R.O.C.

Available online 13 September 2005

Abstract

Ultrananocrystalline diamond (UNCD) films, which possess very smooth surface, were synthesized using CH_4/Ar plasma. 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 average grain size of BEN induced diamond nuclei is about 20∼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 10 nm. They also possess similar Raman spectra, i.e., similar crystallinity. However, the deposition rate can be increased from ∼0.2 to 1.0 μm/h when substrate temperature increased from 400 to 600 °C.

Keywords: UNCD; High speed growth; BEN; MPECVD

1. Introduction

The unique combination of physical and chemical properties of diamond film has 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 ultrananocrystalline diamond (UNCD) films deposited by CH_4/Ar mixture have been established. The detailed 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] has shown the promising future of this nano-material. Even so, no detailed study has been performed on seeding by biased enhanced nucleation (BEN) method to grow uniform UNCD film on the silicon substrate.

The substrate pretreatment strongly affects the initial deposition rate, crystal quality and surface roughness for the diamond film. High deposition rate is primarily important to grow thick diamond films normally required for applications like SAW devices [7] and MEMS [8]. One of the most effective methods of seeding technique is BEN [9,10]. The formation of nano-diamond nuclei on silicon during BEN acts as seeding for the growth of diamond films.

One of the main objectives of the present work is to systematically investigate the nucleation behavior of UNCD on silicon substrate using a BEN technique. Another objective of current study is to find a suitable deposition condition for the uniform growth of UNCD of a high rate. The effect of microwave power, substrate temperature, CH_4 to Ar ratio and total pressure on the growth rate is also reported in this article.

2. Experimental

The seeding layer was grown in CH_4/H_2 plasma using a 2.45 GHz ASTeX 5400 microwave plasma enhanced chemical vapor deposition (MPECVD) system on N-type mirror polished Si (100) substrates. A microwave power of 1.5 kW, total pressure of 55 Torr, 300 sccm H_2 and 45 sccm CH_4 flow rate were used during biased treatment. Different substrates were biased treated (−125 V DC) for 0 to 15 min and the

* Corresponding author. Tel.: +886 2 26268907; fax: +886 2 26207717.
E-mail address: inanlin@mail.tku.edu.tw (I.-N. Lin).

0925-9635/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.diamond.2005.07.030

Table 1
Experimental deposition conditions for UNCD growth on BEN silicon surface

Materials	Pressure (Torr)	CH_4/Ar ratio (%)	Temperature (°C)	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

resulted bias current–time relationship was measured. Silicon substrates after BEN process were used for the deposition of UNCD in CH_4/Ar plasma using an IPLAS MPCVD system. Table 1 presents the detailed experimental deposition conditions used for UNCD growth. The chamber pressure, CH_4/Ar ratio, temperature and microwave power were varied in series -P, -C, -T and -MW, respectively, keeping the 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 spectroscope using 514 nm argon laser beam (Renishaw). Surface topography and roughness was measured with atomic force microscope (PARK).

3. Results and discussion

3.1. Nucleation process

The formation of nano-diamond nuclei during BEN is known for last few years. BEN time is crucial to create uniform nuclei on the silicon. The evolution of bias current during BEN in CH_4/H_2 plasma directly indicates the formation of nano-diamond nuclei on silicon substrate, which is shown in Fig. 1, for the trend of bias current versus time (I_{bias}–t) at a constant negative bias voltage of 125 V. When there was no methane flow, bias current was about −52 mA. This current started to decrease in the first 3 min, which can be ascribed to the increase in methane content in the plasma, since separate experiments showed that the minimum bias current decreased from −50 to −42 mA as that CH_4/H_2 ratio increased from 3% to 15%. The subsequent increase of bias current after 3 min incubation time was due to the formation of nano-diamond seeding on silicon substrate. The bias current was saturated after 10 min, indicating full coverage of seeding on surface. Fig. 2 shows the evolution of diamond nuclei on Si substrate corresponding to the BEN time intervals. The SEM images showed uniform island growth at the beginning after 5 min of BEN (Fig. 2(a)) and subsequent increase in coverage of nano-diamond clusters on the surface after 7 min (Fig. 2(b)). After 8 min of BEN, the whole silicon surface was covered by seeding, forming clusters of nano-diamond. The average size of nano-diamond cluster was around 150 nm and size of each diamond grain in the cluster was about 20∼30 nm (Fig. 2(c)). A saturation of seeding layer formation occurred after 8 min of BEN, covering whole area of silicon substrate. At 10 min of BEN, cluster size of nano-diamond decreased but larger diamond grain (∼50 nm) appeared (Fig. 2(d)). The surface morphology remained almost same after 10 min of BEN. This established the minimum time (8 min) required for the creation of densely populated nucleation centers and uniform seeding layer on silicon. The grain size is also found to be smallest (20∼30 nm) after 8 min of BEN. The thickness of the seeding layer was about 250 nm.

3.2. Growth process

Fig. 3 shows the effect of various parameters on the deposition rate of UNCD. The growth rate of UNCD film was found to depend more significantly on the temperature (T) and the CH_4/Ar ratio (C) in the reactant gas, compared to microwave power (MW) and total pressure (P). There was little increase of deposition rate with the increase of chamber pressure from 100 to 150 Torr (series-P). However, there was a striking increase in deposition rate when CH_4/Ar ratio increased from 0.5% to 2.0% (series-C). The substrate temperature was another important parameter for high deposition rate. The deposition rate was found to increase around 4 times with increase in temperature from 400 to 600 °C (series-T), while all other parameters were held constant. The deposition rate of UNCD varied insignificantly with microwave power from 600 to 1200 W (series-MW).

UNCD film was grown at a deposition rate of ∼1 μm/h with following combination of parameters: 780 W microwave power, 150 Torr pressure, 600 °C temperature and 1% methane to argon ratio. Fig. 4 shows typical SEM image of thus obtained UNCD film. Inset shows the cross-sectional SEM image of UNCD film. Diamond grains of size less than 10 nm had been grown under above described deposition conditions. Unlike the agglomeration observed after BEN, UNCD films showed 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 surface roughness of UNCD films was similar under varied deposition conditions. AFM analysis showed that

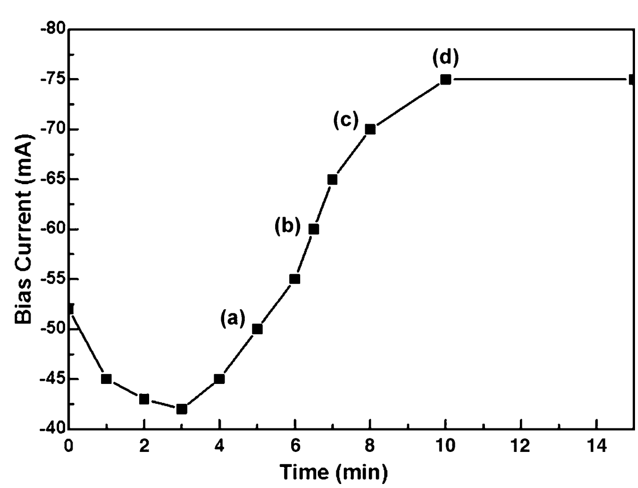

Fig. 1. Evolution of bias current during the bias enhanced nucleation process.

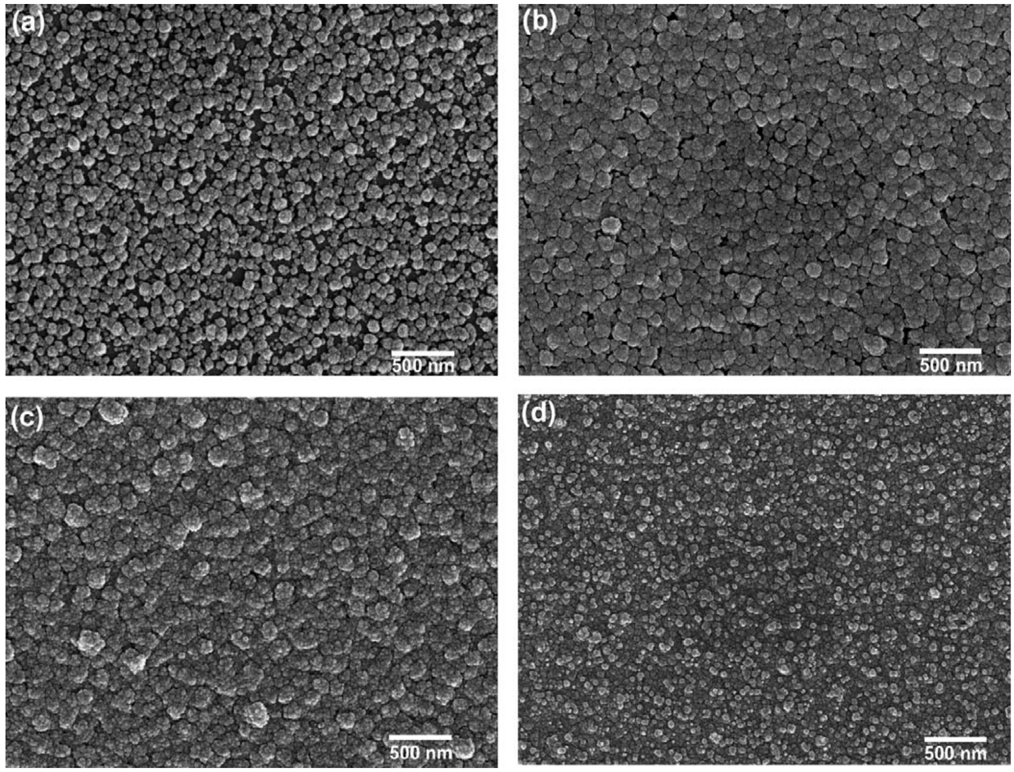

Fig. 2. SEM images of diamond seeding grown on silicon surface after (a) 5, (b) 7, (c) 8 and (d) 10 min of BEN.

the surface roughness of the BEN film using CH_4/H_2 source gas under continuous bias (−125 V) in 8 min period was about 13.2 nm. This surface roughness reduced to about 10 nm after deposition of UNCD using CH_4/Ar plasma. The decrease in surface roughness was 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 seeding layer with 20∼30 nm in diamond grain size formed during BEN.

Raman technique is one of the important non-destructive characterization techniques to study the properties of different types of carbon. Fig. 5 shows Raman spectra of UNCD films which were deposited on silicon at different experimental conditions. These Raman spectra were found very similar to previously reported literatures [11,12]. There are four main peaks normally observed at around 1140, 1350, 1480 and 1580 cm^{-1} in visible Raman spectra of UNCD films [11,12]. The broad peak at 1350 and 1580 cm^{-1} are commonly termed as D band and G band, respectively. The peaks at 1140 and 1480 cm^{-1} were sometimes assigned to nano-crystalline diamond films [13,14]. However, there was certain ambiguity in these two peaks. Ferrari and Robertson [15] and Kuzmany et. al. [16] assigned these two peaks at 1140 and 1480 cm^{-1} to trans-polyacetylene segments presented at the grain boundaries and

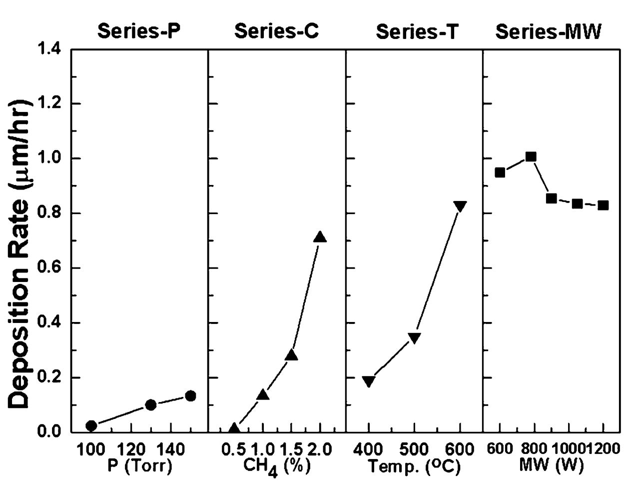

Fig. 3. Effect of total pressure (P), CH_4 to Ar ratio (C), substrate temperature (T) and microwave power (MW) on the deposition rate of UNCD.

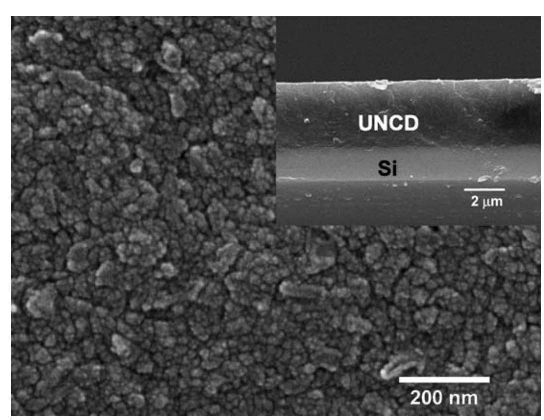

Fig. 4. FE-SEM image of UNCD grown under deposition condition of 750 W microwave power, 150 Torr total pressure, total flow of 200 sccm Ar–CH_4 (CH_4—1%) and substrate temperature 600 °C in 3 h deposition period. Inset shows a cross-sectional view.

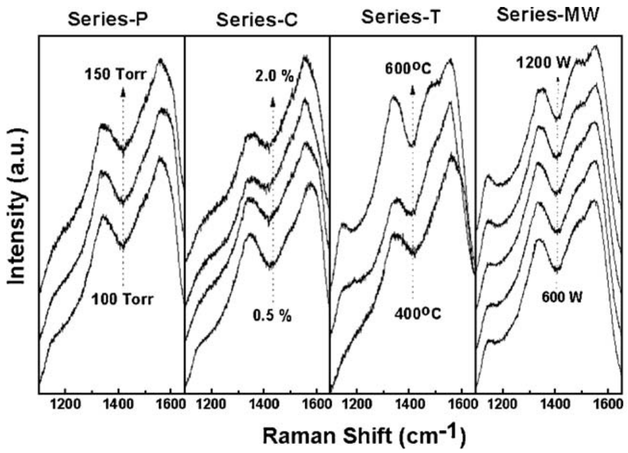

Fig. 5. Visible Raman spectra for UNCD films obtained under different experimental conditions.

surfaces of nano-diamond films. However, these two peaks are generally observed in both UNCD and NCD films [11,12]. Since the sp^2-bonded carbon is highly sensitive to visible Raman spectroscopy than sp^3-bonded carbon, sharp peak at 1332 cm^{-1} was not observed. In our study, the peak height of 1140 and 1480 cm^{-1} suggested the increase in trans-polyacetylne percentage with substrate temperature (series-T). Raman spectra of series -P, -C and -MW samples were almost the same indicating that not much changed in crystallinity of UNCD films by varying pressure, CH_4/Ar ratio and microwave power.

4. Conclusions

UNCD films of diamond grain less than 10 nm were grown on BEN treated silicon substrates. Nucleation density of $\sim10^{12}$ grains/cm^2 was obtained in the growth process. Silicon substrates were biased for different time interval to study the formation of nucleation centers. Our study had shown that a minimum 8 min of BEN was needed for uniform growth of UNCD film. Agglomeration of diamond seeding obtained in BEN process 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 ~10 from 13.2 nm obtained by BEN nano-diamond film. Raman spectra had shown the peaks at respective positions that normally observed in UNCD films.

Acknowledgment

The authors would like to thank National Science Council, R.O.C. for the support of this research through the project No. NSC 93-2112-M-032-010.

References

[1] D. Zhou, T.G. McCauley, L.C. Qin, A.R. Krauss, D.M. Gruen, J. Appl. Phys. 83 (1998) 540.
[2] D.M. Gruen, Annu. Rev. Mater. Sci. 29 (1999) 211.
[3] A. Hartl, E. Schmich, J.A. Garrido, J. Hernando, S.C.R. Catharino, S. Walter, P. Feulner, A. Kromka, D. Sreinmuller, M. Stutzmann, Nat. Mater. 3 (2004) 736.
[4] W. Zhu, G.P. Kochanski, S. Jin, Science 282 (1998) 1471.
[5] K. Wu, E.G. Wang, Z.X. Cao, Z.L. Wang, X. Jiang, J. Appl. Phys. 88 (2000) 2967.
[6] M.D. Fries, Y.K. Vohra, Diamond Relat. Mater. 13 (2004) 1740.
[7] F. Benedic, M.B. Assouar, F. Mohasseb, O. Elmazria, P. Alnot, A. Gicquel, Diamond Relat. Mater. 13 (2004) 347.
[8] L. Sekaric, J.M. Parpia, H.G. Craighead, T. Feygelson, B.H. Houston, J.E. Butler, Appl. Phys. Lett. 81 (2002) 4455.
[9] S. Yugo, T. Kanai, T. Kimura, T. Muto, Appl. Phys. Lett. 58 (1991) 1036.
[10] Q. Chen, Z. Lin, J. Appl. Phys. 80 (1996) 797.
[11] X. Xiao, J. Birrell, J.E. Gerbi, O. Auciello, J.A. Carlisle, J. Appl. Phys. 96 (2004) 2232.
[12] Y. Hayashi, T. Soga, Tribol. Int. 37 (2004) 965.
[13] W.A. Yarbrough, R. Messier, Science 247 (1990) 688.
[14] R.J. Nemanich, J.T. Glass, G. Lucovsky, R.E. Shroder, J. Vac. Sci. Technol., A, Vac. Surf. Films 6 (1988) 1783.
[15] A.C. Ferrari, J. Robertson, Phys. Rev., B 63 (2001) 121405.
[16] H. Kuzmany, R. Pfeiffer, N. Salk, B. Gunther, Carbon 42 (2004) 911.