

*Dedicated to Professor Mircea Diudea
on the Occasion of His 65th Anniversary*

COMPARATIVE STUDY OF NANOCRYSTALLINE DIAMOND GROWTH USING PECVD AND HFCVD TECHNIQUES

ZAHRA KHALAJ^a

ABSTRACT. Diamond coating is one of the hot research topic due to its various industrial applications; for the diamond growth, several techniques, such as PECVD and HFCVD, have been reported. In this paper, we investigate the effects of different CVD techniques on synthesis of diamond crystals, grown on silicon and aluminum substrates, at temperature of 550° C and the reaction pressure of 30 Torr, in which CH₄ and H₂ act as a source and diluting gases, respectively. The hydrogen was used as the etching gas to enhance the diamond nucleation. As a result, we obtained a high distribution of nanodiamond with (111) crystallite structure on gold-coated silicon in HFCVD system. The samples were analyzed using AFM, SEM and XRD.

Keywords: *Hot filament chemical vapor deposition; Plasma enhanced chemical vapor deposition; Etching gas; NCD.*

INTRODUCTION

Diamond coating is a hot research topic because of its high thermal conductivity, large band gap, excellent hardness, robustness, low friction coefficient and stable chemical properties [1-13]. Most of the researches reported the growth of nano crystalline diamond (NCD) and films on silicon substrate, scratching by diamond powder to increase the diamond nucleation by PECVD and HFCVD techniques [13-18]. One of the suitable gases for etching the substrate is the hydrogen. It can increase the ratio of diamond nucleation without using diamond powder. According to some references, the

^a *Department of Physics, Shahr-e-Qods Branch, Islamic Azad University, Tehran, I. R. Iran,
e-mail: khalaj.z@gmail.com*

presence of hydrogen may improve the quality of diamond films, by reducing the graphite content in diamond films [19, 20]. It is generally believed that methyl radicals play the most important role in standard CVD diamond growth, by abstracting the hydrogen from the diamond surface. Therefore, a high concentration of atomic hydrogen at the surface in addition to CH_3 radicals is a prerequisite for a successful microcrystalline diamond deposition [21-26].

In the present paper, we study the effects of simultaneous HFCVD and PECVD systems on the growth of diamond nano structures with (111) crystallite on conductive substrates. Gold coated on silicon and aluminum was used as the substrates in this experiment. Hydrogen gas was used for etching treatment of the substrates. A mixture of methane and hydrogen were used for the growing process in the both systems.

RESULTS AND DISCUSSION

XRD analysis of surface was carried to estimate the crystalline structure of the deposits. Figures 3 and 4 show XRD patterns of diamond grown by HFCVD and PECVD systems on substrates with 2θ angles ranging from 35° to 85° . The study of the parameters show a major peak corresponding to diamond (111) at $2\theta=44.62^\circ$ and $2\theta=44.46^\circ$ on aluminum and gold coated on silicon respectively, performed at $T_F=1800^\circ\text{C}$ by HFCVD system (Fig. 1). The same result for the other aluminum substrate obtained in PECVD system at $2\theta\approx 44.50^\circ$ but here the hydrogen plasma was used for etching the substrate (Fig. 2a). However, we cannot see the diamond peak of (111) crystallinity in the last sample, made by PECVD, but the pattern displays a peak with $2\theta\approx 41.91^\circ$ indicating the diffraction from (101) diamond (See Fig. 2b).

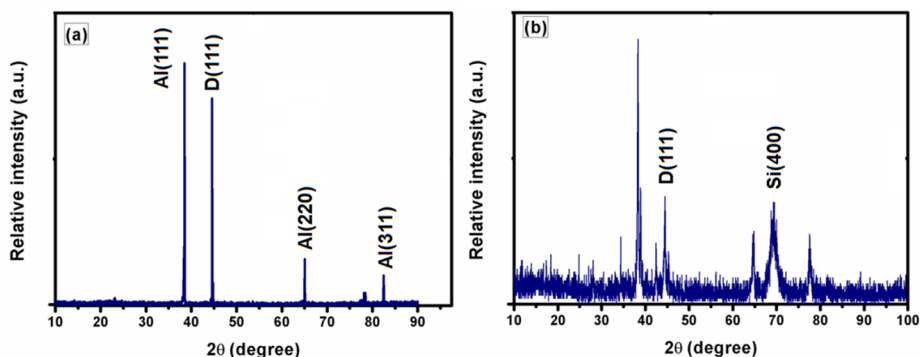


Figure 1. XRD pattern for diamond crystals grown by HFCVD system: (a) Al substrate and (b) Gold coated on silicon.

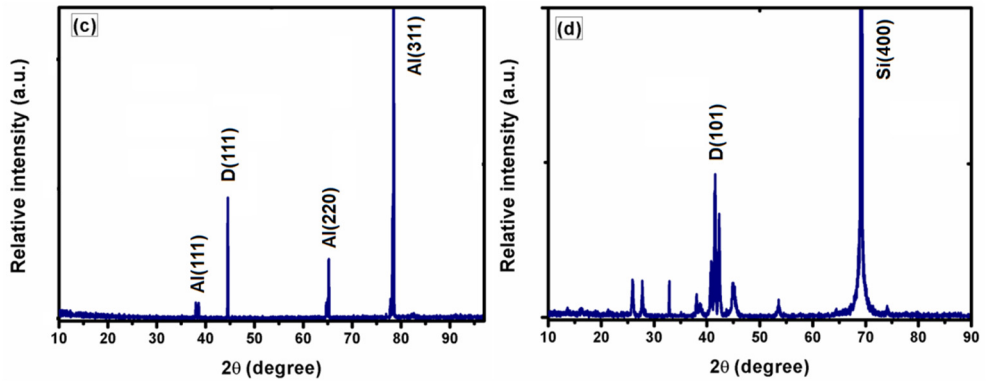


Figure 2. XRD pattern for diamond crystals grown by PECVD system: (a) Al substrate and (b) Gold coated on silicon.

One of the best factors for crystallite quality is Full Width Half Maximum (FWHM) of the XRD patterns. In fact, sharp peaks with small FWHM indicate a high crystal quality [28]. The sharp peaks with small FWHM in Al samples confirm this idea. But a better result in Al sample refers to the sample grown by HFCVD system. The high ratio of reactive gases is the essential parameter for growing diamond nano crystals. Because of the hot filament in HFCVD system, the ionization rate of the reactive gases is much higher than in the case of plasma system of PECVD. On the other hand, in PECVD, in the case of gold coated on silicon substrate, different types of diamond crystals were obtained when different CVD systems were used. The SEM micrographs, in Fig. 3, show the morphology of diamond nano and micro structures, grown on aluminum and gold coated on silicon substrates.

As we can see, diamond single crystals grow in the case of Al substrate, in both the systems (Fig. 3(a)-(b)), whereas a high comparative distribution of nano crystalline diamond can be observed in the case of using gold coated on silicon (Fig. 3(c)). Fig. 3(d) shows some dendritic structures which led to crystals with a regular distribution of nano and micro diamond crystals.

According to Scherer formula, the grain size (T) of diamond crystals is calculated by $T=0.9\lambda/\Delta(2\theta) \cos \theta$, where $\Delta(2\theta)$ is the FWHM in radians and λ is the wavelength in nm [29].

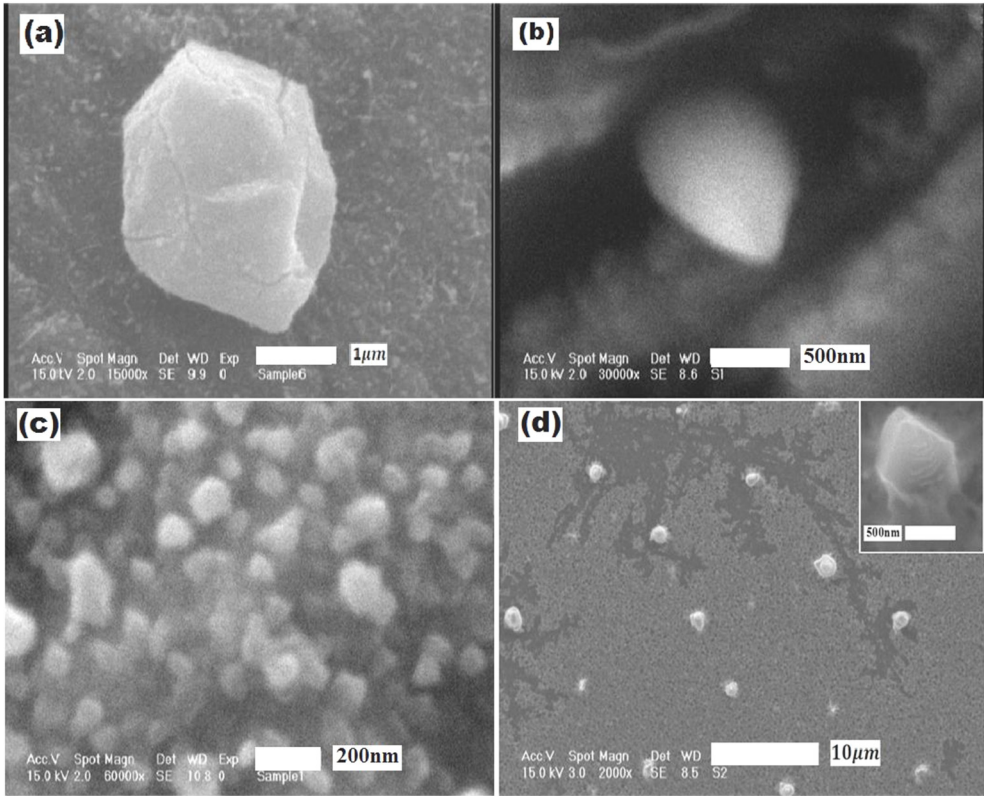


Figure 3. SEM images of nano and microcrystalline diamond grown on: (a) Al substrate by HFCVD, (b) Al substrate by PECVD, (c) Si coated by gold substrate by HFCVD, (d) Si coated by gold substrate by PECVD.

Table 1. Result of XRD studies for diamond crystals grown on gold coated on silicon and aluminum substrates.

Sample	Orientation of plane	$\Delta(2\theta)$ (deg)	T(nm)
Si(HFCVD)	[111]	0.196	44.70
Si(PECVD)	[101]	0.136	66
Al(PECVD)	[111]	0.15	57.75
Al(HFCVD)	[111]	0.09	106.61

The calculated grain size for the diamond crystals grown on the silicon and aluminum substrates measured less than 110 nm. Detailed data for the grain size of the diamond were listed in Table 1.

CONCLUSIONS

In this work, growth of diamond nanocrystals with orientation in (111) plane on gold coated on silicon and aluminum was investigated by two different CVD techniques. Using HFCVD technique, diamond nano and micro crystals with (111) crystallinity were grown on Al and Si substrates. By PECVD technique, a high quality (111) diamond was obtained on Al substrate and (101) diamond crystals on gold coated on silicon. The XRD patterns shown a good quality for the diamond structures grown on aluminum in both techniques, as proved by high intensity and small FWHM in diamond peaks; however, the high concentration and distribution of the diamond nanocrystals on the substrate with lower grain size of the particles were obtained in gold coated on silicon substrates, synthesized by HFCVD. It was proved that the ionization rate of reaction gases has a great influence on diamond nucleation. This is achieved in the case of HFCVD, the hot filament providing a high concentration of ionized gas. It was shown that the usage of H₂ as etching gas in different CVD methods results in diamond nanocrystals, with high concentration of distribution and crystalline quality, on gold coated on silicon substrates.

MATERIALS AND METHODS

Silicon wafers [Si-P typed] with (10mm×10mm) and aluminum (5mm x 5mm) with 99.99% purity were used as substrates in this experiment and pretreated in two steps. For aluminum pretreatment, all the substrates were polished with diamond paste to obtain a smooth surface. Before loading into deposition chamber, the Al substrates were ultrasonically cleaned in a bath of acetone, ethanol and de-ionized water for 15 minutes. The Si samples were ultrasonically cleaned with acetone and ethanol for 15 minutes and a gold nanolayer of 13nm thickness was deposited on the silicon substrate as a catalyst nano layer. Gold deposition was made by a direct magnetron sputtering system, consisting of a cylindrical glass tube and two parallel disks as cathode and anode in its chamber in which a uniform magnetic field was induced for Au coating from outside. In this case, the applied voltage was 2000 V. The argon gas was used as a sputtering gas and the operation pressure was set at 5×10^{-2} Torr. Figure 4 represents the 2D and 3D Atomic Force Microscopy (AFM) image of the gold sputtered substrate; the roughness of the substrate after coating with gold can be seen. The average roughness for the gold coated on silicon was 8.33 Å; this was 15.5 Å for Al polished by diamond paste.

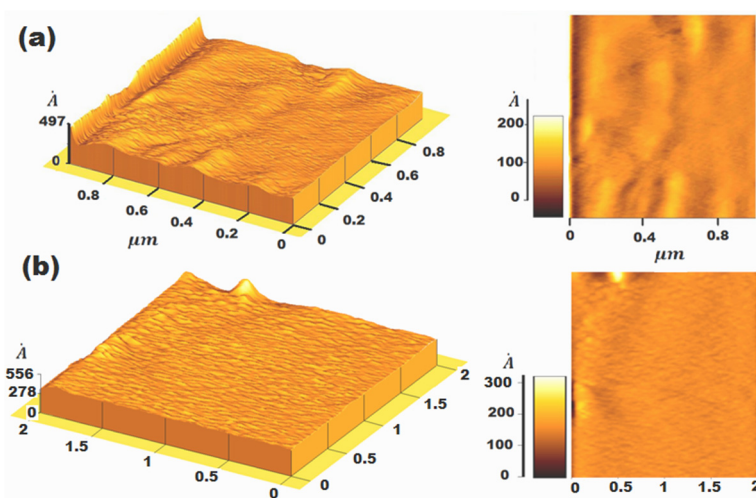


Figure 4. AFM image of the: (a) Aluminum polished by $1\ \mu\text{m}$ diamond paste; (b) Gold coated on silicon substrate.

Deposition of diamond structures carried out in the Hot Filament Chemical Vapor Deposition (HFCVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD) systems. The HFCVD system consists of a gas dispersion system inside a horizontal stainless steel (S.S.316) cylinder as a reaction chamber, a filament network, and an aperture support plate for the substrate (Fig. 5(a)).

The parallel tungsten filaments were employed for activation of gas-phase reactions. The Si coated by gold nanolayer and Al substrates were placed 5mm below to five 0.5mm diameter hot filaments. After the base pressure reached to near to 10^{-5} Torr, the substrate temperature and the temperature of the filament increased up to 450°C and 1600°C , respectively. The hydrogen gas was used for etching the substrates to enhance the diamond nucleation. The H_2 gas was fed into the reaction chamber, at 10 Torr, as the etching pressure, for 45 minutes. For growing the diamond structures, a combination of CH_4/H_2 with 5% flow ratio was fed into the reaction chamber. Prior to diamond deposition, a carbonized interlayer was formed. This layer plays an important and complex role in the diamond nucleation [27]. The reaction pressure and temperature of the filament, for the growth process, were 30 Torr and $\approx 1800^\circ\text{C}$, respectively; the time taken for the growth was 60 minutes. These conditions were preserved for all the samples herein studied. We have done the same experiment in parallel with PECVD system to compare the result of diamond deposition by different CVD methods.

Fig. 5(b) shows the schematic diagram of the DC-PECVD system. After the chamber was pre-evacuated by rotary pump, the base pressure of the system was kept at 1×10^{-2} Torr. The substrate was placed on a furnace right under the anode. The applied voltage and current were 400 V and 25 mA, respectively. The other experimental conditions were same as in the case of HFCVD system. The temperatures of the substrates in both systems were monitored by two thermo-couples, separately.

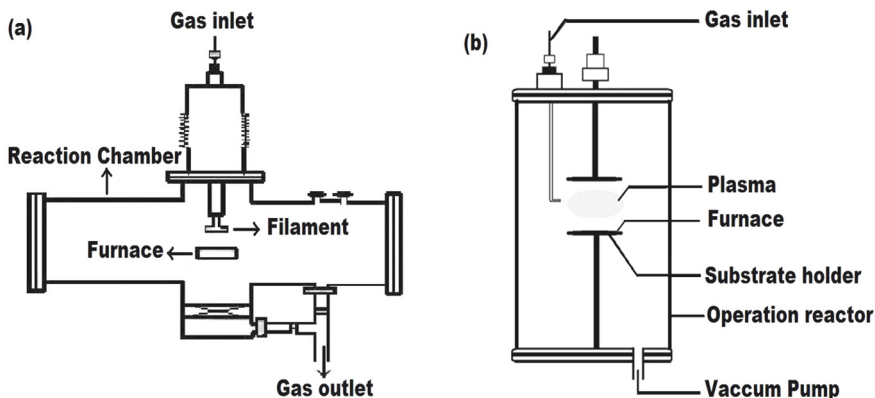


Figure 5. Schematic diagram of: (a) the HFCVD and (b) PECVD, systems.

The morphology of the diamond structures was observed by SEM (XL30, Phillips, Holland), and the crystallinity of the samples was studied by XRD ($\text{CuK}\alpha$, $\lambda=0.154\text{nm}$, $D/\text{Max}=2200$, X-ray diffractometer) analysis.

ACKNOWLEDGMENT

Many thanks are addressed to Professor Mircea V. Diudea for his valuable advice and to Plasma Physics Research Center, Tehran, for technical support.

REFERENCES

1. D. Rommel, F. Scherm, Ch. Kuttner, U. Glatzel, *Surface & Coatings Technology*, **2016**, 291, 62.
2. K. Yamazaki, K. Furuichi, I. Tsumura, Y. Takagi, *Crystal Growth*, **2008**, 310, 1019.
3. A.M. Alexeev, R.R. Ismagilov, E.E. Ashkinazi, A.S. Orekhov, S.A. Malykhin, A.N. Obraztsov, *Diamond and Related Materials*, **2016**, 65, 13.

4. X. Sun, Y. Li, B. Wan, L. Yang, Q. Yang, *Surface and Coatings Technology*, **2015**, *284*, 139.
5. H.E. Zhoutong, Y. Shumin, L. Qintao, Z. Dezhang, G. Jinlong, *Nuclear Science and Technology*, **2008**, *19*, 83.
6. Y. Takano, M. Nagao, T. Takenouchi, H. Umezawa, I. Sakaguchi, M. Tachiki, H. Kawarada, *Diamond and Related Materials*, **2005**, *14*, 1936.
7. B. Aldwell, Sh. Yin, K.A. McDonnell, D. Trimble, T. Hussain, R. Lupoi, *Scripta Materialia*, **2016**, *115*, 10.
8. L.G. Wang, L.W. Jiang, L. Ren, J. M. Liu, Q.F. Su, R. Xu, H.Y. Peng, W.M. Shi, Y.B. Xia, *Transactions of Nonferrous Metals Society of China*, **2006**, *16*, 289.
9. N. Kohmura, K. Sudoh, K. Sato, K.K. Hirakuri, K. Miyake, G. Friedbacher, *Diamond and Related Materials*, **2005**, *14*, 283.
10. A. Bogus, I.C. Gebeshuber, A. Pauschitz, M. Roy, R. Haubner, *Diamond and Related Materials*, **2008**, *17*, 1998.
11. M.S. You, F.C.N. Hong, Y.R. Jeng, S.M. Huang, *Diamond and Related Materials*, **2009**, *18*, 155.
12. I.E. Monje, E. Louis, J.M. Molina, *Scripta Materialia*, **2016**, *115*, 159.
13. S. Yang, Z. He, Q. Li, D. Zhu, J. Gong, *Diamond and Related Materials*, **2008**, *17*, 2075.
14. C.J. Tang, A.J. Neves, S. Pereira, A.J.S. Fernandes, J. Gracio, M.C. Carmo, *Diamond and Related Materials*, **2008**, *17*, 72.
15. S.A. Rakha, S. Yang, Z. He, I. Ahmed, D. Zhu, J. Gong, *Current Applied Physics*, **2009**, *9*, 698.
16. J. Hirmke, S. Schwarz, C. Rottmair, S.M. Rosiwal, R.F. Singer, *Diamond and Related Materials*, **2006**, *15*, 536.
17. X.T. Zhou, H.L. Lai, H.Y. Peng, C. Sun, W.J. Zhang, N. Wang, I. Bello, C.S. Lee, S.T. Lee, *Diamond and Related Materials*, **2000**, *9*, 134.
18. A. Bogus, I.C. Gebeshuber, A. Pauschitz, M. Roy, R. Haubner, *Diamond and Related Materials*, **2008**, *17*, 1998.
19. K.C. Yang, Y.B. Xia, L.J. Wang, J.M. Liu, I.F. Su, R. Xu, H.Y. Peng, W.M. Shi, *Transactions of Nonferrous Metals Society of China*, **2006**, *16*, 321.
20. Y. Yamazaki, K. Ishikawa, N. Mizuochi, S. Yamasaki, *Diamond and Related Materials*, **2005**, *14*, 1939.
21. Yu. A. Mankelevich, P.W. May, *Diamond and Related Materials*, **2008**, *17*, 1021.
22. O. Matsumoto, H. Tushima, Y. Kanzaki, *Thin solid films*, **1985**, *128*, 341.
23. B.V. Spitsyn, L.L. Bouilov, B.V. Derjaguin, *Crystal Growth*, **1981**, *52*, 219.
24. M. Tsuda, M. Nakajima, S. Oikawa, *Japanese Journal Applied Physics*, **1987**, *26*, L527.
25. M. Frenklach, *Applied Physics*, **1989**, *65*, 5142.
26. Y. Mitsuda, Y. Kojima, T. Yoshida, K. Akashi, *Material Science*, **1987**, *22*, 1557.
27. K.I. Itoh, C. Morishima, K. Ubukata, A. Chiba, H. Aida, O. Matsumoto, *Diamond and Related Materials*, **2000**, *9*, 140.
28. S. Schwarz, C. Rottmair, J. Hirmke, S. Rosiwal, R.F. Singer, *Crystal Growth*, **2004**, *271*, 425.
29. M. Pandey, R. D'Cunha, A.K. Tyagi, *Alloys and Compounds*, **2002**, *333*, 260.