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EFFECT OF CATALYST LAYER THICKNESS ON GROWTH OF CVD DIAMOND

FATEMEH SHAHSAVARI[a, b], MAHMOOD GHORANNEVISS[a, †], ZAHRA KHALAJ[a], MIRCEA V. DIUDEA[c]

ABSTRACT. Tungsten Nanocrystalline Diamond (NCD) films were grown on silicon substrates by Hot Filament Chemical Vapor Deposition (HFCVD) method using three different catalyst layer thicknesses. At first, the silicon substrates are ultrasonically cleaned in acetone; ethanol and demonized water for 15 minutes in each step to remove organic contaminants, then gold layers were deposited on silicon substrate by DC magnetron sputtering. Nitrogen gas 80 Sccm was introduced into HFCVD chamber for 40 minutes and the growing process were done in a mixture of CH_4/H_2 for 75 minutes. Crystal structure investigations were carried out by X-ray diffraction (XRD) measurements for deposited films. The XRD spectra of the NCD films demonstrated different diffraction peaks for different catalyst layer thicknesses that confirmed the presence of crystalline diamond. Morphology of the diamond films were investigated by scanning electron microscopy. The thickness of the gold nanolayer of each substrate was measured by DEKTAK surface profile measuring system.

Keywords: *Nanocrystalline diamond films, Catalyst, Hot filament CVD, Etching*.

INTRODUCTION

Synthesis of diamond films by chemical vapor deposition (CVD) have been extensively studied during the last decades because of their unique properties and potential applications in mechanics, optics and electronics [1-7]. Diamond films could be produced by various chemical vapor deposition (CVD) methods, including microwave plasma [8-12], hot filament [13-17], arc plasma jet system [18-20] and magnetically enhanced radio frequency assisted plasma [21-22] methods. Among these methods, hot filament chemical vapor deposition (HFCVD) has been one of the most common methods for synthesis of diamond films.

† *E-mail address: Ghoranneviss@gmail.com*
[a] *Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran. P.O. Box:14665/678*
[b] *Eghbal Techno-Center, Yazd Scientific and Technology Park, Yazd, Iran*
[c] *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj, Romania*

During the HFCVD system, various gas species formed on and near the filament which their transport to substrate play an important role in growing of diamond film [17]. Therefore the parameters, such as the gas pressure [16-17, 23], the temperature of filament and substrate [24-28], the composition of the source gas [13, 16, 29-30] play an important role in CVD diamond growth. Another important part in growing of CVD diamond deposition is nucleation. Various nucleation processes were used such as bias enhanced nucleation (BEN) [24, 31-33], seeding the substrates by scratching with diamond powder, and ultrasonic agitation of substrate with diamond powder [16, 34-36]. It can also be done by etching gas [37]. In the present work, nitrogen used as etching gas to provide suitable nucleation sites for growing nano diamonds.

Using catalyst nano layer, is a useful method to reduce the time from over than four hours to about one hour in HFCVD systems [16], so we used catalyst nano layer to reduce time into around one hour. To study the effect of different catalyst layer and find the best catalyst thickness layer on the growth of NCD films, different catalyst nano layer's thickness were deposited on the substrates. The XRD spectra of the NCD films demonstrate different diffraction peaks for different catalyst thicknesses layer which confirm the presence of crystalline diamond. Scanning electron microscopy (SEM) shows the various morphologies of the films.

RESULTS AND DISCUSSION

1. Catalyst Layer Thickness Measurements

The thickness of the catalyst nano layer varied within the range of 21.6-62nm. The Fig. 1 shows the thickness measurement of the catalyst nano layer for the three samples by Dektak3 profilometer. Fig.1 (a) shows the 21.6 nm thickness for the first sample. Fig. 1(b) and Fig. 1(c) corresponded to second and third sample with thickness of 49 and 62.4 nm for catalyst layer, respectively. These three samples were named A, B and C, respectively.

2. Morphology study

Fig. 2 shows the SEM morphology of the NCD films deposited at different layer thicknesses of the catalyst. The morphology of the samples are similar, as shown in the Fig. 2, revealing diamond films with cauli-flower like structure.

A wide dispersion of NCD structures were observed in sample A with a lowest thickness layer (Fig.2a). By increasing the catalyst thickness layer to 49nm in sample B, the film morphology became denser and smoother and the whole surface is covered by diamond film (see Fig. 2b). In the sample C with the highest catalyst thickness layer, the crystal size increased

around 200nm (see Fig. 2c). In Fig. 2c there is also changes in nucleation density and the films became less dense. For comparing the grain size of samples B and C was shown in the inset of Fig. 2. The smallest grain size with around a couple of tens nanometers corresponded to sample B. The second nucleation made bigger particles in sample C.

3. X-ray diffraction

XRD patterns of the diamond films deposited for different catalyst layer thicknesses were shown in Fig. 3. For diamond films in sample A, XRD patterns exhibit four peaks from (1 1 1), (104), (110), and (311) crystal planes of diamond. By increasing the layer thickness in sample B, five different crystalline structure of(101), (1 0 2), (104), (108) and (311) was observed, in which the best quality of the diamond peaks refer to the structure with (101) crystallinity. For sample C, the diamond peaks with (111) and (106) crystal planes were only observed. To investigate more, the XRD results were summarized in Table 1. Crystalline structures of (104) and (311) existed in both sample A and B, which they had a higher relative intensity and FWHM in sample B. Regarding to Sherrer's formula, sample B had a better quality and smaller grain size. There was the same crystalline structure of (111) for sample A and C which had the same amount of FWHM and different relative intensities. In XRD spectra of sample C, a sharper peak at 16.3˚ and 33.13˚ corresponded to non-diamond structures. The results show that, by increasing the thickness of the catalyst layer, from 49nm to 62nm, we can see some extra structures. It can be concluded that catalyst thickness layer directly changed the quality, grain size and even crystalline structure of deposited diamond films. XRD studies confirmed previous observation in SEM images that the smallest grain size was corresponding to sample B, which has also the best quality of diamond films. In all samples, the peak at 2theta≈69.2˚ corresponded to Si, the substrate.

CONCLUSIONS

In this study, the effect of different thicknesses layer of the Au catalyst was investigated in HFCVD system. Different thicknesses of nano catalyst layers within the range of 21-62nm, has different effects on CVD diamond growth. XRD characterizations presented changes in diffraction peaks of crystalline diamond within changing the catalyst thickness layer. Optimized catalyst layer thickness found in sample B with the sharpest peak and small FWHM which indicates the higher quality of CVD diamonds. In sample C with the highest catalyst layer thickness, the quality of diamond films decreased and other non diamond structures appeared.

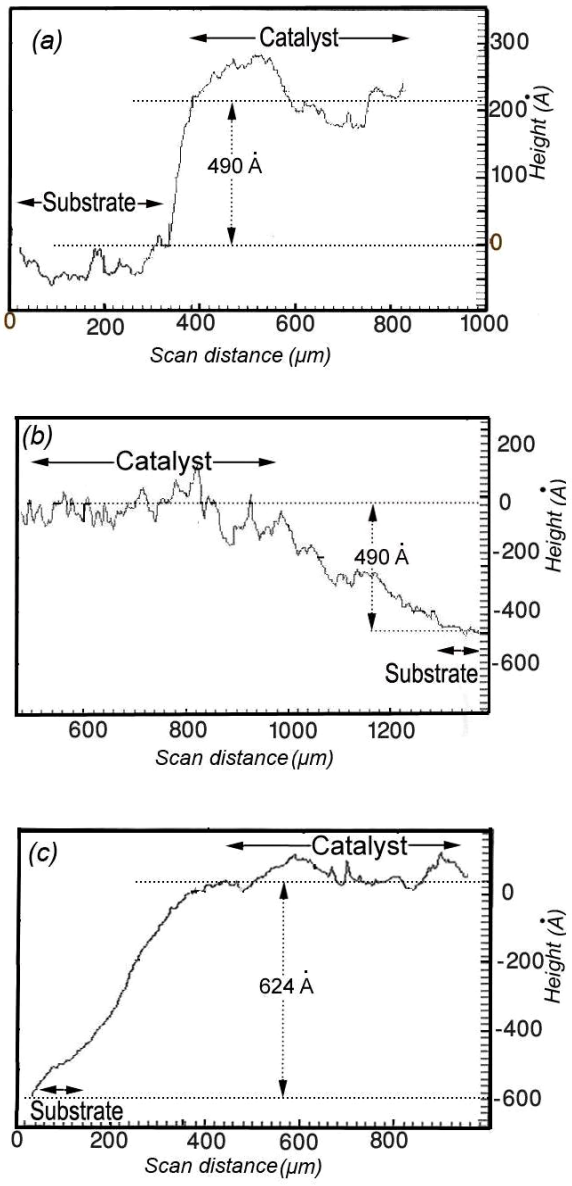

Fig. 1. DEKTAK profilometer results show:
a) sample A with 21.6nm, b) Sample B with 49nm, and
c) sample C with 62.4 nm, for thickness layer.

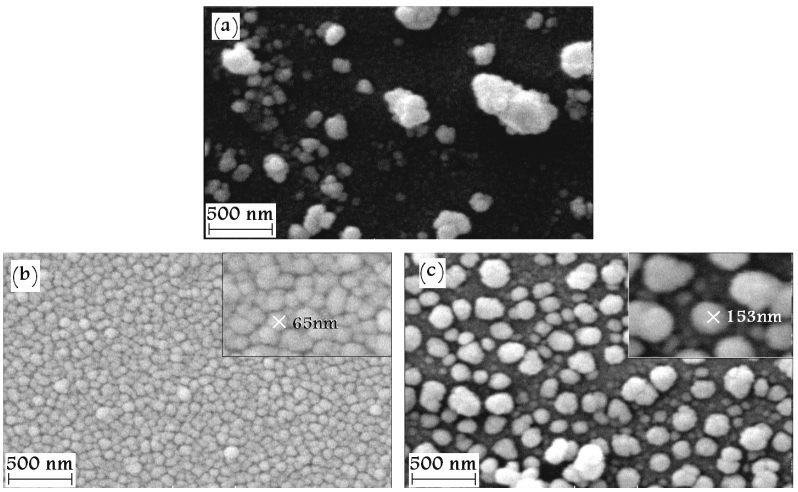

Fig. 2. SEM morphologies of the nanocrystalline diamond deposited in various thicknesses of catalyst layers: (a) sample A, (b) sample B, and (c) sample C. The inset shows the Increasing of the grain size in 200nm scale by increasing the thickness of the nano catalyst layer from sample B to C.

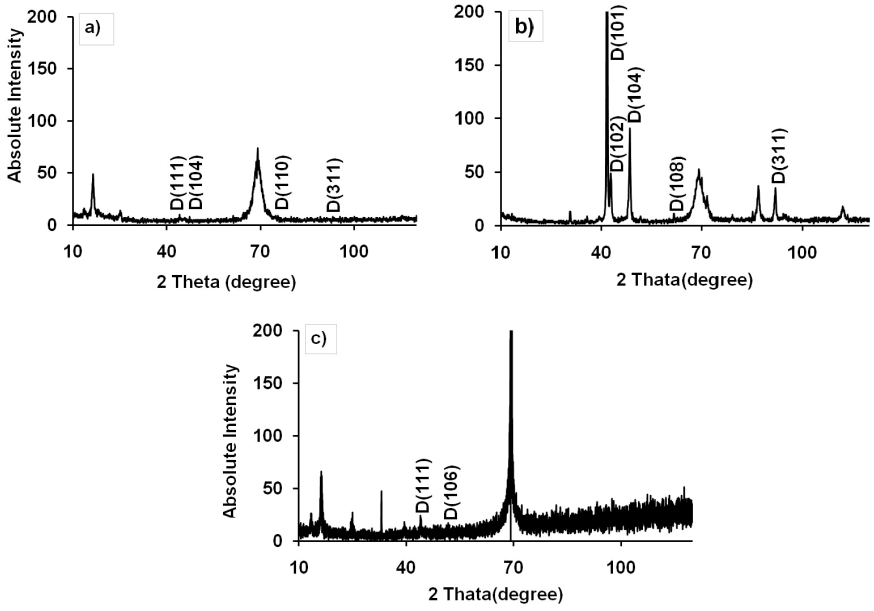

Fig. 3. X-ray diffraction spectra of the diamond films for (a) sample A, (b) sample B, (c) sample C.

Table 1. Results of the XRD studies of the diamond films grown at different catalyst layer thicknesses

Sample	Catalyst layer thickness	Orientation of plane	Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	Rel. Int. [%]
A	21.6 (nm)	[111]	44.02	2.89	0.315	6.98
		[104]	47.28	2.72	0.236	6.58
		[110]	75.55	2.15	0.315	5.19
		[311]	92.48	1.15	0.197	2.78
B	49 (nm)	[101]	41.68	279.04	0.275	100
		[102]	42.88	38.67	0.315	13.86
		[104]	48.55	84.73	0.275	30.36
		[108]	61.69	6.66	0.197	2.39
		[311]	92.02	28.74	0.275	10.3
C	62.4 (nm)	[111]	44.07	10.76	0.315	0.06
		[106]	53.40	2.28	0.236	0.01

EXPERIMENTAL SECTION

A hot filament CVD system was used for deposition of nanocrystalline diamond in which the tungsten filament was 1.1mm in diameter and about 1.5 cm in length. P-type silicon wafers with [100] orientation were used as the substrates. The substrates were ultrasonically cleaned in acetone, ethanol and deionized water for 15 minutes in each step to remove organic contaminants.

After pretreatment of Si substrates, to deposit different catalyst layers of gold [38], they were loaded in a DC magnetron sputtering system at 1.3 Pa (10^{-2} Torr) in Ar with Au target. The thickness of the gold nano layer of each substrate was measured by DEKTAK3 surface profile measuring system. Then the substrates put into the stainless steel subholder below the hot filament wires. The distance between filament and substrates was 1.5 cm. The chamber was pumped down to the base pressure of 1.3 Pa with a rotary pump and after that reached to 2×10^{-2} Pa (1.5×10^{-4} Torr) with diffusion pump.

In the first step, argon gas with flow ratio of 208 sccm was introduced into the chamber for etching the substrates with total pressure of 4 KPa (30 Torr) for 45 minutes. In the second step, nitrogen was introduced into the chamber as an etching gas with flow rate of 80 sccm. At this time, the filament was reached to about 1600°C. The working pressure was kept in 667 Pa (5 Torr) and duration of time was 40 minutes. In the last step, for growing the nanocrystalline diamond, a mixture of precursor gases of methane and hydrogen were introduced into the chamber. Methane and hydrogen were introduced to the reaction chamber with a total flow rate of 150 sccm to keep the CH4/H2 ratio at 10%. The working pressure in this step was 4 KPa

and nanocrystalline diamond was grown after only 75 minutes. During each step, the substrate temperature was controlled by the thermocouple and was kept on 600°C.

The deposited films were characterized by scanning electron microcopy (SEM, XL30), X-ray diffraction spectroscopy (Cu Kα, λ=0.1541 nm), and DEKTAK3 version 2.13 at room temperature.

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