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DEPOSITION AND CHARACTERIZATION OF NANO CRYSTALLINE DIAMOND ON DIFFERENT SUBSTRATES BY PLASMA ENHANCED CVD TECHNIQUE

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ABSTRACT. In this paper, we report the results concerning characterization of the nanocrystalline diamond with different crystallite structures with the purpose of determining the parameters responsible for the texture, crystallinity, and surface morphology. Beyond the influence of the substrate on these characteristics, the role of the etching gas on diamond growth is studied. It is shown that the grain size is a strong function of the substrate's material. Crystalline grain size is estimated by broadening the X-ray diffraction peaks using the Scherer equation. Other techniques for structural and morphological characterization used in this study are Raman spectroscopy and Scanning electron microscopy and Fourier Transform Infrared spectroscopy.

Keywords: *Etching gas, Crystallinity, NCD.*

INTRODUCTION

Synthesis of Microcrystalline Diamond (MCD) films and Nanocrystalline Diamond films (NCD) by variety of Chemical Vapor Deposition (CVD) techniques, have generated a great interest. Scientists are interested on growth of NCD and MCD with carbon containing gas mixture such as CH_4/H_2, $H_2/CH_4/O_2$, $H_2/CH_4/N_2$ or other gases of different composition [1-8]. In the two last decades because of outstanding properties and useful applications of diamond films such as high thermal conductivity and low electrical conductivity or optical transparency, scientists studied about growing and using diamond coating for instruments such as cutting tools, modern biomedicine, or micro- and nano-electromechanical and optical systems [9-11]. It is believed that $C\text{-}H_x$ radicals played major roles in NCD growth the same as in MCD growth [12]. Most of the researches preparing nanocrystalline diamond thin films have been done by using plasma enhanced CVD, microwave and hot filament CVD process or pulsed laser deposition [13-20].The fundamental aspect of beneficial's Plasma Enhanced Chemical Vapor Deposition(PECVD) uses electron energy as the activation method to enable deposition to occur at low temperature and at reasonable rate [25]. Investigating the effect of substrate on crystallinity of the diamond films by DC-PECVD method is the

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purpose of this project. Using chemical or physical etching of substrate is another effective way to increase the diamond nucleation. Using hydrogen as etching gas provides suitable sites for nucleation and growth of CVD diamond. Besides, C.K. Lee et al in 2008 reported that Hydrogen plasma treatment of as-grown CVD diamond surfaces provide a smoother surface [21]. It is proved that nanocrystalline diamond thin films could be deposited on gold coated silicon as the best substrate in this study. We investigate surface morphology and the formation of diamond crystals. Scanning electron microscopy (SEM), X-ray diffraction (XRD), DEKTAK profilometer, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy was used for analyzing the samples.

RESULTS AND DISCUSSION

The instrument used in this experiment for coating Au nanolayer was direct magnetron sputtering system. This system consists of a cylindrical glass tube with 18 cm high and 16 cm in diameter, and two parallel disks as cathode and anode in its chamber [15]. Argon was selected as a sputtering gas. A uniform magnetic field was induced for Au coating from outside. Silicon wafers were coated by gold for 8 minutes. The thickness of the gold catalyst layer for these substrates was 50 nm given by DEKTAK profilometer 3, version 2.13 that reveals in Figure 1.

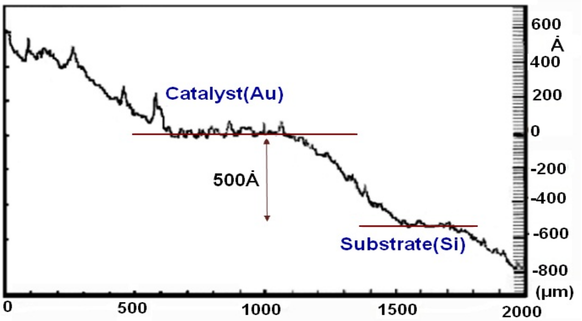

Figure 1. The thickness of gold coated silicon substrate measured by DEKTAK profilometer

The surface morphologies of the deposited films were investigated by scanning electron microscopy reveals that the morphology of nanocrystalline diamond. As shown in the Figure 2 (a-c), different nanocrystalline diamond grows in various substrates. NCD films grown on S_1 substrate can be seen in Fig. 2 (a). Because of the lower density of nano crystalline diamond and low distribution was obtained from this sample, this substrate was further declined [22]. Figure 2 (b) illustrates the NCD films grown on S_2 substrate. Finally, more concentrate NCD films are produced on the S_3 substrate (See Fig. 2 (c)).

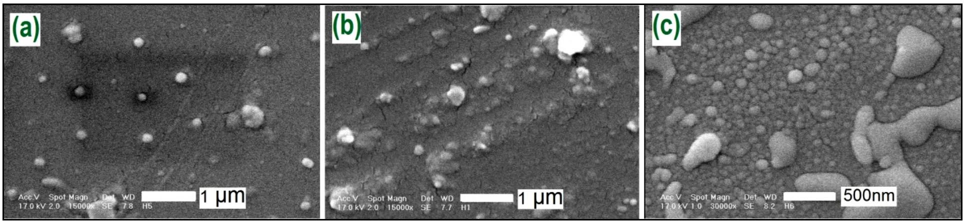

Figure 2. The surface morphology of the NCD films deposited on different substrates: (a) S_1, (b) S_2 and (c) S_3.

Diamond crystals can be investigated by means of X-ray diffraction spectroscopy, an imaging technique based on Bragg diffraction as shown in Figure 3(a–c). The crystal size varies from 14 nm to 50 nm, as deduced from the XRD spectra (Figure 3(a)).There is one peak at 2θ= 42.65° that indicates the diamond (102) on sample S_1. Oxygen in this sample reduces the diamond crystallite by increasing the sp^2 amorphous carbon phase content. According to the Scherrer formula, the grain size of the nanocrystalline diamonds, d, were calculated by $d = 0.9\lambda/\Delta(2\Theta)\cos\Theta$, where $\Delta(2\Theta)$ is the FWHM in radians and λ is the wavelength [23].

The grain size of NCD for S_1 was estimated 30 nanometers by using the Scherrer formula. Three peaks with relatively large FWHM at 42.61° and 66.50° and 90.26°are clearly observed for S_2 substrate. In addition, we note that the XRD pattern indicates the presence of diamond (102), (109), (202) crystallites structure (Figure 3(b)). For S_3, there are three main diffraction peaks at 2θ= 41.58°, 43.44°, 66.50° that give evidence for the diamond type (101), (008), (109), respectively (See Fig. 3 (c)). Using the Scherrer formula, the grain size was calculated as 30, 20 and 67 nm for sample S_3.

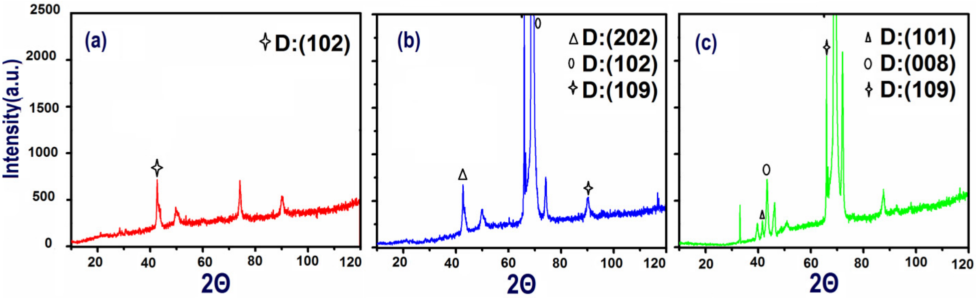

Figure 3. Representative XRD spectra of the NCD film grown on different substrates: (a) S_1, (b) S_2 and (c) S_3.

Raman scattering is one of the most important method to characterize the diamond quality which approximately 50 times more sensitive to small grain size or amorphous diamond and graphite, hence, it is frequently used to characterize CVD diamond films [25,26]. The Raman spectra of the diamond deposited films, measured by 628 nm excitation wave length of Nd: YLF laser are shown in Fig. 4. The Raman spectra of the NCD films grown on S_1 substrate display one major features at around 1150 cm^{-1}which are corresponding to diamond while a sharp peak at 1326 cm^{-1} that be observed for the NCD films deposited on S_2 substrate, both of them confirming that the major phase in the films is diamond and show variation of NCD films. Whereas, in Figure 4(c), the D peak for the grown NCD films on S_3 substrate is observed at 1332 cm^{-1}. One of the best factors for crystallite quality in Raman and XRD is Full Width Half Maximum (FWHM) of the patterns. In fact, sharp peaks with small FWHM indicate high crystal quality. The intensity of the Raman peaks increases from S_1 to S_3, however the FWHM of the peaks are reduced in this case. As can be seen verifies occurrence of the characteristic diamond and suggesting a better crystallite of sp^3 diamond phase, respectively that are finding agreeing well with literature data which is in good agreement with XRD measurement. Briefly, the Raman spectroscopy and XRD analysis reveals that the crystallites of the deposited films has changed by different substrates also indicated that a greater sp^2 bonded carbon component containing at sample S_1. Therefore, the crystallites and quality of the films increases in the following order, $S_1 < S_2 < S_3$.

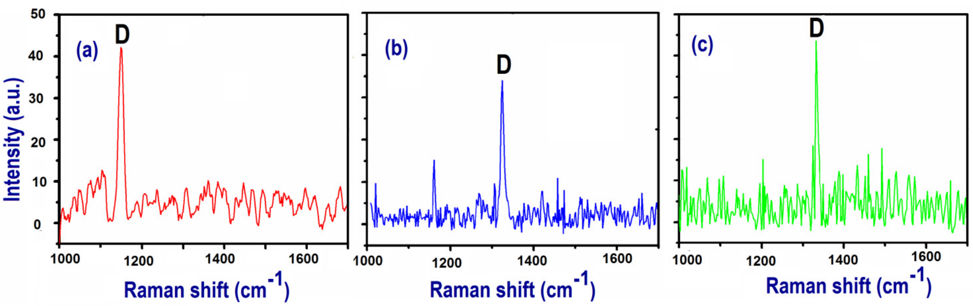

Figure 4. Raman spectrum of the deposited films on: (a) S_1, (b) S_2 and (c) S_3

Fourier Transform Infrared (FTIR) spectroscopy is a spectroscopic technique used to characterize the chemical bonds, molecular structures and $C\text{-}H_n$ (n=1, 2, 3) bonding configurations in carbon materials. It is allowed to analyzing in more details the nature of chemical bonding in all tested carbon nanomaterials. The typical infrared spectra of the diamond films deposited on S_1, S_2 and S_3 substrates, in the range of 1000-4000 cm^{-1}, are shown in Figure 5. The peaks at 2852 cm^{-1} and 2921 cm^{-1} are related to the $C–H_2$ and

$C–H_2$ which refers to the symmetric and asymmetric stretch vibrations of $C–H_2$, respectively. These are reveals clearly the absorption bands of CVD diamond. For all samples there are no peaks in the region of 3000–3150 cm^{-1}, which would imply the presence of unsaturated hydrocarbons.

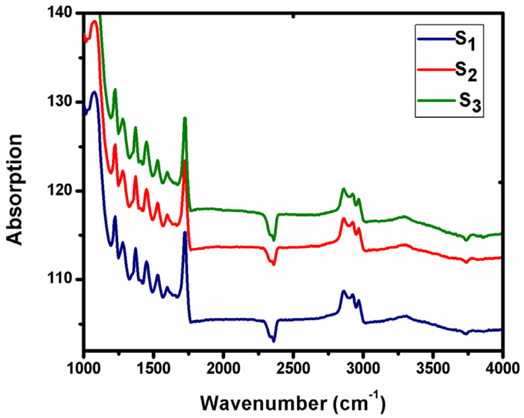

Figure 5. FTIR absorbance spectra of the diamond films grown on S_1, S_2 and S_3

CONCLUSIONS

In this paper, growth of nanocrystalline diamond films on different substrates was investigated by DC-PECVD method. Using gold coated silicon, good quality diamond nano crystals with different crystallite structures were grown on pretreated substrates. The XRD and Raman analysis patterns show that diamond nano crystals grown on Si covered Au has a higher quality due to their high intensity and small FWHM in diamond peaks. The FTIR analysis in this case shows an absorption band in CVD diamond with peaks at 2852 cm^{-1} and 2921 cm^{-1}, which are believed to be caused by symmetric and asymmetric stretch vibrations of $C–H_2$, vibrations. The results show that substrate pretreatments, hydrogen etching gas and coating gold nanolayer, have great influence on diamond nucleation and growth.

EXPERIMENTAL PROCEDURE FOR DEPOSITION OF DIAMOND FILMS

The NCD films have been synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD) system. The plasma glow discharge system consists of a cylindrical pyrex wall of vertical type reactor chamber having a diameter about 28 cm and length 45 cm. The substrate holder is a stainless steel plate square. A schematic of the deposition chamber is presented in Fig. 6 [26]. After getting the base pressure, a mixture of the gases inserted to the system.

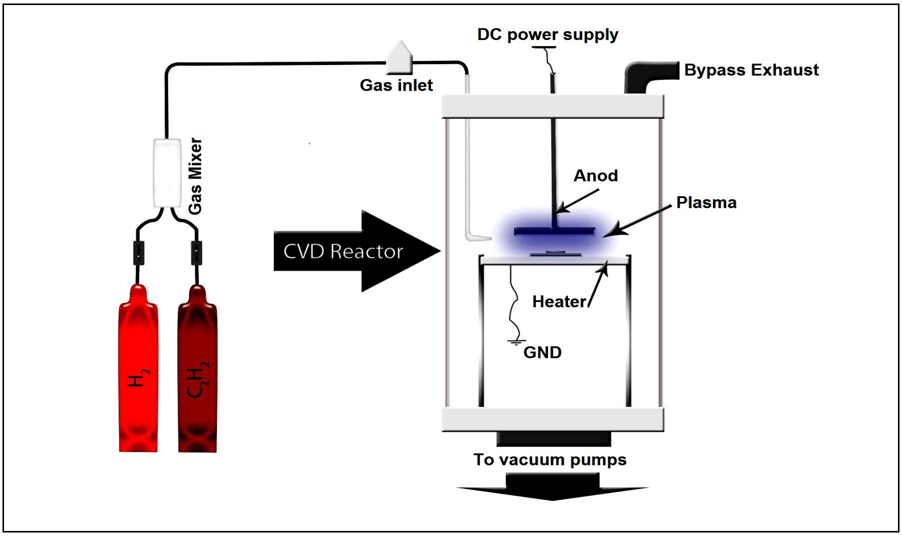

Figure 6. Schematic of the PECVD system which manufactured by our group in Plasma Physics Research Center

The inert gas and the reactive hydrocarbon precursor were premixed in a definite ratio and introduced into the deposition chamber from the top of cylinder. The plasma was produced by application of DC-supply between the substrate and the grounded wall of the deposition chamber.

EXPERIMENTAL PROCEDURE FOR DEPOSITION OF DIAMOND FILMS

The NCD films were deposited on glass, Si and Si coated with Au as catalysts layers by sputtering system which called S_1, S_2 and S_3 respectively. The silicon wafers which used in this study were P-typed with (100) orientation. The substrates were ultrasonically cleaned with acetone, ethanol and de-ionized water for 10 minutes separately before loading into the deposition chamber. The system was evacuated to the base pressure. Prior to deposition of the film, the substrate was etching treated by H_2 plasma at base pressure of 7 Torr with the flow rate about 210 Sccm for 15 minutes. The mixture of hydrogen and acetylene gas was introduced in the chamber and the pressure was adjusted to the required level. The ratio of H_2 and C_2H_2 gas was adjusted by controlling flow rate of these gases independently. DC voltage was applied to the plates after the pressure and flow rate of the gases fixed. The films were allowed to deposit for 1 hour. The substrate temperature and working pressure was kept ~280° C and 12 Torr respectively.

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