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PREPARATION AND CHARACTERIZATION OF DIAMOND-LIKE CARBON FILMS ON VARIOUS SUBSTRATES BY PECVD SYSTEM

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ABSTRACT. Diamond–like carbon (DLC), a form of amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C: H) has been actively studied due to its interesting properties in many fields of industry. In this work, Diamond-like carbon films were deposited on silicon, glass and quartz substrates via DC plasma enhanced chemical vapor deposition (DC-PECVD) system at the substrate temperature of 180°C from gaseous mixtures of C_2H_2/H_2. The deposited films were characterized by Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR) and Raman spectroscopy. FTIR measurements depict the C-H and C-C vibration mode assignments in DLC structures in all of the samples. The Raman spectra confirm the formation of DLC structures due to the existence of the D and G peaks. The surface morphology of the grown films was investigated by AFM analysis.

Keywords: *DLC, FTIR, Plasma Enhanced CVD.*

INTRODUCTION

Diamond-Like Carbon film is an amorphous phase of carbon and atomically, it is consist of sp^2-bonded clusters interconnected by a random network of sp^3-bonded atomic sites [1-2]. These films are classified into two main groups: amorphous carbon (a-C) with approximately no hydrogen and hydrogenated amorphous carbon (a-C: H) with some hydrogen. During the last decades, DLC films have been intensively studied and also utilized in many fields of industry, owing to their outstanding properties like high hardness, low friction coefficient, chemical inertness, and etc [3-5]. DLC films used as protective coatings for magnetic recordings [6] antireflective layers for silicon solar cell [7], solid lubricant coatings for vacuum applications [8] and, so on. Also they can be used as gate dielectrics, intermetal dielectrics and passivation layers for microelectronic purposes [9-10].

A wide range of various deposition techniques have been devised to deposit DLC films such as sputtering [11], ion beam deposition (IBD)[12], cathodic vacuum arc [13], microwave electron cyclotron resonance (ECR) plasma

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CVD[14], plasma enhanced chemical vapor deposition (PECVD) [15-17], because deposition of DLC films requires their surfaces to be continuously bombarded by high energetic ions [18]. The most common deposition methods, suitable for depositing DLCs are DC and RF Plasma Enhanced Chemical Vapor deposition.DLC films deposited by DC-PECVD technique exhibit smaller stress values in comparison with RF-PECVD technique [3, 18]. The possibility of the deposition on a large area and at low temperature is the main advantage of the PECVD technique [15].In this paper, DLC films were coated on quartz, glass and silicon substrates by DC-PECVD system in a mixture of acetylene (C_2H_2) and hydrogen (H_2) in total flow ratio of 200 sccm (C_2H_2/H_2:25 vol. %). The topography of samples was carried out by AFM analysis (Park Scientific instruments, Auto probe cp) in contact mode. Raman measurements were performed using an Almega Thermo Nicolet Dispersive Raman Spectrometer with 532 nm of an Nd: YLF laser. The bonding structures of the DLC films were characterized by Fourier transform infrared (FTIR).

RESULTS AND DISCUSSION

Morphology of the films

Atomic Force Microscopy (AFM) images provide more detailed information involving the surface morphology of the films. Figure 1 show the 3D AFM images of the DLC films produced on S_1, S_2, S_3 and S_4 substrates. The root mean square (RMS) surface roughness is one of the most important parameters to characterize of surface structures. The RMS surface roughness of all samples is less than 5nm over the area of 3μmx3μm. It shows that the DLC films grown on various substrates have a smooth surface. Fig.1 (a) shows the 3D AFM image of the as-deposited DLC on the surface. It can be seen that the surface of the film has tightly packed configuration and smooth surface morphology. The homogeneity and packed configuration of the films were reduced in S_2 and S_3 (see Fig.1 (b, c)). Whereas, The RMS surface roughness of the films deposited on S_4 is increased to 4.68nm, as shown in Fig.1 (d).

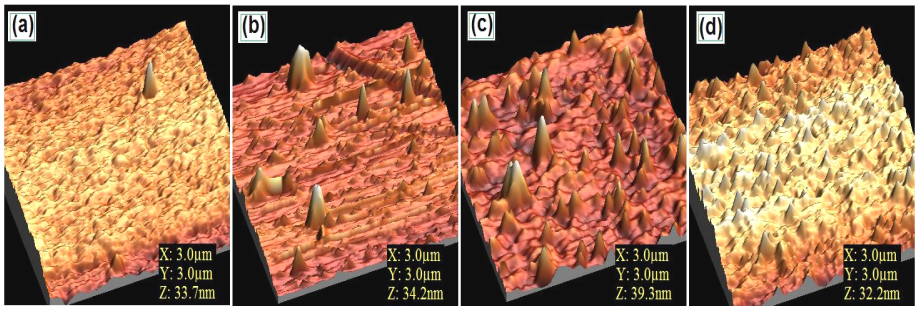

Figure 1. Three dimensional AFM images of the DLC films deposited on different substrates

Figure 2 shows kinds of height changes in a segment AFM images. Existence of valleys in the Figure is related to DLC homogeneity of the surface. As we can see in figure 2(a, b), the peak and valley intensities are near to each other which result in a more homogeneous film deposition on the surface. However, this homogeneity reduces for S_3 and S_4 (see Fig. 2(c, d)). The results of the AFM studies are listed in Table 1.

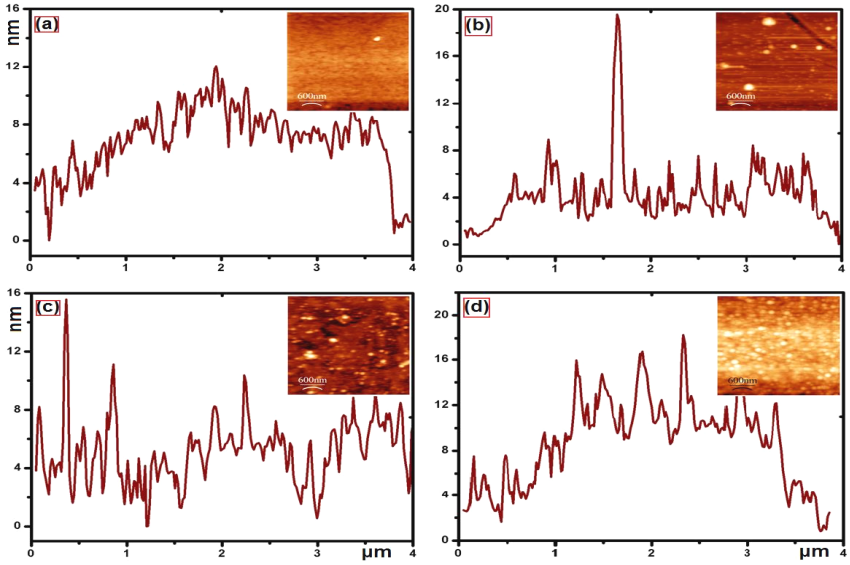

Figure 2. Height changes of the as-deposited DLC on samples (a) S_1, (b) S_2, (c) S_3, (d) S_4

Table 1. AFM studies of the as-deposited DLC on various substrates.

No.	Sample	Etching gas	RMS. rough. (nm)	Ave.Rough (nm)
S_1	glass-Au	H_2	3.29	2.57
S_2	glass	H_2	2.76	1.70
S_3	quartz-Au	H_2	3.90	2.62
S_4	Si -Au	H_2	4.68	3.86

Raman spectroscopy

Raman spectroscopy is a powerful tool for investigating the detailed bonding structure of the DLC films [19]. Fig.3 shows the Raman spectra of the DLC samples, which were measured by Nd: LYF laser at 532nm excitation wave length. The DLC coatings usually have two main features in their Raman

spectra which are commonly well-known as the D and G peaks. The G peak corresponds to the zone center phonons of E_{2g} symmetry while the D peak attributed to the breathing mode of A_{1g} symmetry that contains phonons near the K zone boundary [20]. As shown in Fig. 3, there are two major peaks in these spectra; the peak which is located at a wave number of 1392.80 cm^{-1} is related to the D (labeled 'D' for disorder) bond and another peak at around 1527.72 cm^{-1} is attributed to the G(labeled 'G' for graphite) bond, whereas the D peak for the DLCs deposited on S_2 sample are observed approximately at 1392.47 cm^{-1} and the G peak shifted toward higher wave number at about 1533.6 cm^{-1}[21]. In principle, in the Raman spectra of carbon based materials the G-peak positions move to higher wave number due to two processes: the high sp^2 content or cluster size and due to higher compressive stress [26]. Also we observed the D peak for the DLC samples deposited on S_3, S_4 substrates appeared at around 1395.55 cm^{-1}, 1392.37 cm^{-1}, and the G peak at about 1527.14 cm^{-1} and 1529.30 cm^{-1} [22], respectively. The intensity ratio of the D and G peaks, I_D/I_G and the position of the G peak, Pos (G), have been widely used for qualitative estimation of sp^3 content in DLC [23]. S. Zhang et. al. display that the sp^3 fraction is inversely proportional to the band ratio I_D/I_G [24, 25]. Spectra of the samples show that the intensity ratio, I_D/I_G, is decreased from 1.80 to 1.44, 1.40 and finally 0.95 (See Fig. 4). Therefore, the DLCs deposited on S_1 substrate have more SP^3 bonded carbon atoms and it has a better quality in comparison with samples.

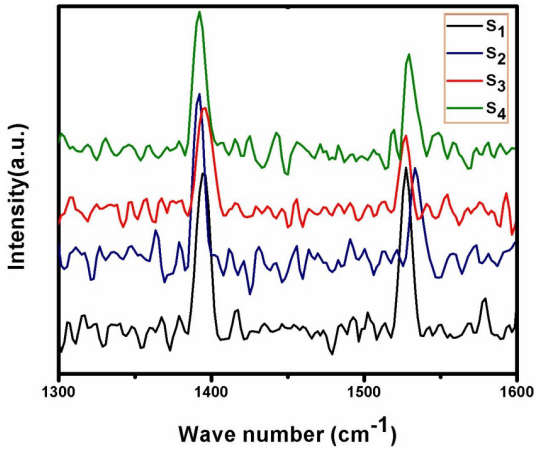

Figure 3. Raman spectra of the DLC films deposited on:
(a) S_1, (b) S_2, (c) S_3 and (d) S_4

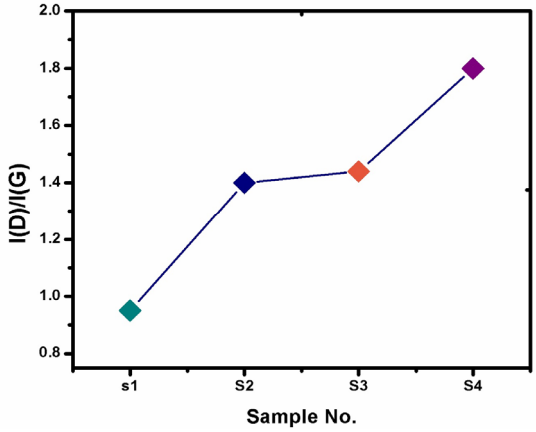

Figure 4. Intensity ratio versus different type of samples

Fourier transform infrared spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is such a spectroscopic technique to characterize the chemical bonds, molecular structures and C-H_n (n=1, 2, 3) bonding configurations, in DLC films and another carbon material. The infrared spectra of the DLCs deposited on S_1, S_2, S_3, S_4 substrates in the range of 600-3500 cm^{-1} are shown in Fig.5. It is composed of bending vibration (1300-1700 cm^{-1}) and stretching vibration (2700-3100 cm^{-1}) regions of C-H groups. The FTIR spectrum of carbon films grown on samples indicates the major peaks (See Fig. 5). The peak at around 913.85 cm^{-1} can be attributed to CH_2 (olefinic) bond in sp^2 type carbon. The absorption peak at around 1373.05 cm^{-1} may arise due to sp^3 CH_3 configuration and the band at approximately 1449.94cm^{-1} is due to C-H_2 vibration mode. The other absorption peak appeared at about 1596.92 cm^{-1} could be related to sp^2 C-C vibration mode. The peaks near 2861.54 cm^{-1} and 2864.61 cm^{-1} [27], assigned to stretching vibrations of sp^3 CH_3 groups in S_3, S_4 and S_1, S_2 samples, respectively. In addition, the peak which is located around 2969.33 cm^{-1} can be associated with sp^3 CH_3 configuration. IR vibrational mode assignments of the samples are summarized in Table 2.

Table 2. FTIR results for DLC deposited on samples

Samples	Wave numbers (cm^{-1})	*Assignment*
S_1 S_2 S_3 S_4	913.85	Olefinic sp^2 C-H_2
	1373.05	sp^3 C-H_3
	1449.94	sp^3 C-H_2, Olefinic sp^2 C-H_2
	1596.92	Olefinic sp^2 C-C
	2864.61, 2861.54	sp^3 C-H_3
	2969.33	sp^3 C-H_3

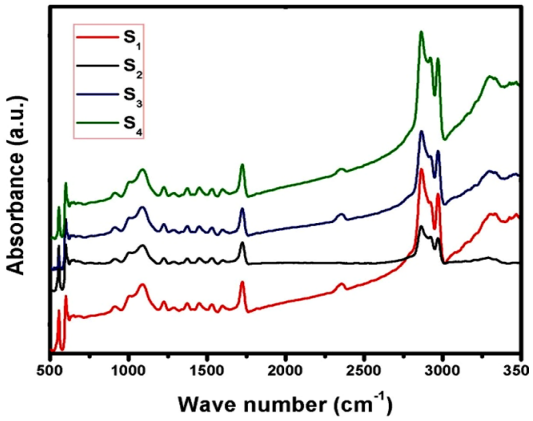

Figure 5. FTIR absorbance spectra of the DLC films grown on S_1, S_2, and $S_3$and S_4 substrates

CONCLUSIONS

In this paper, growth of DLC films on glass-Au, glass, quartz-Au and Si-Au, substrates were investigated by DC-PECVD method. The morphology and the root mean square roughness (R_{rms}) of the DLC films on various substrates were investigated by AFM. The results of the AFM show three-dimensional morphological images of the DLC films. It presents detailed data on the variation of R_{rms} of the diamond-like carbon films. In all cases, the roughness of the films remained low between 2.76 nm and 4.68 nm. However, DLC films maintain their smooth surface and the FTIR spectra indicative of the formation of sp^2 and sp^3 hybridized bonds in all samples. It was observed that the intensity ratio, I_D/I_G, in Raman spectra decreased from S_4 to S_1. Consequently, the DLCs grown on S_1 substrate have better quality compared with the other samples.

EXPERIMENTAL DETAILS AND METHODOLOGY

Substrate treatments and Film synthesis

Diamonds like carbon (DLC) films were prepared using DC-Plasma Enhanced Chemical Vapor Deposition (PECVD) system. The characteristic of the system were discussed in our previous works [15]. Glass, quartz and P type silicon (100) wafers were used as substrate and pre-cleaned with acetone, ethanol, and de ionized water for 15 minutes in an ultrasonic bath. The samples were coated by gold using DC magnetron sputtering system. The DLC films were deposited on glass-Au, glass, quartz-Au and Si-Au after in situ

etching treated with hydrogen ion for 15 minutes. Deposition was carried out at a fixed pressure of C_2H_2 and H_2 mixture gas (C_2H_2/H_2 25 vol. %), with flux rates of 200 sccm. The chamber pressure was adjusted at 15 Torr, and the stage temperature was set at 180°C during deposition. The applied current and voltage in this experiment were 50 mA and 400 V respectively.

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