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The effects of deposition potential on the optical, morphological and mechanical properties of DLC films produced by electrochemical deposition technique at low voltages

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Diamond-like carbon (DLC) films were electrochemically deposited onto indium tin oxide (ITO) substrates using acetic acid and deionized water as electrolyte at low deposition voltages (2.4 V and 60 V). The transmittance of the films was investigated by UV spectrometry. Transmittance measurements versus wavelength revealed that the films transmit 86 % to 89 % light in visible region and band gap of the films varies between 3.87 eV and 3.89 eV. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used for structural characterization to evaluate surface morphology of the DLC films. The grain size and the surface roughness increased for the films prepared at higher deposition potential, while their measured average height decreased. The mechanical properties (hardness H and elastic modulus E_r) were determined from load-displacement curves which were obtained by using nanoindentation method. Hardness and elastic modulus of the films increased as the deposition voltage of the films increased from 2.4 V to 60 V.

Keywords: *DLC films; optical properties; morphological properties; mechanical characterization*

1. Introduction

"Diamond-like carbon" (DLC) is a name given to semi-stable amorphous carbon (a:C) containing sp^2 and sp^3 bonds or amorphous carbon (a-C:H) containing hydrogen [1]. Importance of diamond-like carbon among engineering materials is increasing day by day for their potential in variety of industrial applications such as microelectronics, optical and mechanical transportation, and biomedical coatings due to their attractive mechanical and optical properties such as high resistance against abrasion and friction, high hardness, chemical inertness, infrared transmittance, wide band gap and high thermal conductivity [1–6]. The properties of DLC structures are related to the volumetric ratio of the sp^3 bonds that can be controlled by the coating mechanism [7]. Therefore, the sp^2/sp^3 bond ratio may vary depending on the deposition process and deposition parameters of the films or coating method [7].

Common synthesis methods for DLC films reported in the literature include: Radio Frequency (RF) Magnetron Sputtering Method [8], Chemical Vapor Deposition (CVD) [9], Physical Vapor Deposition (PVD) [10] and Ion-Beam [11]. Diamond-like carbon films have recently been reported to be prepared through the electrochemical

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deposition technique with organic solvents [1–3, 12–16]. Electrochemical deposition technique has great advantages over the others. First of all, the deposition temperature is very low (close to the room temperature). Therefore, the instruments used in the production process are much simpler and cheaper; for example, there is no need for vacuum devices, pumps, big chambers or furnaces to melt or evaporate materials. On the other hand, the films produced by electrochemical technique are limited by organic liquids that are used as production and deposition electrolytes as the boiling points of the organic liquids determines the deposition characteristics [15].

The mechanical properties of materials are significant in terms of usability or applicability. By using conventional methods, it used to be difficult and often impossible to accurately define the mechanical properties of a coated film that is few micrometers thick. However, recent advancements in nanoindentation techniques enable researchers to define mechanical properties of materials accurately and precisely. Hence, in this work, diamond like carbon films were electrochemically synthesized at voltages of 2.4 V and 60 V and investigated by the nanoindentation method. Effect of different deposition voltages upon mechanical properties, such as elastic modulus E_r and hardness H was determined. We also focused on the optical and morphological properties of DLC films prepared using different deposition voltages.

2. Materials and methods

2.1. Electrochemical deposition

Diamond-like carbon films were deposited on indium tin oxide (ITO) coated glass through electrochemical deposition technique using a mixture of acetic acid (CH_3COOH) and deionized water as an electrolyte. The acetic acid concentration in water in the deposition process was 10 %. The deposition was performed at room temperature at two different potentials (2.4 V, 60 V). The graphite sheet was used as anode and the ITO coated glass as cathode; the distance between anode and cathode surfaces was set to approximately 0.7 cm.

The deposition took 9 h and the experiment was performed at room temperature. The surface topography of the films was measured by using Ambios Qscope atomic force microscope (AFM) in contact mode and the optical transmission spectra were recorded by PerkinElmer Brand UV-Vis spectrometer. Regarding to the optical properties and thickness of the films, energy band gaps were determined from equation 1 and equation 2, respectively. Mechanical characterization of the films was carried out using a 120° angled, three-side pyramid diamond Berkovich tipped NH-2 nanoindentation device (CETR) and the Oliver and Pharr model [17].

3. Results and discussion

3.1. Raman spectroscopy

Raman spectroscopy is a commonly used technique to define the composition and structure of carbon-based materials. Amorphous carbon materials exhibit two broad peaks in the range of 1200 cm^{-1} to 1700 cm^{-1} in the Raman spectrum. These are two broad peaks in the range of 1200 cm^{-1} to 1450 cm^{-1} for the D band and in the range of 1500 cm^{-1} to 1700 cm^{-1} for the G band. The Raman spectra for DLC films electrochemically synthesized at 2.4 V and 60 V are shown in Fig. 1. As is observed in Fig. 1, the films show two peaks in the range of 1200 cm^{-1} to 1700 cm^{-1}. The first peak is G peak which is a common feature of diamond-like carbon films obtained through different deposition methods and which occurs at around 1540 cm^{-1}. The second peak at 1400 cm^{-1} is the D peak which is characteristic of the extraordinary diamond formation. D and G bands are the characteristic peaks of DLC films [1, 3].

3.2. Optical analysis

Thickness of films deposited at 2.4 V and 60 V potentials was estimated from equation 1:

$$x = \frac{\lambda(1)\lambda(2)}{2\left(n_f(1)\lambda(2) - n_f(2)\lambda(1)\right)} \quad (1)$$

where n_f is the refractive index of the film, $\lambda(1)$ and $\lambda(2)$ are the wavelengths between two consecutive peaks or pits [18, 19]. The thickness
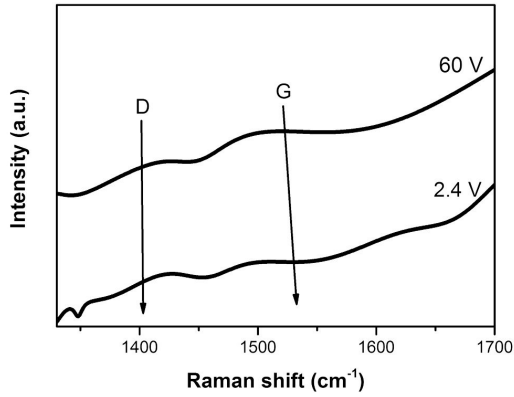
Fig. 1. Raman spectra of DLC films deposited at 2.4 V and 60 V.

of the films was calculated using equation 1 as 218 nm and 259 nm for the films deposited at 2.4 V and 60 V, respectively. This indicates that the deposition rate of the carbon films increased with the increasing potential. As can be seen in Fig. 2 regarding to optical transmittance-wavelength graph, the optical transmittance of the films shows that the transparency of the films changes between 85 % and 89 % in the visible region.
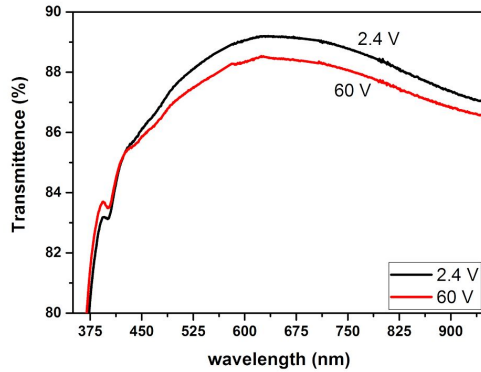

Fig. 2. Optical transmittance spectra of DLC films prepared at 2.4 V and 60 V.

The forbidden energy gap E_g of DLC films deposited at 2.4 V and 60 V potentials were calculated from equation 2, where the absorption coefficient of a direct ($m = \frac{1}{2}$) band gap of DLC film is expressed as a function of E_g

$$\alpha(h\upsilon) = A^*(h\upsilon - E_g)^{\frac{1}{2}} \qquad (2)$$

where α is the absorption coefficient, $E = h\upsilon$ is photon energy, A^* is a constant for different transitions and E_g is forbidden energy band gap [2, 20]. Forbidden energy band E_g can be obtained from the intersection of tangent line of (($\alpha h\upsilon)^2$ – $h\upsilon$) graph with the energy axis. Here, ($\alpha h\upsilon)^2$ – $h\upsilon$ graph is the square of the multiplication of absorption coefficient α by energy, drawn against energy (Fig. 3a and Fig. 3b). The forbidden energy band gap values E_g for the DLC films prepared at 2.4 V and 60 V were calculated as 3.87 eV and 3.89 eV, respectively.

(a)

(b)
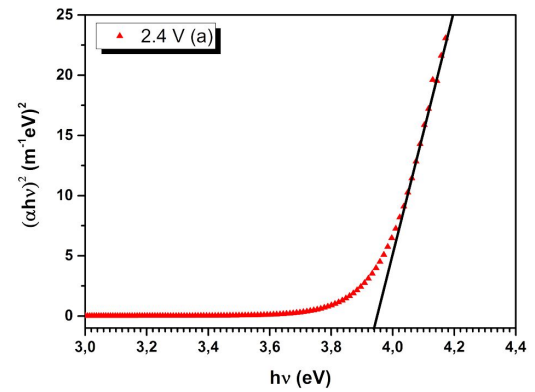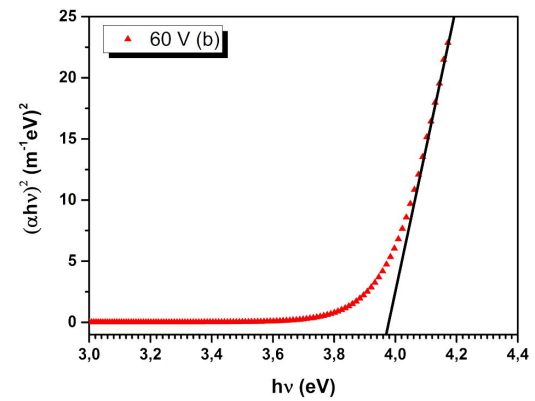
Fig. 3. ($ahv)^2$ vs. hv plots of DLC films prepared at (a) 2.4 V and (b) 60 V.

The energy gaps calculated for the films which were produced by our group are slightly larger than those reported by some other authors [2, 13]. It was noted that the energy gap of the clusters depends

on the shapes and number of atoms constituting the cluster. This would mean that the size, shape and distribution of carbon clusters (or grains), which are forming the DLC films, determine the energy band gap. Therefore, the curves obtained from the $(\alpha h v)^2 - h v$ graphs could give an average band gap energy. In addition, it was reported that the band gap energy also depends on the deposition technique, so the band gaps of the synthesized DLC films may vary from 0.5 eV to 4 eV [2, 13, 14]. The variation occurs due to hydrogen content in amorphous carbon matrix which may cause an increase in band gap. It was also seen in our experiment that the deposition rate of the carbon films increased when the deposition potential was increased.

3.3. Surface morphologies

SEM images of the DLC films are presented in Fig. 4. Microscopy investigation of the films revealed that the surfaces of the films are covered with grains smaller than 50 nm. They are mostly uniformly and randomly spread onto the surface. SEM micrographs of the samples show that the coverage and grain size increased when the deposition voltage was increased.

Fig. 5 and Fig. 6 show atomic force microscopy (AFM) images of the films deposited at 2.4 V and 60 V, respectively. It is also observed in the AFM images that the surface morphology of the DLC films have been affected by the applied voltage. The AFM images support the result that grain sizes and the surface roughness increase when the films are deposited at higher voltage. However, it has been observed that the average height has decreased. The average heights of the films deposited at 2.4 V and 60 V were found to be ∼23 nm and ∼18 nm, respectively. The main reason of the decrease in the height can be attributed to the increase in the coverage; the gaps between the grains were filled more densely for the deposition at higher voltage (60 V) which caused the measured average height to decrease.

3.4. Mechanical analysis

Nanoindentation technique is a standard method for studying the mechanical behavior
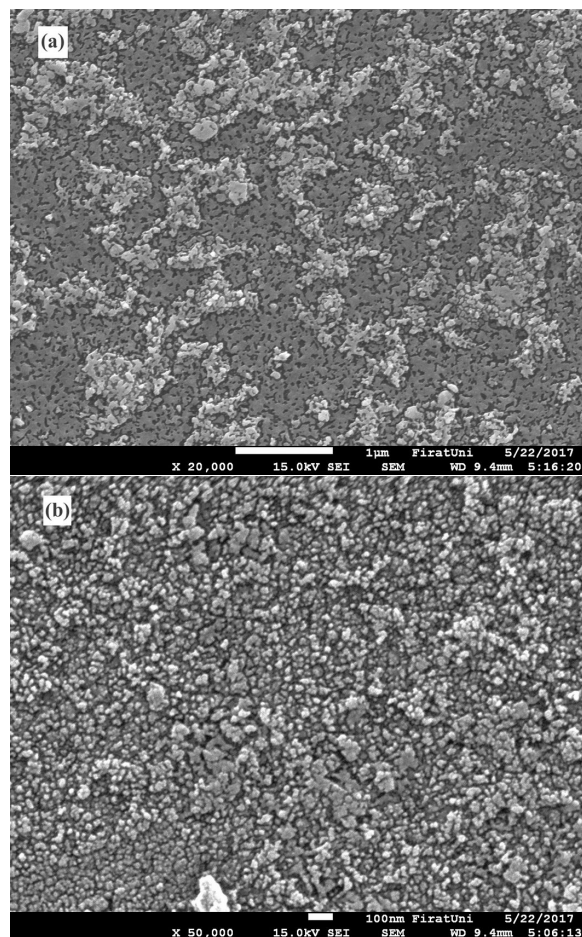
Fig. 4. SEM surface images of DLC films deposited at (a) 2.4 V and (b) 60 V.

of thin films even in very small scales, where the data in high resolution are obtained using a nanoscaled sharp tip. In this technique, a nanoindenter (the nano scaled sharp tip) applies a load to the surface (pushed towards the surface) of the material and then it is retracted (pulled back). Displacement of the tip and the load applied to the surface is continuously recorded. Two mechanical properties (reduced elastic modulus E_r and indentation hardness H) can be obtained from the load-displacement data of the indenter. Different calculation methods have been developed in the literature to derive these mechanical properties from load-displacement data [21]. Maybe, one of the most popular calculation methods is the Oliver-Parr (O-P) method which is based on the elastic
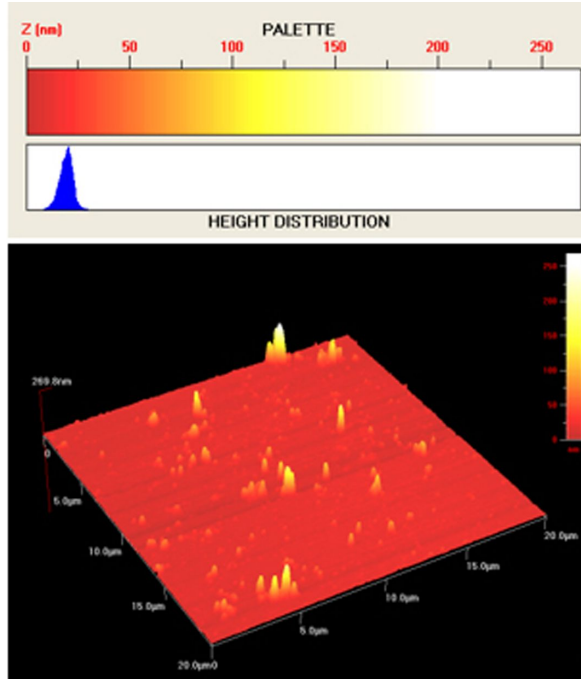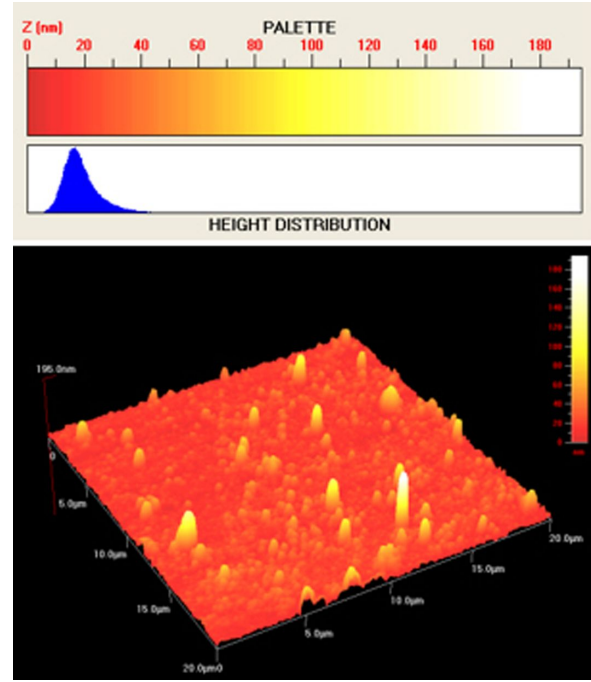
Fig. 5. AFM images of DLC film prepared at 2.4 V.

Fig. 6. AFM images of DLC film prepared at 60 V.

contact model [17]. In this method, the contact stiffness S and the contact area A_c are measured at the onset of the unloading. The reduced elastic modulus E_r is then calculated using the contact mechanics relation in equation 3:

$$E_r = \frac{\pi}{2} \frac{S}{A_c} \qquad (3)$$

In addition, the ratio of the peak of indentation load P_{max} to the projected area of the hardness impression A_c gives the indentation hardness H:

$$H = \frac{P_{max}}{A_c} = \frac{P_{max}}{24.5h_c^2} \left(A_c = 24.5h_c^2 \right) \qquad (4)$$

where A_c is a geometric function of the contact depth h_c and is defined as the contact area [17].

Hardness and elasticity modulus values were obtained using Oliver-Pharr analysis of load-displacement data. The load-displacement data of the films were recorded at peak load levels of 0.5 mN, 1 mN and 3 mN. Indentation tests were performed at four different positions on the sample to enhance the reliability of the process.

The variation of the reduced elasticity modulus E_r and hardness H values calculated from the load-displacement data regarding to the applied load is

shown in Fig. 7 and Fig. 8. E_r values were calculated in the range of 85 to 135 GPa and H values were calculated in the range between 10 GPa and 35 GPa, respectively.
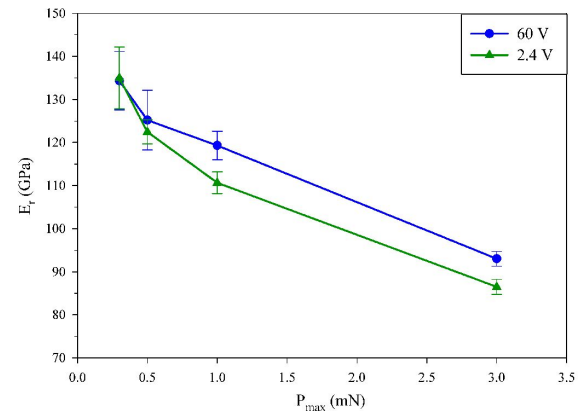

Fig. 7. Variation of reduced elastic modulus with applied peak load at two different deposition voltages.

It is seen that the E_r and H values of the films increased with the increasing deposition voltage (from 2.4 V to 60 V). Previously, Yan et al. [3]
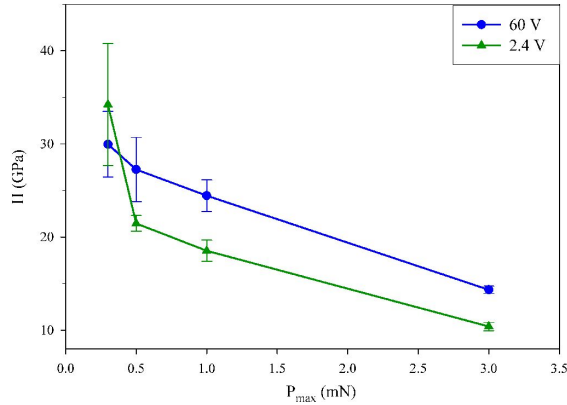
Fig. 8. Variation of hardness with applied peak load at two different deposition voltages.

reported a similar result for hydrogenated amorphous carbon (a-C:H) films which were deposited on Si substrates by electrolysis in a methanol solution using various high deposition voltages (from 800 V to 1600 V). They mentioned in the paper that the sp^3/sp^2 ratio, H and E_r values of the a-C:H films increase with increasing deposition voltage. It was assumed that more hydrogen and hydrocarbon radicals are created by higher deposition potentials which may be beneficial to reducing the sp^2 carbon phase and may lead to an increase in the sp^3 carbon phase. Also Bartali et al. [22] studied the mechanical behavior of the hard a-C:H films deposited onto Si and PET by using RF sputtering technique. They found nanohardness and Young modulus as 12.1 GPa and 160 GPa, respectively. Uzun et al. [21] and Bartali et al. [22] noted that hardness is one of the most important parameters and its determination is affected directly by different factors such as surface roughness, tip shape, material state (bulk or thin film), the applied loads, loading rate, oxide layer etc. In addition, we found that the E_r and H values of the films decrease with the increasing loads applied by nanoindenter. The measured hardness is generally found high at very low load levels applied to the surface, but when the load is increased, the measured hardness decreases. In the literature, this phenomenon is referred as indentation size effect (ISEs) and presumably occurs due to a non-negligible tip defect, imperfection of the indenter used or a tip/machine

miscalibration [21, 23]. However, in our present work, the main reason of this phenomenon has been attributed to the substrate effect (or non-coated layer) which is caused by the penetration depth of the indenter and the E_r and H values obtained at higher loads are shadowed by the substrate.

4.   Conclusions

In this study, the effects of the deposition potential on the optical, morphological and mechanical properties of DLC films synthesized by low voltage electrodeposition technique using acetic acid was investigated. Raman spectroscopy results confirmed that the films showed DLC characteristics. Transmittance analyses were performed to characterize optical properties of the films. It was stated that the thickness of the DLC films increased with increasing the deposition voltage whereas transmittance was slightly decreased. The slight decrease in the transmittance was attributed to the increase in the thickness of the films that affected the transmittance of light. It was also confirmed that the transmittance of the films changed between 86 % and 89 % in visible region. Morphological investigations of the DLC films revealed that the thin films consisted of atomic grains smaller than 50 nm. Changing of the deposition voltage affected the grain size and surface roughness. Grain size and surface roughness increased when the deposition voltage was increased whereas average height of the grains decreased. The decrease in the average height was attributed to filling of the gaps between the grains. High voltage provided higher deposition rate that enabled the gaps between grains to be filled. Lastly, hardness H and elasticity modulus E_r of DLC films were investigated by using nanoindentation technique. Nanoindentation results were evaluated by using Oliver-Pharr analysis. In the Oliver-Phar analysis, load-displacement values were used as a function of deposition voltage. It was found that the H and E_r values of DLC films increased for the films deposited at higher voltage. On the other hand, E_r and H values of the films decreased when the applied loads increased. It was noticed that the phenomenon is quite common in thin film investigations and is

attributed to substrate effect causing that measured hardness and elasticity modulus values of films are dominated by the substrate instead of the thin films themselves.

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