

Preparation and characterization DLC thin films using atmospheric pressure plasma Jet

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Abstract. Diamond-like carbon, amorphous hydrogenated films forms of carbon, were pretreated from cyclohexane (C₆H₁₂) liquid using plasma jet which operates with alternating voltage 7.5kv and frequency 28kHz. The plasma Separates molecules of cyclohexane and Transform it into carbon nanoparticles. The effect of argon flow rate (0.5, 1 and 1.5 L/min) on the optical and chemical bonding properties of the films were investigated. These films were characterized by UV-Visible spectrophotometer, X-ray diffractometer (XRD) Raman spectroscopy and scanning electron microscopy (SEM). The main absorption appears around 296, 299 and 309nm at the three flow rate of argon gas. The value of the optical energy gap is 3.37, 3.55 and 3.68 eV at a different flow rate of argon gas. For XRD analysis, The presence of diamond peaks and graphite peaks in the x-ray spectrum for these films Indicates that there is an occurrence of local ordered sp³ and sp² for carbon domains and graphite respectively. Raman spectroscopy analysis revealed two broad bands D band and G band. The upshift of D band of diamond and downshift of the G band of graphite with is indicative of the presence of DLC films.

Keywords: Atmospheric pressure plasma jet, carbon nanoparticles, Diamond-like carbon, Raman spectroscopy

1. Introduction

In the last one decade, the atmospheric pressure plasma jet research is extremely increased because of its significant applications in different fields. Plasma jet is non-equilibrium systems, that's mean the electron temperature is greatly upper than ion temperature [1]. one of the essential characteristics of plasma jet approach it to room temperature and does not require vacuum equipments. Plasma jet has a very easy design as it consists of a syringe needle, is used as High voltage electrode. Gas flows through the electrode at diverse flow rate measured by unit (l/min). Flow velocity can be controlled by a flow meter [2]. This system is characterized by high efficiency, easy to design, flexible and non-heat. The small size of plasma jet enables it to deal with large areas, also its advantageous in dental treatment in medical use, which requires high correctness [3]. As well as this systems can be used for deposition oxides, nitrides and other materials of thin films on different substrate types [4]. Plasma jets were moreover suggested as chemical reactors for decomposition of toxic impurities in the air [5]. Along with that, the atmospheric plasma jet systems have a higher rate of deposition than low-pressure systems [6].

In this work, plasma jet was used to deposit a-C: H nano-thin films. There are three types of films a-C: H depending on the sp³ fraction and hydrogen content. These types are polymeric amorphous carbon (PAC), diamond-like carbon (DLC), and graphitic amorphous carbon (GAC)[7]. Hydrogenated amorphous carbon (a-C: H) films are interesting because of its distinctive properties such as high



hardness, electrical insulation, chemical stability, and high optical transparency [8]. All of these qualities make these films appropriate for many applications such as shielding and antireflection coatings, wear-resistant overcoats, and low friction wear-resistant and biocompatible coatings [9].

2. Experimental part

Numerous methods have been used to systematize a-C: H thin films like R.F. sputtering technique, chemical vapour deposition and reactive (D.C., magnetron) sputtering. In this research, carbon nano-thin films were synthesized on quartz substrates via a plasma jet. Figure. 1. Shows the plasma jet system used to prepare the DLC thin films. The torch was generated using Argon gas flow through a nebulizer which contained Cyclohexane (C_6H_{12}). The mixed of cyclohexane and argon gas was transformed into an aerosol, the aerosol was guided by the Argon gas through Teflon tube to the plasma jet. The plasma was ignited by using an electric source at a fixed frequency (28.0 kHz) and high voltage 7.5kv. The deposition system used in this work is shown schematically in figure (1). The distance between the substrate and plasma torch is fixed 2.5 cm while the flow rate of argon gas is variable (0.5, 1 and 1.5) L/min. The film thickness was measured using the optical interferometer method employing laser of (532nm), the films thickness (t) was determined using the formula[10]:

$$t = \frac{\lambda}{2} \cdot \frac{\Delta x}{x} \quad (1)$$

Where ΔX is the width of the fringe, x is the position of the fringe and λ is the wavelength of the used laser light. Structural analysis of carbon nanoparticles thin films performed by (Shimadzu XRD-6000 Japan) diffractometer with CuK_{α} radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and 30 mA in the scanning angle (2θ) from 20° to 80° with the scanning speed of 0.05 deg/s. The surface morphology was examined by Scanning electron microscopy (SEM) under ambient condition. The optical transmission spectra of the deposited films were recorded using UV-VIS double-beam spectrophotometer in the wavelength range 200-1100 nm.

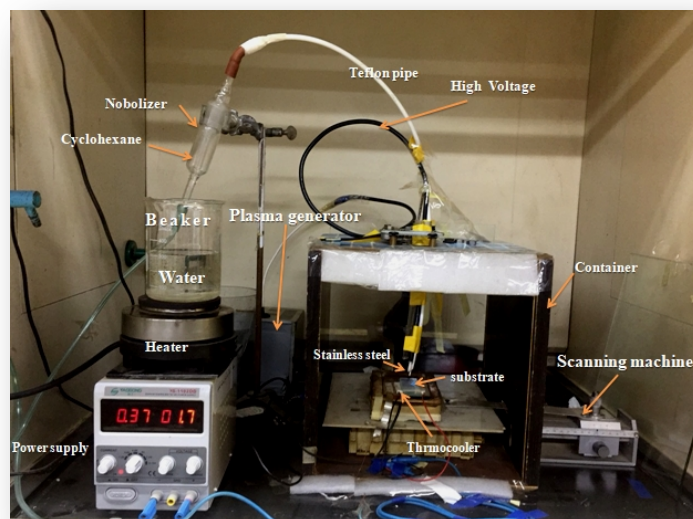


Figure 1. The plasma jet system used to synthesize the DLC thin films.

3. Results and discussion

3.1 Measurements of optical properties

The optical properties of the a-c: H films deposited via a plasma jet on quartz substrates with 2.5 cm as a distance between the substrate and plasma torch have been investigated using the UV-Visible spectrophotometer (Metertech Inc SP-8001, wavelength range: 190-1100nm). the absorption spectrum

of the a-c: H films is shown in figure.2. Many Layers of carbon nanoparticles deposited on quartz substrates with a thickness 140, 135, 135 nm at a different flow rate of argon gas (0.5, 1 and 1.5) L/min, respectively. The main absorption appears around 296, 299 and 309nm at the three flow rate of argon gas. The figure shows that the increase in the flow rate of argon gas guide to shifting the peak position ($\lambda_{\max}$) toward the infrared region of the electromagnetic spectrum. Also, the peak width increases when the flow rate increases.

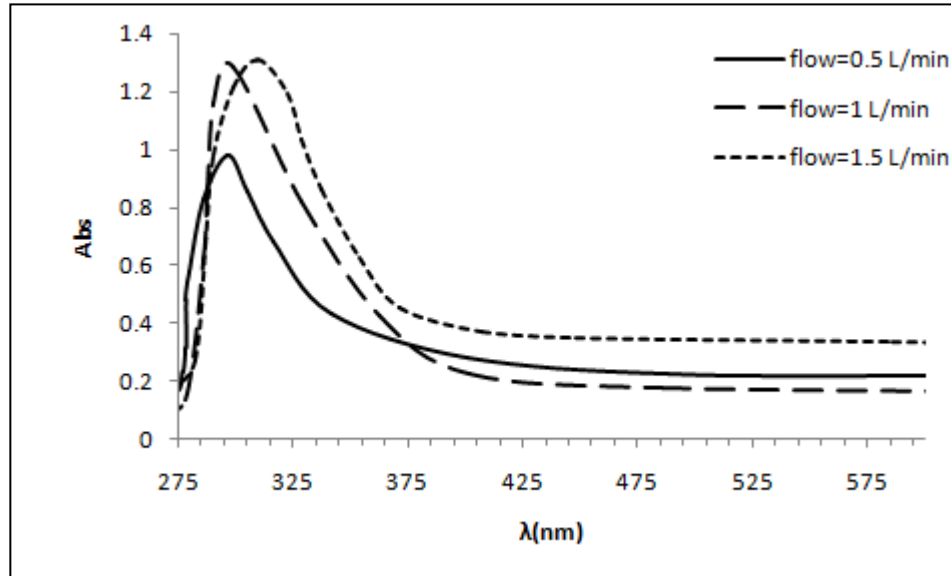


Figure 2. Absorption spectra for a-C: H thin films thin film at a different flow rate of argon gas (0.5, 1 and 1.5) L/min.

For the study of the optical properties of the synthesized a-C: H thin films, the band gap was determined, which were calculated by means of the optic absorption spectrum. The type of transition was directly allowed transition as the dependence of (α) on the photon energy ($h\nu$) was found to follow the subsequent relationship [11]:

$$\alpha h\nu = \beta (h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

Where β is a constant that depends on the properties of the material and E_g is the optical band gap.

The value of the optical energy gap as shown in Fig. 2. are 3.37, 3.55 and 3.68 eV at a different flow rate of argon gas (0.5, 1 and 1.5) L/min, respectively. it can be seen that the optical energy gap increases when the flow rate of argon is decreased. A decrease in the E_g can be credited to an increase in sp^3 fraction a-C: H thin films [12].

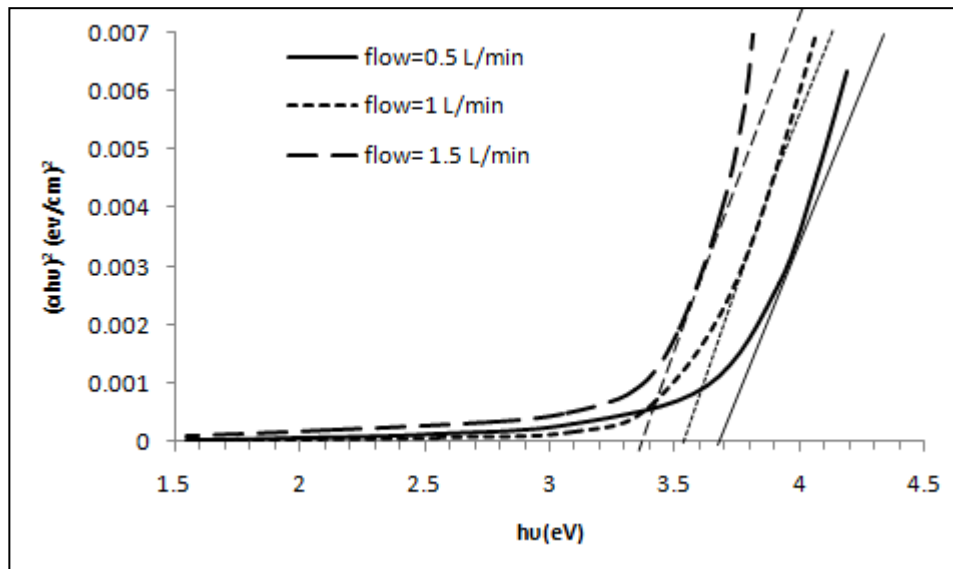


Figure 3. The Variation of $(\alpha h\nu)^2$ versus the Photon Energy ($h\nu$) of a-C: H thin films thin film at a different flow rate of argon gas (0.5, 1 and 1.5) L/min.

3.2 The scanning electron microscope analysis:

The morphological characteristics of the DLC films were studied by The scanning electron microscope (SEM) to check the nanostructure of the films under the influence of different flow rates of argon gas. Figures 4-a, 4-b and 4-c illustrate the surface morphology of the carbon films with flow rates of argon gas 0.5, 1 and 1.5 l/min respectively. One can observe that the morphologies radically changed with the increase in flow rates of argon gas. The size of the nanoparticles decreases when the flow rates of argon gas decreases end become continuous and denser.

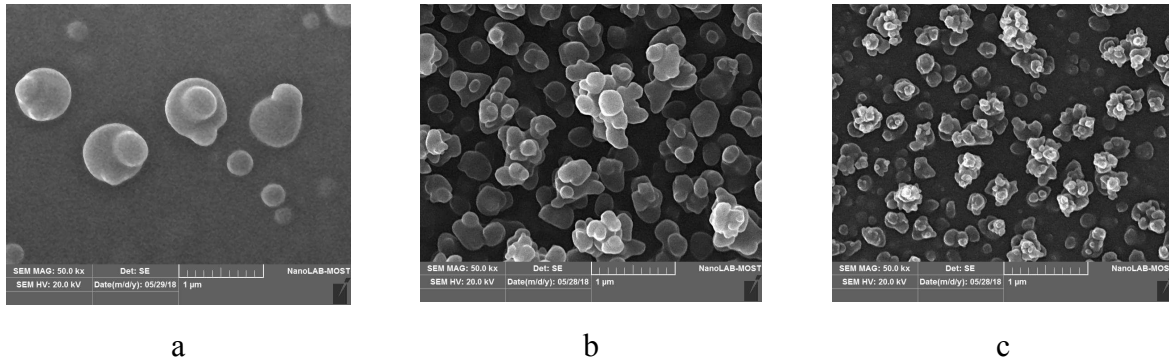


Figure 4. SEM of the fractured surface of DLC thin films at flow rates of argon gas a- 0.5 l/ min. b-1 l/min. C- 1.5 l/min.

3.3 X-ray diffraction patterns

Figures 5,6 and 7 show the x-ray diffraction pattern of the carbon films with flow rates of argon gas 0.5, 1 and 1.5 l/min respectively. The broader peak which found in each figure refer to that these films are found to be Nanocrystalline in nature. In fig. 5., There are four diffraction peaks were found in the spectra at 2θ values Two of them at 2θ 26.66° , 51.9° which could be identified with reflection form (002) and (102) plane of graphite and the peaks at 2θ 43.52° and 73.94° could be assigned to the (111) and (220) lattice spacing of cubic diamond. While in fig. 6., the peaks at 2θ 26.62° , 51.76° could be contribution to graphite (002) and (102). The sharp peaks centred at 2θ 43.48° , 73.94° corresponding to the (111) and (220) diamond plane. The strong peaks for the hexagonal structure of graphite are located at 2θ 26.52° , 51.72° in fig. 6. In fig. 6., Two clear peaks can be observed at 43.52° , 73.99° could be suggested to identified with reflections form (111) and (220) diamond plane.

The presence of diamond peaks and graphite peaks in the x-ray spectrum for DLC films reveals that there is a presence of local ordered sp^3 and sp^2 for carbon domains and graphite respectively.

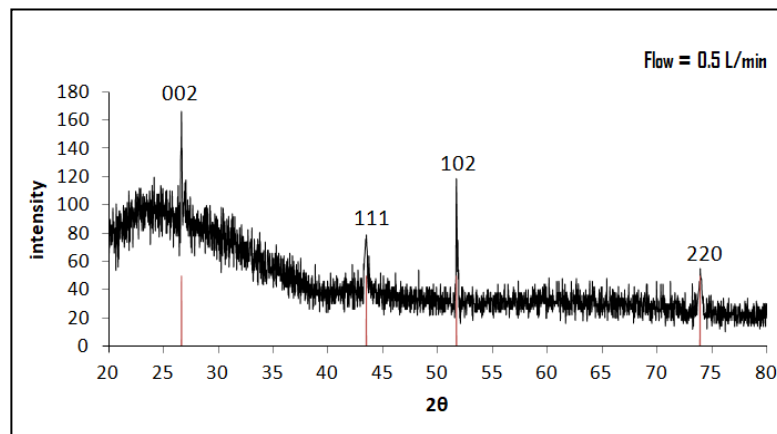


Figure 5. XDR for DLC thin film at flow rate of argon gas 0.5 L/min

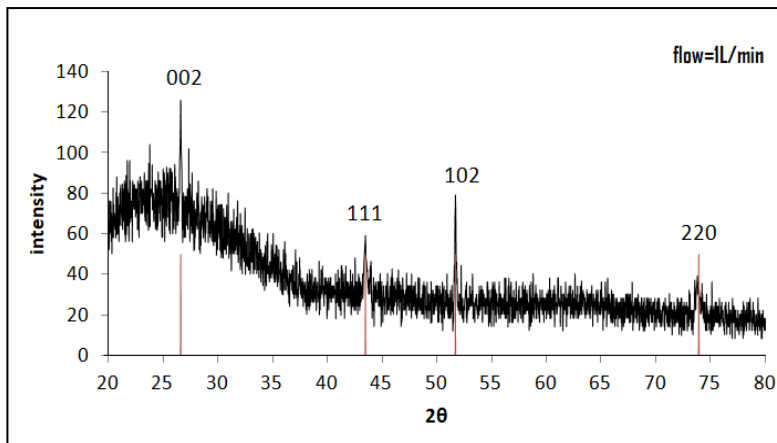


Figure 6. XDR for DLC thin film at flow rate of argon gas 1 L/min.

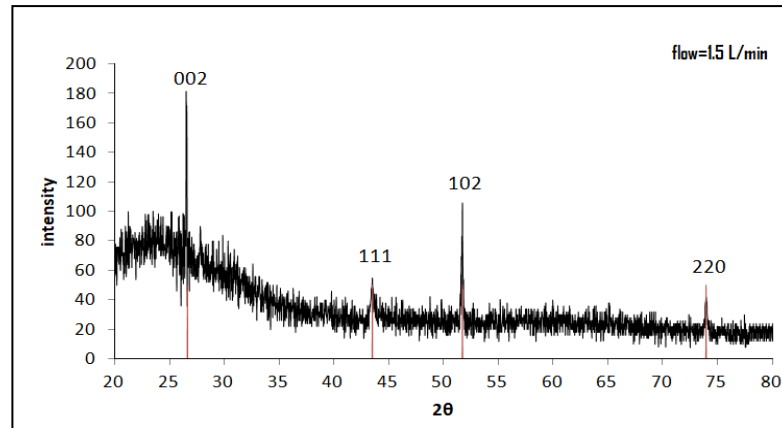


Figure 7. XDR for DLC thin film at flow rate of argon gas 1.5 L/min.

3.4 Raman analysis

Raman spectroscopy was used to distinguish the superiority of the a-C: H films, amorphous hydrogenated or non-hydrogenated forms of carbon, obtained from cyclohexane (C_6H_{12}) liquid using plasma jet with a fixed distance (2.5 cm) and different flow rate of argon gas (0.5, 1 and 1.5) L/min. The DLC thin film were analyzed by laser Raman spectroscopy (Laser 532nm-Nd:YAG). There are two typical wide peaks in the a-C: H spectra the 'D' peaks and 'G'. The D band corresponds to breathing modes of the aromatic rings related with disordered carbon structure (it is common to sp^3 carbon system) and The stretching of the C-C bond in graphitic materials contributes to G-band Raman feature which is common to sp^2 carbon system. Structure of carbon film can be characterized as graphite-like or diamond-like comparing the positions and intensities of G and D peaks. Structure of carbon film can be characterized as diamond-like or graphite-like comparing the positions and intensities of G and D peaks. From figures 8,9 and 10 can be seen that the D band peaks were positioned around 1516, 1431 and 1428 cm^{-1} for the DLC films at flow gas 0.5, 1 and 1.5 L/min respectively (shifting towards lesser wavenumbers with increasing the flow of argon). While, the G band peaks were centred at 1610, 1612 cm^{-1} and 1625 cm^{-1} for the DLC films with flow gas 0.5, 1 and 1.5 L/min respectively. That signifies the films are representative DLC films with mixed structured of sp^2 and sp^3 carbon. It can be observed a shift in the position of D and G peaks due to the nanostructure of these films. The incidence of upshifting and broadening in the D band indicates an increased level of disorder and a decrease in the graphitic domain size. It is clear that the G-peak is shifted towards higher wavenumbers with increasing the flow of argon. This indicates to increase of the graphite-like concentration in these films. From table 1 can be observed that the value of I_D/I_G ratio rises with increasing flow of argon. The diminishing of I_D/I_G ratio indicates the reduc in the quantity of sp^3 atomic site in the carbon films.

Table 1: Position, Fwhm, and intensity of D and G peaks and the intensity ratio of peaks as a function of flow gas.

The flow of the gas (L/min)	Position of D peak (cm^{-1})	Position of G peak (cm^{-1})	Fwhm of D peak (cm^{-1})	Fwhm of G peak (cm^{-1})	I_D	I_G	I_D/I_G
0.5	1516	1610	64	48	90	187	0.481
1	1431	1612	55	73	77	153	0.503
1.5	1428	1625	34	78	59	109	0.541

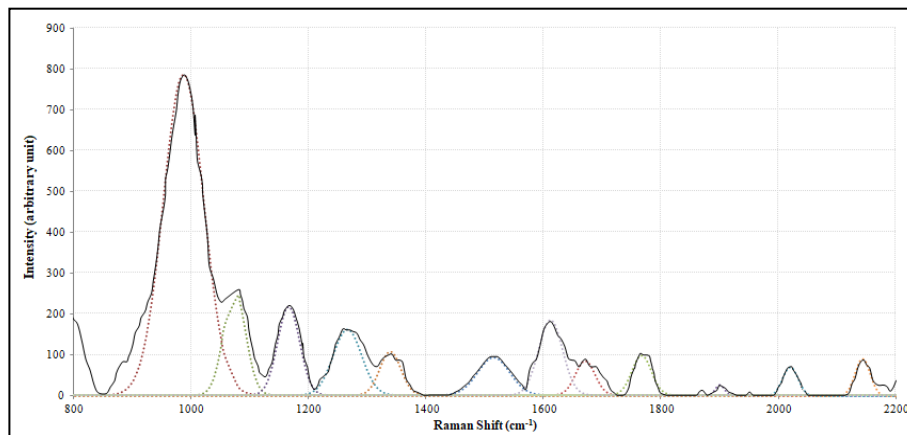


Figure 8. Raman spectra of DLC thin film at flow rate of argon gas 0.5 L/min.

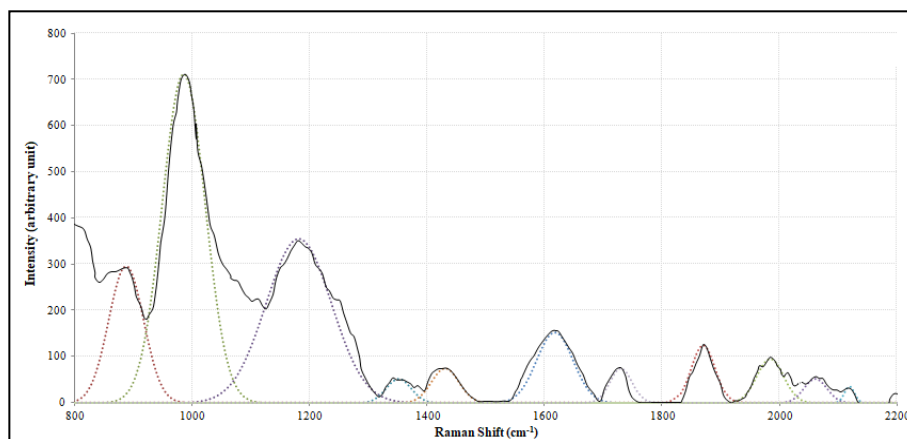


Figure 9. Raman spectra of DLC thin film at flow rate of argon gas 1 L/min.

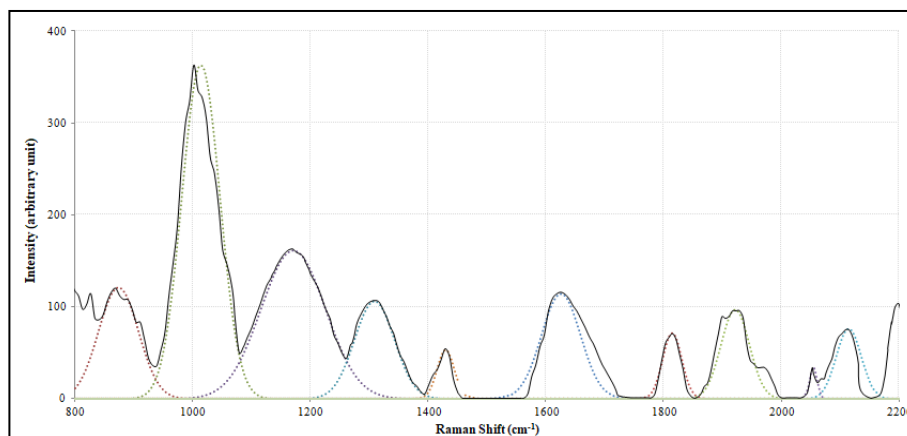


Figure 10. Raman spectra of DLC thin film at flow rate of argon gas 1.5 L/min.

4. Conclusions

Nanostructured DLC films were successfully deposited on a quartz substrate using the atmospheric pressure plasma jet. The experimental results are proved that the optical energy gap can be controlled by proper selection of deposition parameters. Compact and uniform DLC films can be monitor by SEM images. The X-ray spectrum includes peaks for the crystalline structure of diamonds and others for graphite. Compact and uniform films were observed by SEM. For Raman spectra analysis, the D

bands peaks were located around 1516, 1431 and 1428 cm^{-1} for the DLC films at flow gas 0.5, 1 and 1.5 L/min respectively and, the G band peaks were positioned at 1610, 1612 cm^{-1} and 1625 cm^{-1} for the DLC films with flow gas 0.5, 1 and 1.5 L/min respectively Which confirms the existence of the diamond and graphite phase in films. The Raman spectra clarify the ratio of the bonding sp^2 and sp^3 as found to be increasing with increasing flow rate of argon gas.

5. References

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