Preparation and Characteristics Study of Diamond - Like Carbon (DLC) Film onn-Si Substrates by Electrolysis of Methanol

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Received on: 5/11/2015 & Accepted on: 19/5/2016

ABSTRACT

The electrolysis of methanol was used to deposit diamond-like carbon (DLC) film on an-type Si (100) substrate under constant voltage (1200V) at ambient pressure and temperature40^{o}C. The surface morphology and composition of the synthesized film was characterized by scanning electron microscopy (SEM), energy dispersive x-ray (EDX), atomic force microscopy (AFM), and Raman spectroscopy.Deposited DLC film has a compact structure of dense grains, and the film contained irregular shape particles (clusters) of DLC. Raman spectraconfirmed that the DLC film contains carbon atoms with sp^{3}hybridization.

Keywords: Electrolysis, diamond - like carbon (DLC), thin film, Raman spectra

INTRODUCTION

Diamond like carbon (DLC) is a metastable form amorphous carbon containing a significant fraction of (sp^3) bond. DLC is characterized by high mechanical hardness, chemical inertness, optical transparency, wide band gap semiconductor of (1-4 eV), low mobility semiconductor and low electron affinity. The wide properties range of DLC is coming from atomic orbitals are hybridized during making chemical bonds and the complex structure involving different bonding configurations, and the incorporation of hydrogen in the films [1-3]. Therefore DLC film was used in various applications such as protective coatings, magnetic storage disks, and biomedical coatings, additionally DLC films used as semiconductors coatings for electronic application [4-6].

Various synthesis methods have been studied for fabricating DLC films.The using of CVD method is hypothesized that hydrogen is necessary for the formation of sp^3 bond in DLC films. PVD method based on energetic ablation of carbon like pulsed laser deposition (PLD) demonstrated that hydrogen is not necessary for the formation of sp^3 bond[7].

The disadvantages of these depositions are using high voltage, high vacuum and therefore high cost. Electrodeposition is offered a novel route to synthesis DLC films. The electrodeposition methods, compared with (CVD) and (PVD), have demonstrated some obvious advantage in terms of simple setup, low temperature and low cost [8].

The first attempt to deposit diamond phase carbon films from an organic solution (ethanol) was achieved by Namba [9], who was successfully deposited DLCfilm on single crystal silicon substrate at a temperature less than 70C^0. Suzuki et.al[10]deposited carbon films by electrolysis of water ethylene glycol solution. Zhang et al.prepared DLC films on Si substrate by electrodeposition from solution of acetonitrile and deionized water as electrolyte under low voltage [11]. Raid A. Ismail et.al [12] deposited DLC films by electrolysis of ethanol with

https://doi.org/10.30684/etj.34.5B.10
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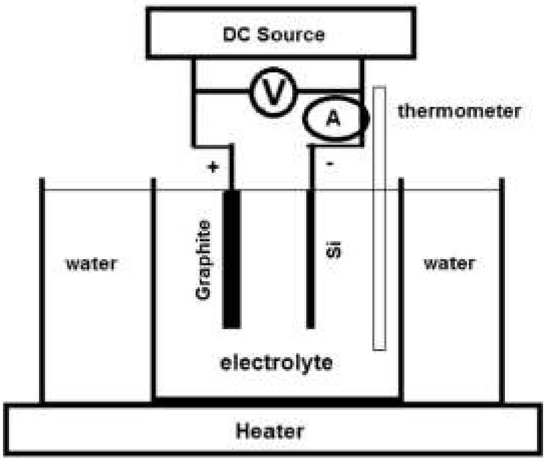
different volume ratios of methanol at 60 ^{o}C. In this study, thin film of DLC has been deposited on Si substrate by electrodeposition technique using electrolysis of methanol, and the structural properties of DLC film were investigated.

Experimental

A setup similar to that in figure (1) was used to deposit the DLC thin films.The beaker was open and the deposition was carried out under atmosphere pressure and bath temperature set at 40°C by providing an external water jacket.



Figure(1)Schematic diagram of the experimental setup [12].

Single crystallinemirror-like Si (100) n-type substrates with resistivity of (0.5-3) Ω.cm and size of 5mm x20mm x 0.5mm was mounted as cathode. The native oxide layer was removed from silicon substrates prior to deposit by dipping in HF 20% for 5 minutes and subsequently cleaned by ultrasonic treatment in ethanol.A high purity graphite plate was used as anode with distance adjusted to be 1.5mm to the cathode. DC power supply was used to provide a constant voltage of 1200V. Analytically pure methanolwas used as electrolytesolution. By using He-Ne laser (632.8 nm), the thickness was calculated by using the equation1 [13]:

$$d = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad \text{......(1)}$$

Where

d: thickness of the film (nm) , λ: Laser wave length (nm)

Δx: the distance between two fringes (dark region), x: light fringes width.

Surface morphology of DLC film was investigated by using FESEM (JSM 6500F thermal field emission scanning electron microscope) and AFM (SPM AA3000, Angstrom Advanced Inc., 2008, USA, Contact mode). EDX was used to study the chemical composition of the DLC film. Raman spectrum was employed using (RenishawinVia Raman microscope with 514nm wavelength) to investigate how the carbon atoms are bonding in the deposited DLC film.

Results and Discussion

The applying of high potential, the dipoles (methanol molecules) in the electrolytes align themselves in the direction of the field to minimize the energy, the high field leads to partial breakdown of the electrolyte, the decomposition (ionization) of CH_3OH in liquid phase:

$CH_3OH \rightarrow CH_3O^- + H^+$ [14]

$CH_3OH \rightarrow CH_3^+ + OH^-$ [15]

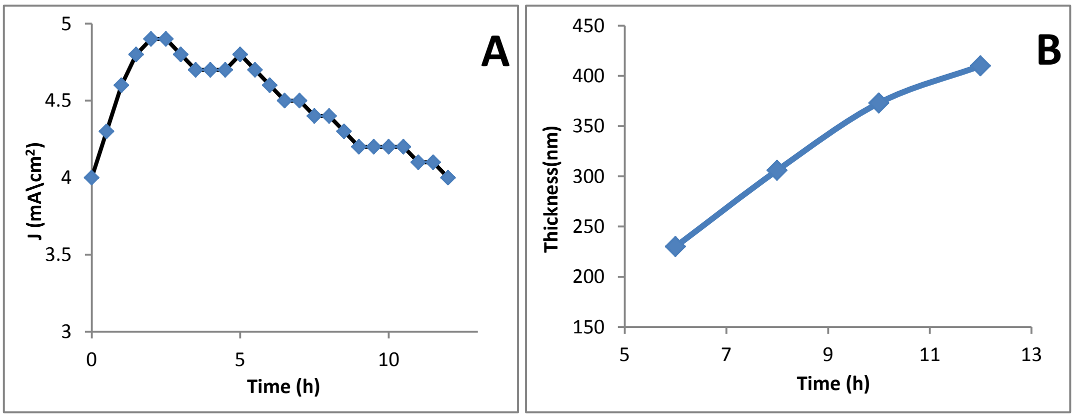
In this work, gas bubbles could be recognized on both electrodes, which mean; two types of ionization have been taken place in the electrolytes. The H^+ and CH_3^+ ions are absorbed on the negative electrode (substrate), the DLC films will be generated on the substrate surface via the reactions of the CH_3^+ groups with each other (quickly coalesce and nucleate) to form carbon network.

$CH_3^+ + ne \rightarrow$ DLC (on cathode)

The H^+ ions take electrons and convert to H gas. On the other hand the CH_3O^- and OH^- ions reach the anode and reaction occurs between them to produce CH_3OH and O gasses. Another reaction takes place during the ions migration between H^+ and OH^- ions and this reaction led to produce H_2O molecules, H^+ may react with CH_3OH to produce CH_3^+ and H_2O.Therefore the electrical resistance of the electrolyte will reduce and this explains the increase in current during the deposition process as it shown in figure1.

The figure(2a) shows the variation of the current density with deposition time.It is obvious that the current density of the electrolyte solution increases within the first of two hours and then decreased slowly with deposition time. This could be due to the increase in the electrode resistivity after the deposition of DLC and also due to the continuing addition of electrolyte to compensate the loss because of evaporation. It could be assumed that there is a series resistors: R_{anode} ,$R_{cathode}$, and $R_{electrolyte}$, the resistance of cathode increases with the increase of DLC thickness, the electrolyte resistivity decreases because of the chemical reaction, and water production.

DLC film thickness was increased with the deposition time, the deposition rate was 30.4nm/h, which calculated from figure (2b).The deposited DLC film has a pale brownish color and that results agree well with other studies [16,17].



Figure(2) a: Time dependence of the current density, b:Deposition Rate of DLC films

Figure(3) showed the SEM image, the deposited DLC film has a compact structure of dense grains, and the film contained irregular shape particles (clusters) of DLC (as proved by EDX) with sizes about several tens of nanometers, this result agrees with those reported by Ismail et.al [18] and Honglertkongsakul et.al [19].

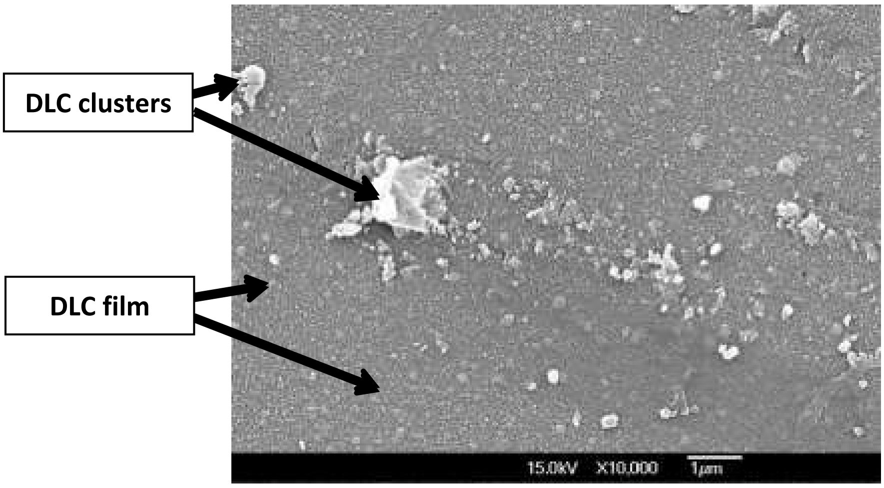


Figure (3) SEM images of DLC film.

The applying of EDX spectrum, the chemical composition of the deposited DLC film was extract, a typical EDX pattern of the DLC film was shown in figure (4), it could be seen that mainly existence four bands belong to carbon, oxygen, gold ,and silicon. The oxygen existence could be due to keep the film in air or from the solution [20,21], the presence of gold band at~2.2keV results from the sputtered gold film which was used to improve the SEM images.

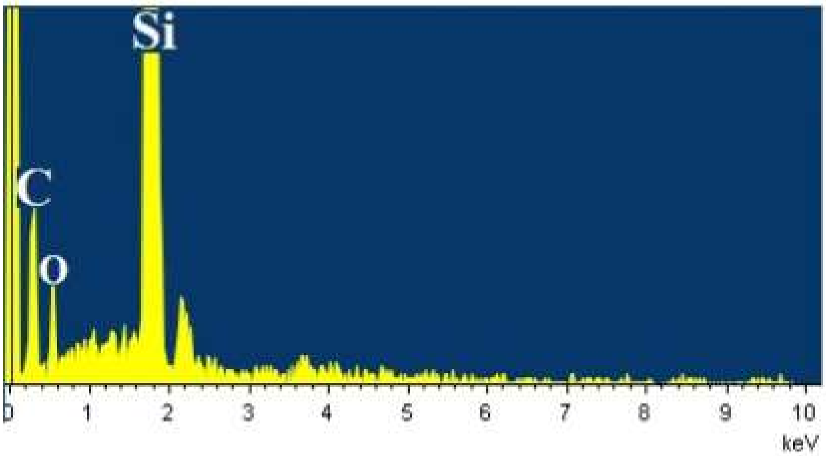


Figure (4) EDX Spectrum of the DLC film

The irregular small clusters on the film have the same composition of DLC surface with a higher oxygen percentage and lower carbon percentage as illustrated in Table 1.

Table (1) EDX results of the DLC films

Sample name	C		O		Si	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
DLC surface	33.47	52.29	6.48	7.6	60.04	40.11

DLC cluster	21.49	36.01	14.31	18.00	64.20	46.00

The AFM investigation illustrated in figure 5which shows the 3D image and particle size distribution of the deposited DLC film, the film was uniform and composes of non-spherical grains. The average grain size was (58.14nm) and the root mean square roughness was 0.712nm. Deposited DLC film showed Gaussian distribution (normal distribution).

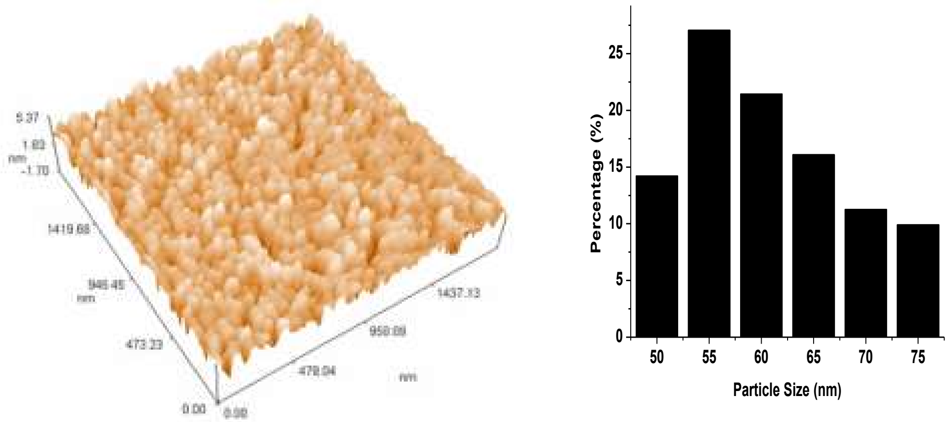


Figure (5) 3D AFM image of the DLC(a) and the grain size distribution(b)

Raman spectrum of DLC film on silicon substrate deposited at 40 ^oC and 1200 volt is shown in figure 6, this spectrum can be deconvoluted into three peaks: The G peak (centered at approximately 1656 cm^{-1}) is responsible for graphite-like layers of sp^2microdomains (1580 cm^{-1}), while the D peak (centered at 1311cm^{-1}) may be referring to the presence of cubic diamond structure (1332cm^{-1}), or (1305cm^{-1}) which refers to a hexagonal diamond, or (1180cm^{-1}) refers to nanocrystalline diamond or hexagonal diamond or sp^3- rich phase [22-24].The high intensity of D peak relative to G peak mean that film has amount of (sp^3-carbon atom) higher than (sp^2-carbon atom) [12].The (I_d/I_g) or (sp^3/sp^2) ratio for the deposited DLC film was approximately 1.1, and this meansthe number of sp^3 carbon atoms slightly larger than the sp^2 carbon atoms in the deposited DLC film [25]. There was another broad peak at ~ 1450 cm^{-1} for the deposited film assigned to amorphous diamond-like carbon [26,27], or could be ascribed to a tetrahedrally bonded diamond precursor phase [28,29]. This peak may also be assigned to the symmetrical deformation frequency of C-CH with sp^2-hybridized C-C bonding (from the -CH_2- various stretch vibration mode). This can be explained on the basis that some alkyl structures in the films and the films are hydrogenated diamond-like carbon [26,28].

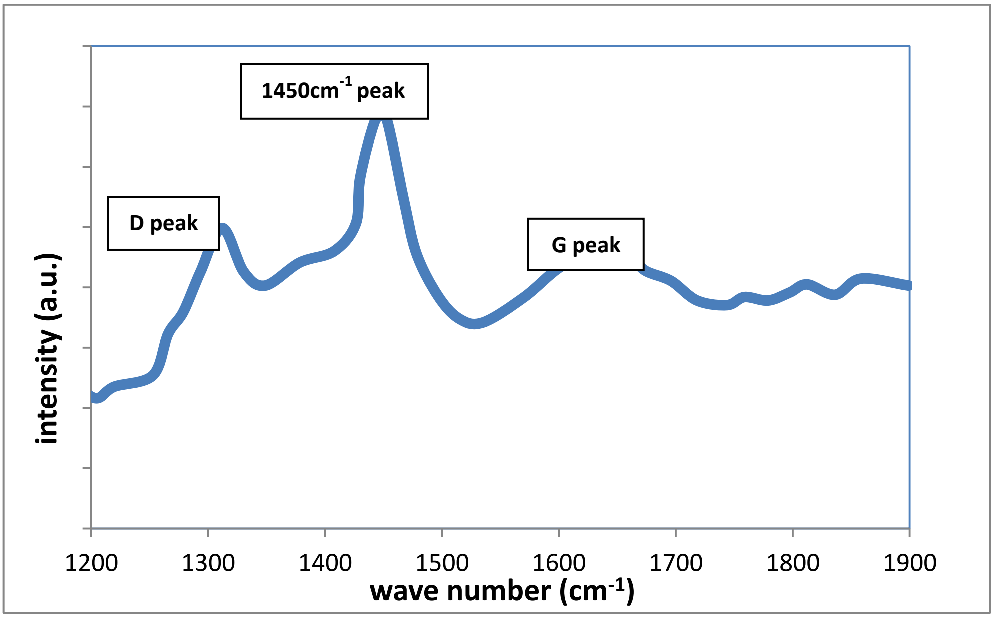


Figure (6) Raman spectrum of DLC film

The FTIR absorption spectrum of the DLC film deposited from methanol is presented in figure (7).

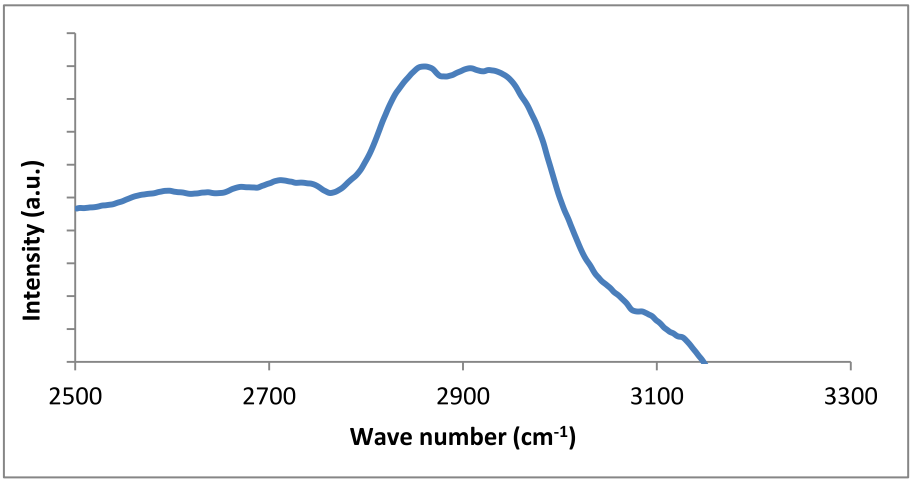


Figure (7) FTIR absorption spectrum of the DLC films

The deposited DLC film has uncertain peak at 2960 cm^{-1} within the shoulder of the peak centered at 2924 cm^{-1} due to sp^3-CH_2 (asymmetric vibration) [1,30,31]. Table (2) illustrates all the predicted and observed frequencies of the deposited DLC film. It could be easily concluded that deposited DLC film is hydrogenated, and the peak intensity depends on the existing of the type of carbon hybridization, and the hydrogen amount.

Table (2) Absorption bands of the prepared DLC films [1,30,31].

Samples	Predicted wave no. (cm^{-1})	Observed wave no. (cm^{-1})	Configurations
M100E0	2855	2860	sp^3 CH_2 (symmetric)
	2915	2906	sp^3 CH
	2925	2924	sp^3 CH_2 (asymmetric)
	2960	2960	sp^3 CH_3 (asymmetric)

CONCLUSIONS

DLC films were synthesized by electrodeposition under constant voltage 1200V and temperature 40°C, on silicon substrates, the electrolyte was the pure methanol. DLC film composes of a compact, and homogeneous grains, the surface contain irregular small clusters of DLC. The EDXpattern of the DLC film shows the mainly existence four bands belong to carbon, oxygen, gold, and silicon.A Raman spectrum shows that deposited DLC film has a mixture of sp^2 and sp^3 bonded carbon, and it was amorphous. FTIR spectrum ensures that DLC film was hydrogenated.

REFERENCES

[1] J.Robertson,"Diamond-like amorphous carbon", Materials Science and Engineering, R 37, (2002), 129-281.

[2] Alfred Grill, "Diamond-like carbon: state of the art", Diamond & Related Materials, 8, (1999), 428-434.

[3] A.C.Ferrari, and J.Robertson, "Resonant Raman spectroscopy of disorderd, amorphous, and diamond like carbon", Physical review B, 64, 075414.

[4]. X.B.Yan, T. Xu, S.R Yang, H.W.Liu, and Q.J.Xue," Characterization of hydrogenated diamond-like carbon films electrochemically deposited on a silicon substrate",J.phys D: Appl. Phys., 37, (2004), 2416-2424.

[5]. R.K. Roy, B.Deb, B.Bhattacharjee, and A.K.Pal, "Synthesis of diamond like carbon film by novel electrodeposition route", Thin solid films, 422, (2002), 92-97.

[6]. R.S. Li, M.Zhou, X.J.Pan, Z.X.Zhang, B.A.Lu, T.Wang, and E.Q.Xie, "Simultaneous deposition of diamondlike carbon films on both surfaces of aluminum substrate by electrochemical technique", J.Appl.Phys., 105, 066107, (2009).

[7] Pankaj Gupta, "Synthesis, Structure And Properties OfNanolayered DLC/DLC Films", Louisiana State University andAgricultural and Mechanical College,MSc.thesis, (2003).

[8] Minhua Chen, "ElectrodepositionOf Diamond-Like Carbon Films", University Of North Texas, MSc thesis, (2002).

[9]. Y. Namba,"Attempt to grow diamond phase carbon films from an organic solution", Vac. Sci. Technol. A, 10,(5), (1992), 03368.

[10]. T.Suzuki, Y.Manita, T.Yamazaki, S.Wanda, T.Noma," Deposition of carbon films by electrolysis of a water-ethylene glycol solution", Journal of Materials Science, 30, (1995), 2067-2069.

[11]. J. Zhang, L. Huang, L.Yu, and P.Zhang, "Synthesis and tribological behaviors of diamond-like carbon films by electrodeposition from solution of acetonitrile and water", Applied Surface Science, 254, (2008), 3896 – 3901.

[12]. Raid A. Ismail, Ali M. Mousa, and Mustafa A. Hassan, "Synthesis and characterization of diamond-like carbon film on silicon by electrodeposition from solution of ethanol and methanol", Materials Science in semiconductor processing, 27, (2014), 461-467.

[13] Mustafa Amer Hassan, "Studying the Effect of Doping in Some Physical Properties of Copper Oxide Thin Film", Eng. & Tech. Journal, 30, (14), (2012), 2421-2430.

[14]. K. Sreejith, J. Nuwad, and C.G.S.Pillai," Low voltage electrodeposition of diamond like carbon (DLC)", Applied Surface Sci., 252, (2005), 296 – 302.
[15]. X.Yan, T.Xu, G.Chen, S.Yang, and H.Liu,"Study of structure, tribological properties and growth mechanism of DLC and nitrogen-doped DLC films deposited by electrochemical technique", Applied Surface Sci., 236, (2004), 328–335.
[16] C. Cao, H. Zhu, and H.Wang, "Electrodeposition diamond like carbon films from organic liquids", Thin solid films, 368, (2000), 203-207.
[17] WenLiang He, Rui Yu, Hao Wang, and Hui Yan," Electrodeposition mechanism of hydrogen-free diamond-like carbon films from organic electrolytes", Carbon, 43, (2005), 2000–2006.
[18] R. Ismail, W.Hamoudi, K.Saleh,"Effect of rapid thermal annealing on the characteristics of amorphous carbon/n-type crystalline silicon heterojunction solar cells",Mater.Sci.Semicond.Process., 21, (2014), 194–199.
[19] K. Honglertkongsakul, P.W. May, and B. Paosawatyanyong," Effect of temperature on sulfur-doped diamond-like carbon films deposited by pulsed laser ablation", Diamond & Related Materials, 20, (2011), 1218–1221.
[20]. S.Zeb, A.Qayyum, M.Sadiq, M.Shafiq, A.Waheed, and M.Zakaullah, "Deposition of Diamond-like Carbon Films using Graphite Sputtering in Neon Dense Plasma", Plasma Chem Plasma Process, (2007), 27:127-139.
[21]. Sk.F.Ahmed, M.K.Mitra, and K.K.Chattopadhyay," Low-macroscopic field emission from silicon-incorporated diamond-like carbon film synthesized by dc PECVD", Applied Surface Science, 253, (2007), 5480-5484.
[22] T.Falcade, T.E.Shmitzhaus, O.G.Reis, A.L.M.Vargas, R.Hubler, I.L.Muller, and C.F.Malfatti,"Electrodeposition of diamond-like carbon films on titanium alloy using organic liquids: Corrosion and wear resistance",Applied Surface Science, 263, (2012), 18–24.
[23] C. Cao, H. Zhu, and H.Wang,"Electrodeposition diamond like carbon films from organic liquids",Thin solid films, 368, (2000), 203-207.
[24] J. Schwan, S. Ulrich, V. Batori, and H. Ehrhardt, and S. R. P. Silva, "Raman spectroscopy on amorphous carbon films", J. Appl. Phys., 80, (1), 1 July (1996).
[25] Raid A. Ismail, Ali M. Mousa, Mustafa A. Hassan, Walid K. Hamoudi, "Synthesis of diamond-like carbon films by electrodeposition technique for solar cell applications", Opt Quant Electron, (2016), 48:16 DOI 10.1007/s11082-015-0298-8.
[26]. Z.Sun, Y.Sun, X.Wang, "Investigation of phases in the carbon films deposited by electrolysis of ethanol liquid phase using Raman scattering", Chemical Physics Letters, 318, (2000), 471 - 475.
[27] K.Ma, G.Yang, L.Yu, and P.Zhang, "Synthesis and characterization of nickel-doped diamond-like carbon film electrodeposited at a low voltage", Surface & Coatings Technology, 204, (2010), 2546–2550.
[28] S.Wan, H.Hu, G.Chen, and J.Zhang, "Synthesis and characterization of high voltage electrodeposited phosphorus doped DLC films", Electrochemistry Communications, 10, (2008), 461–465.
[29] H.Wang, M.Yoshimura," Electrodeposition diamond like carbon films in organic solvents using a thin wire anode", Chemical Physics Letters, 348, (2001), 7-10.
[30] S. B. Singh, M. Pandey, N. Chand, A. Biswas, D. Bhattacharya, S. Dash, A. K. Tyagi, R. M. Dey, S. K. Kulkarni and D. S. Patil," Optical and mechanical properties of diamond like carbon films deposited by microwave ECR plasma CVD" Bull. Mater. Sci., 31, (5), October, (2008), 813–818.
[31] D.S.Patil, K.Ramachandran, N.Venkatramani, M.Pandey, S.Venkateswaran, and R.D Cunha," Microwave plasma chemical vapour deposition of diamond like carbon thin films", Jurnal of Alloys and Compounds, 278, (1998), 130-134.