

Effect Of Bipolar Pulsed Voltage On Properties Of DLC Films Deposited By Inductively Coupled PECVD

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Abstract

Diamond-like carbon (DLC) is a metastable form of amorphous carbon having large sp^3 bonding. DLC films have unique properties such as high hardness, low-friction, good transparency in IR region, chemical inertness and biocompatibility. To have better performance of the coating one should have proper selection of different parameters for deposition. In the present study, DLC films were deposited on p-type silicon (100) substrates using methane (CH_4) and hydrogen (H_2) as source gases in an inductively coupled RF plasma CVD system. Bipolar pulsed bias voltage source at 10 KHz frequency used for substrate shows proper DLC film. The DLC films were characterized for surface morphology & roughness, hardness & Young's modulus, IR absorption and micro-Raman spectroscopy. Deposited DLC film images show that the roughness decreases, hardness & Young's modulus increases and the I_d/I_g ratio decreases with the increase of pulse bipolar bias voltage. Raman result shows that disorder decreases. The correlation plotted between I_d/I_g , hardness and roughness.

Key words: Bias, Bombardment, Diamond-like carbon, Microstructure, Nanohardness, Nanoindentation, PECVD.

1. Introduction

Diamond-like carbon (DLC) is a form of amorphous carbon, which is metastable containing a greater fraction of sp^3 bonds [1]. DLC is gaining an increasing demand because of its vast area of applications, as protective coatings in magnetic storage disks, optical windows, micro-electromechanical devices (MEMs) and automobile industry. Its unique combination of properties, such as chemical inertness, high electrical resistivity and mechanical hardness, low friction coefficient, high optical transparency and wear resistance, determine its wide applicability in a variety of fields ranging from optics to tribology, from electronics to biomedical as stated before. [1, 2, 3] Highly corrosive environments exploit the chemical inertness of DLC

and the bio-compatibility of DLC is regarded as a boon in the bio-medical field. These properties of DLC depend mainly on its structure resulting from the combination of sp^3 bonding as found in diamond and sp^2 bonding as found in graphite. The structure or the sp^3 to sp^2 ratio is tailored by the various deposition methods available [4].

Different methods have been devised for deposition of DLC, both in physical vapor deposition (PVD) as well as in chemical vapor deposition (CVD). PVD techniques include sputtering, both magnetron and ion beam sputtering, ion beam assisted deposition (IBAD), pulsed laser deposition (PLD) to name a few. Similarly CVD techniques consist of plasma enhanced chemical vapor deposition (PECVD) and electron-cyclotron resonance CVD (ECR-CVD) [5]. Of these, PECVD seems to be the ideal choices for DLC deposition since CVD techniques give a better control, reproducibility, and importantly independence in the choice of substrates wherein substrates with complex geometry can also be coated. In PECVD it has been shown that film composition is determined mainly by parameters such as gas composition, pressure and plasma parameters. The ion flux and energy of ions from the plasma that bombard the growth surface during film growth has been shown to be important process parameters that determine the film composition and properties.

In case of capacitive coupled PECVD the self bias generated by the asymmetric geometry provides the ion energy. Inductive Coupling leads to high density plasma and enhancement in the quality of deposited film because of a higher degree of ionization of the atoms in gaseous phase. This gives a maximum control over the deposited films by lowering the process temperature and also maintaining the deposition rate same. [6] However, an independent control of ion energy, separate from the plasma generation source, will give a better control over the ion bombardment and hence on the composition and properties of film. A separate biasing can be used to provide additional energy by way of RF or DC bias. [6, 7] The energy supplied by the additional ion bombardment provides

rearrangement of adsorbing species to change the films composition and morphology. DLC has also been deposited using plasma based ion implantation with bipolar pulses with an idea to enhance the adhesion of the deposited film by giving a graded carbon interface. [8] In the present study the role of bias voltage on the properties of DLC films deposited in inductively coupled plasma CVD (ICP-CVD) is presented.

2. Experimental procedure

The DLC films were deposited in an inductively coupled plasma system [9] Silicon, p type (100), was used as the substrates for the DLC coating. Before deposition the substrates were cleaned ultrasonically in acetone, dried and loaded in to the vacuum chamber. The vacuum chamber was pumped to a base pressure of 2×10^{-6} mbar by diffusion pump and purged with methane and hydrogen. The samples were cleaned in hydrogen plasma for 15 minutes at 50W RF power. After the cleaning process, methane and hydrogen in the desired ratios were introduced and the pressure was maintained at 1.4×10^{-4} mbar. The flow rate was maintained by MKS make mass flow controllers. Experiments were carried out at 90:10, 80:20 and 75:25 of methane to hydrogen ratio. The RF (13.56MHz) power was kept constant at 50W. The substrates were kept on an insulated electrode and biased by a separate bias power supply and the bias voltage was varied from 60V to 150V in the pulsed as well as continuous DC mode. In the case of pulsing, both bipolar and unipolar pulses were employed. For bipolar pulsing, the frequency was kept constant at 10 KHz and the positive voltage was

kept constant at 30V while the negative voltage was varied.

The IR absorbance of the DLC coatings were measured in the near infrared (IR) range of 4000 cm^{-1} to 400 cm^{-1} using VECTOR 22 FTIR Spectrometer (Bruker Make) and the Raman spectra by Labram 010 model micro Raman Spectrometer (DILOR-JOBIN-SPEX make) with laser of 632nm wavelength and 3mW power. The nanohardness measurements and AFM imaging were performed with an instrument consisting of a nanohardness Tester (CSEM Instruments) and an integrated optical (Nikon)/Atomic Force Microscope (Surface Imaging) Systems. Indentation profiles were recorded with a maximum load of 5mN and AFM images were obtained on $5 \mu\text{m} \times 5 \mu\text{m}$ area.

3. Results and Discussion

Experiments were carried out with different bias voltages and gas compositions of CH_4 and H_2 , for 30 minutes and the same are tabulated in the TABLE 1. The samples were systematically studied by Raman spectroscopy, AFM, NHT, and FTIR spectroscopy for different properties. In this table roughness, hardness, Young's modulus and I_d/I_g ratio of the DLC films are listed. The results for films deposited with 75:25 gas compositions at a bias frequency of 10 KHz and 50 W RF power are presented here to emphasize the effect of different bias voltage.

Table 1 Experimental Details of DLC films deposited at 50W RF power and 10 KHz bias frequency.

Run No.	Gas composition (%) $\text{CH}_4:\text{H}_2$	Bias Voltage (V)			Roughness (nm)	Young's Modulus (GPa)	Hardness (GPa)	I_d/I_g
		+ve	-ve	pulsing				
C20	75:25	30	60	Y	2.62	191.65	15.59	0.724
C30	75:25	30	80	Y	2.22	196.85	17.54	--
C23	75:25	30	100	Y	2.10	204.10	19.6	0.695
C21	75:25	30	120	Y	1.94	198.90	25.34	0.634
C22	75:25	60	130	Y	2.02	196.28	16.52	--
C25	90:10	60	150	Y	--	187.01	23.45	--
C31	90:10	60	100	Y	2.71	177.22	15.64	--
C33	90:10	--	100	N	1.91	158.99	13.52	0.811
C36	90:10	--	-80	N	--	--	--	--
C38	90:10	50	--	N	2.39	189.13	15.27	--
C39	90:10	60	120	Y	--	--	--	--
C40	90:10	60	100	Y	--	--	--	--

The properties of DLC films are strongly connected to their hydrogen concentration, which plays an important role in the microstructure of film matrix. Thus, the study of hydrogen content is

of great relevance to achieve a good control of optical, electric, mechanical and surface properties of DLC. IR transmittance spectra of DLC films grown at 10 KHz pulse frequency and at -150, 130,

-100 V, +50 V and +100 V bias are shown in Fig.1 in the wavelength range of 2800 cm^{-1} to 3100 cm^{-1} . Three peaks are present in Fig.1; they are centered at 2962 cm^{-1} , 2854 cm^{-1} , and 2925 cm^{-1} wave numbers. These three peaks are due to the stretching of C-H bond. [10, 11, 12] The resulting peaks of absorption spectra appear centered approximately at 2920 cm^{-1} , wave number that is

associated with the major presence of hydrogen bonds in the form of $\text{sp}^3\text{-CH}_3$ and $\text{sp}^3\text{-CH}_2$ groups. TABLE 2 shows that the intensity of peak centered at 2924 cm^{-1} with applied bias voltage increases. IR absorbance of DLC films were estimated by measuring the intensity of the peak (2924 cm^{-1}) of each samples with the base line correction as a first approximation.

Table 2 Intensity dependence (2924 cm^{-1} peak) of DLC films on the bias voltage.

Sample	Bias Voltage (V)	Bias condition	Absorbance
C22	100	Bi polar Pulsed	0.330
C31	60	Bi polar Pulsed	0.400
C38	+50	Simple bias	0.390
C36	-80	Simple bias	0.345
C39	120	Bi polar pulsed	0.465
C40	100	Bi polar pulsed	0.471
Silicon substrate	No	---	0.165

The decrease of the absorption (Fig.1) from 0.8 to 0.2 as the bias voltage increases from -100 to -150 V and for +50 and +100 indicates a reduction in hydrogen bonding. This result is interpreted as a

lowering of hydrogen content in DLC samples, since the integrated absorption in the C-H stretching band is correlated with the hydrogen density in DLC.

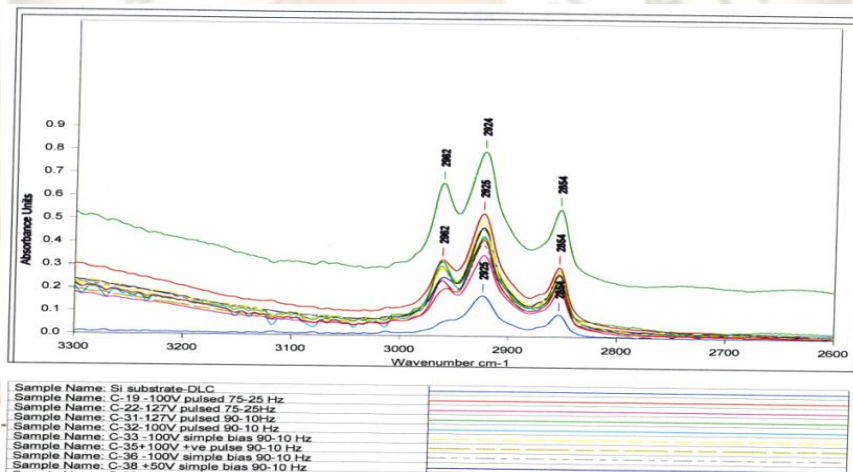


Figure 1 FTIR spectra of DLC coatings

Data for C39 and C40 is for films deposited for 4hrs and shows that the absorbance of the samples decreases with the increase of the negative bias keeping other parameters, such as gas composition 90:10, RF Power 50W, frequency for the bias pulsing 10 KHz, constant. This shows that the hydrogen concentration decreases with the increase of the bias voltage.

Fig.2 (a) to (d) show the Raman spectra of the DLC coatings deposited with different bias voltages on silicon substrate. These spectra were fitted with Gaussian peaks after subtracting a linear background. The spectra have two peaks at approximately 1340 cm^{-1} (D-band) and 1560 cm^{-1} (G-band). TABLE 1 lists the I_d , I_g and the ratio I_d/I_g of DLC films deposited with 75:25 gas ratio, 50 W RF power and at different bipolar pulse bias voltage with constant pulse frequency of 10 KHz.

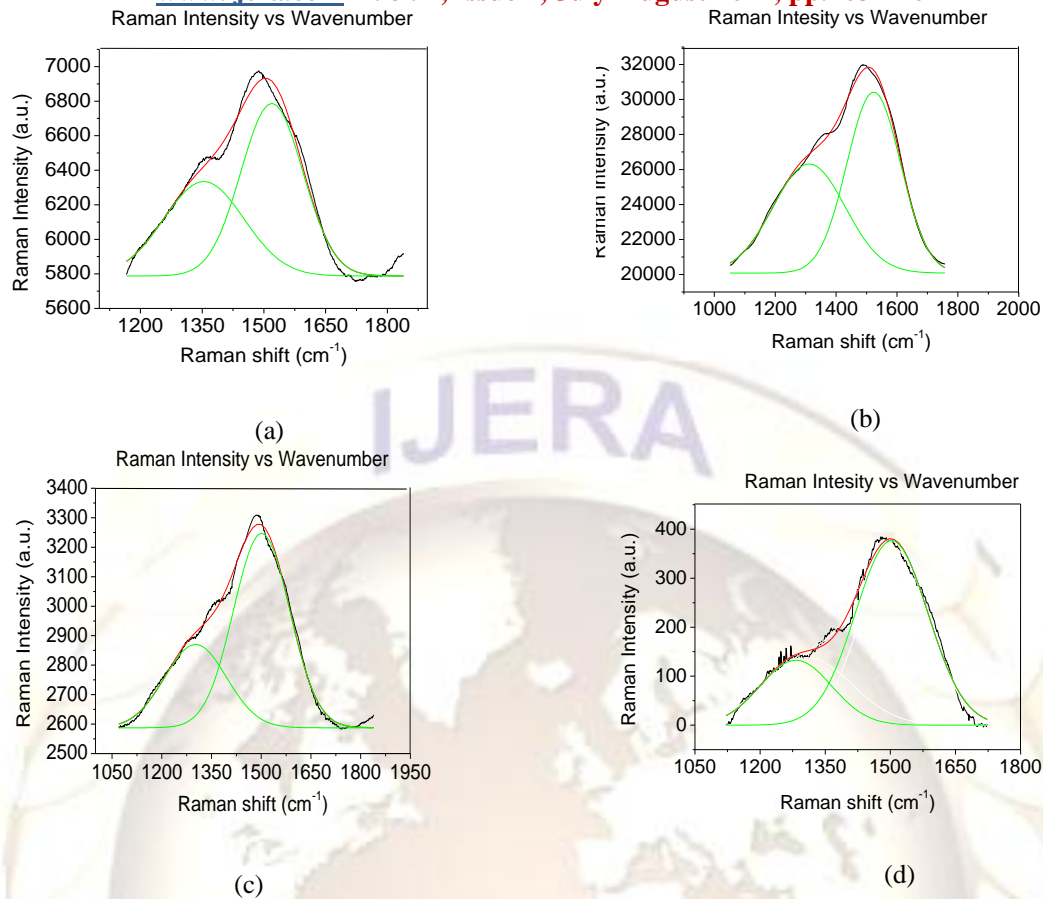


Figure 2: Raman spectra fitted with Gaussian curves to determine sp^3 and sp^2 ratio. DLC films deposited with a gas composition of $CH_4:H_2$ in 75:25 ratio at 50W RF power.

The variation of I_d/I_g ratio with substrate bias voltage is shown in the Fig.3. The ratio decreases with bias, especially at higher bias. Decrease of

I_d/I_g ratio has been identified with decrease of disorder in the film. [12, 13, 14].

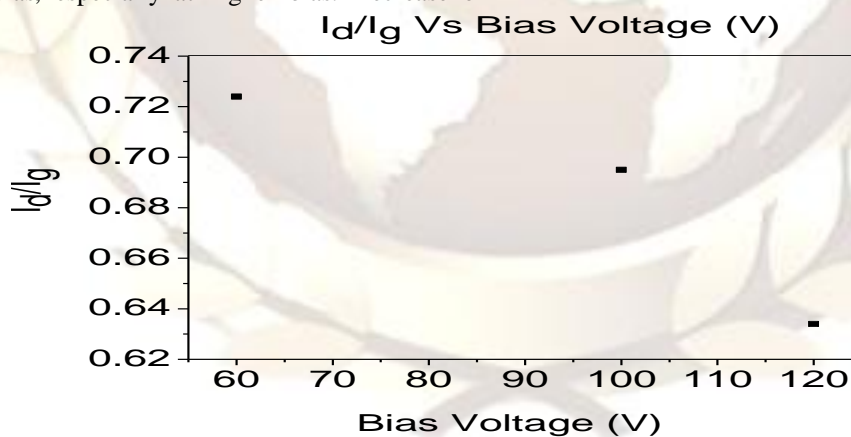


Figure 3 I_d/I_g vs. Negative pulsed Bias Voltage (V) plotted using the Gaussian curve fitting data.

Fig.4 show the AFM images for the substrate and DLC films coated on silicon samples. From the images and the roughness values, the films appear smoother than the silicon substrate which has an RMS roughness of 8.54nm. The dependence of the roughness on pulse bipolar bias voltage is shown in

Fig.5 and in the TABLE 1 as well. Roughness varies from 2.6nm at -60V bias to 1.9nm at -120V. The roughness could be seen decreasing with increasing applied bias voltage. Higher bias shows smoother surface as a consequence of bombarding effect of the incoming ions [15, 16, 17].

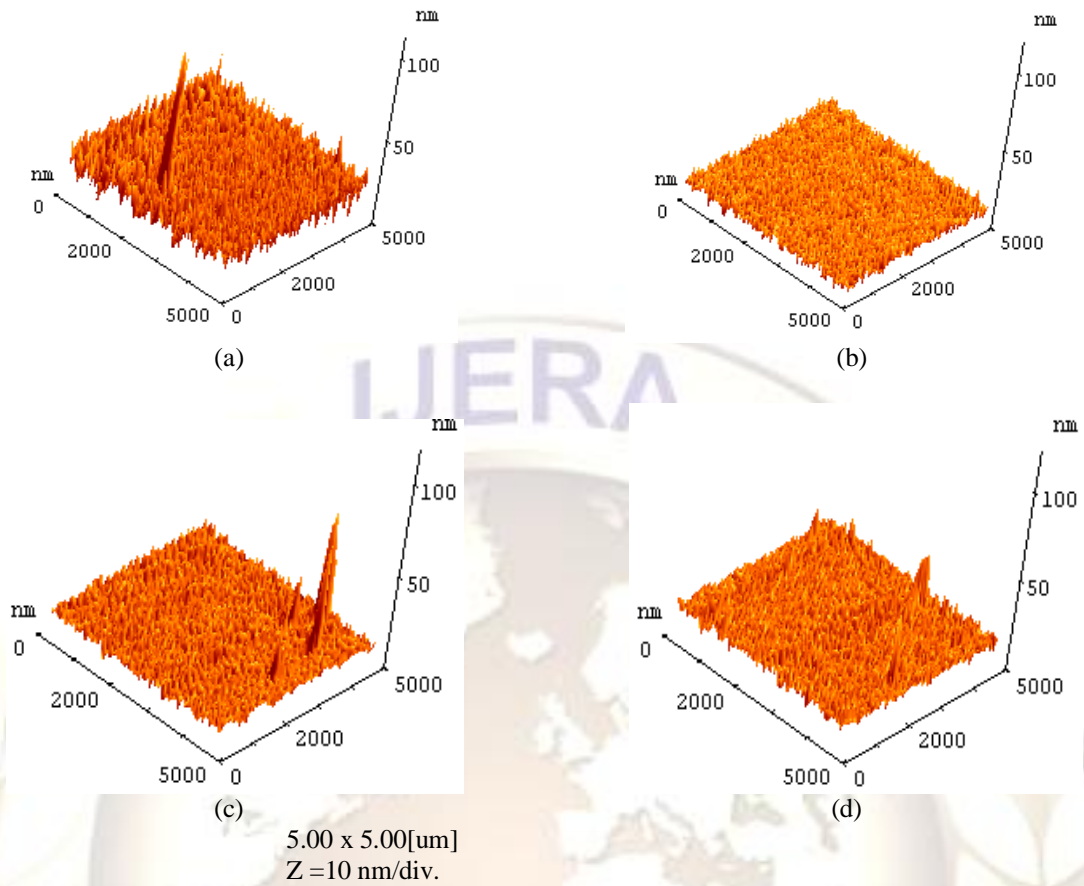


Figure 4 Surface morphology of DLC films deposited with a gas composition of $\text{CH}_4:\text{H}_2$ in 75:25 ratio at 50W RF power with (a) -60V, (b) -80V, (c) -100V and (d) -120V

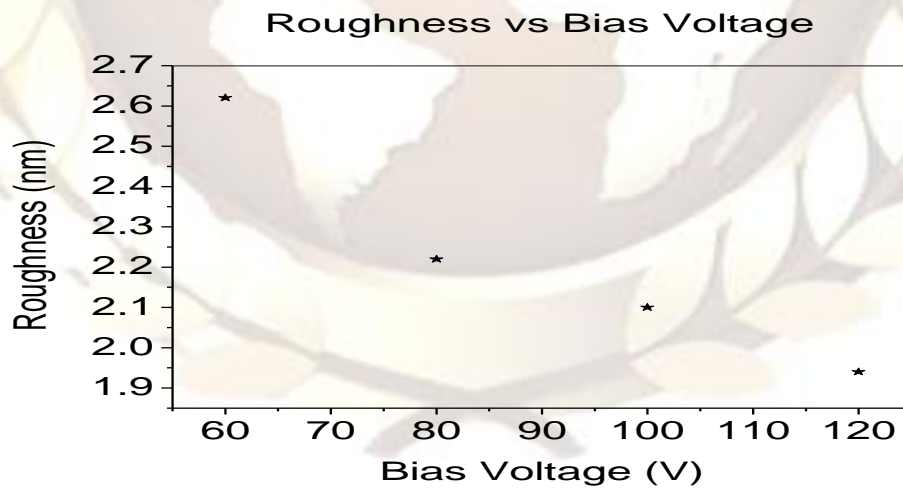


Figure 5 Dependence of R_a on negative pulsed bias voltage at a gas composition $\text{CH}_4:\text{H}_2$ in 75:25 ratio and 50W RF power

The nanohardness (H) and Young's modulus (E) of the coatings deposited on silicon substrate were measured by nanoindentation. The nanohardness was measured at different points on the coating with 5mN load. Nanohardness and Young's modulus was estimated from the indentation profiles following Oliver-Pharr method. [18] Indentation profiles for the DLC coating deposited

at different parameters are shown in Fig.6. Indentation profiles show smoother loading and unloading behavior. The repeatability of hardness measurements and uniformity of the film's hardness at different places are highlighted by the profiles measured at different places on the sample as shown in the graphs below.

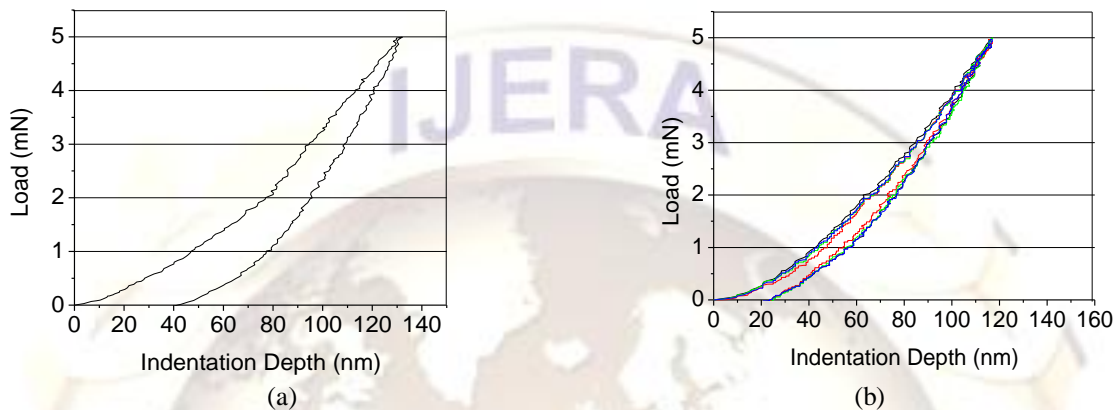


Figure 6: Indentation profiles at 5 mN load for DLC coatings on Silicon Sample deposited with a gas composition of $\text{CH}_4:\text{H}_2$ in 75:25 ratio at 50W RF power and 10 KHz bias frequency with different negative bias (a) -100V (b) -130V

Fig.7 shows the dependence of hardness (H) on the applied bias. It is observed from the graph that hardness depends on the applied bias. [19] The hardness seems to be marginally affected by voltage up to 80V and then increases with applied bias. In TABLE 1 hardness and Young's Modulus values are listed against applied pulse bipolar bias for DLC coatings deposited with 75:25 gas ratio,

50W RF power with a bias frequency of 10KHz. Hardness is found to increase from 16GPa at -60V to 25GPa at -120V bias voltage. [19] Fig.8 depicts the dependence of the Young's modulus (E) on bias voltage. Graph shows increase of E from 191 GPa for a bias of -60V to 204.1 GPa for a bias of -100V and then it decreases to 198.9GPa at a bias of -120V.

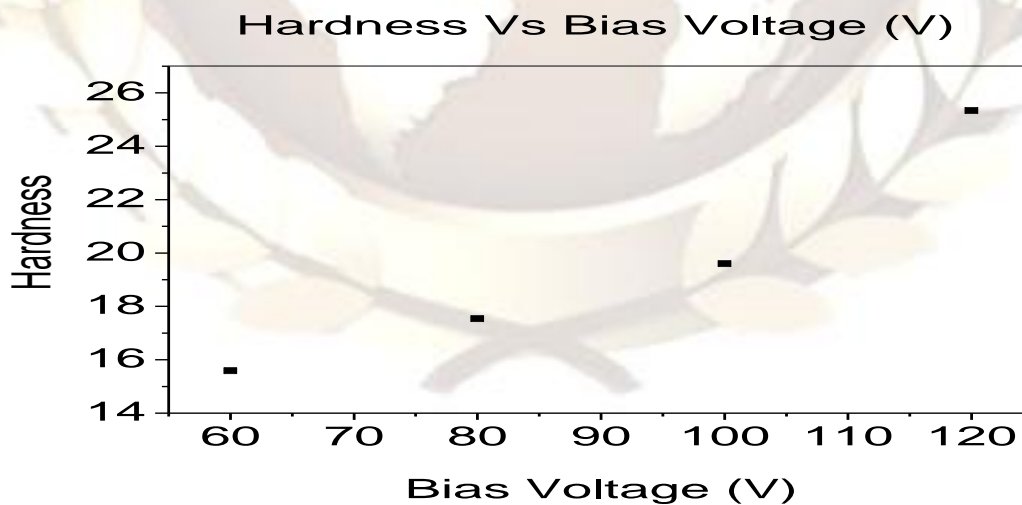


Figure 7: Dependence of hardness on the applied negative bias voltage. (Gas composition $\text{CH}_4:\text{H}_2$ in 75:25 ratios, 50 W RF power and 10 KHz bias frequency)

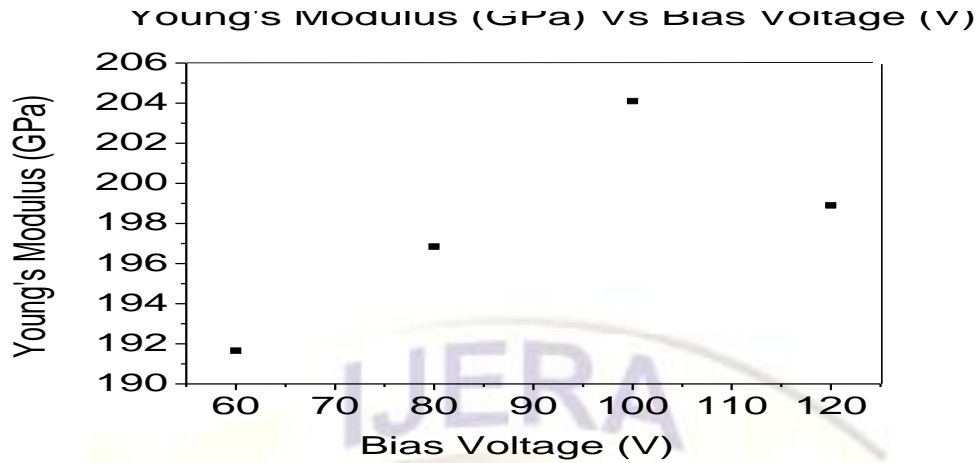


Figure 8: Dependence of Young's modulus on the applied negative bias voltage. (Gas composition CH₄:H₂ in 75:25 ratio, 50 W RF power and 10 KHz bias frequency)

In TABLE 1, the nanohardness, Young's modulus, roughness, the sp³ / sp² ratio are listed against applied bias for DLC films deposited with 75:25 gas ratio, 50W RF power with a bias frequency of

10KHz. Fig.9 shows the dependence of the hardness and roughness on I_d/I_g ratio and Fig.10 shows the dependence of Young's modulus and absorbance on I_d/I_g ratio. [13, 20]

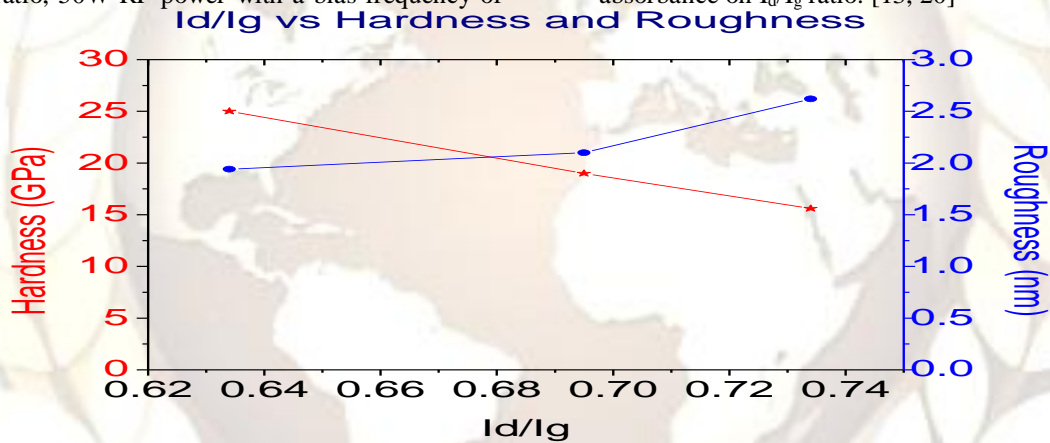


Figure 9: The I_d/I_g ratio of sp³ and sp² shows the dependence with the hardness and roughness.

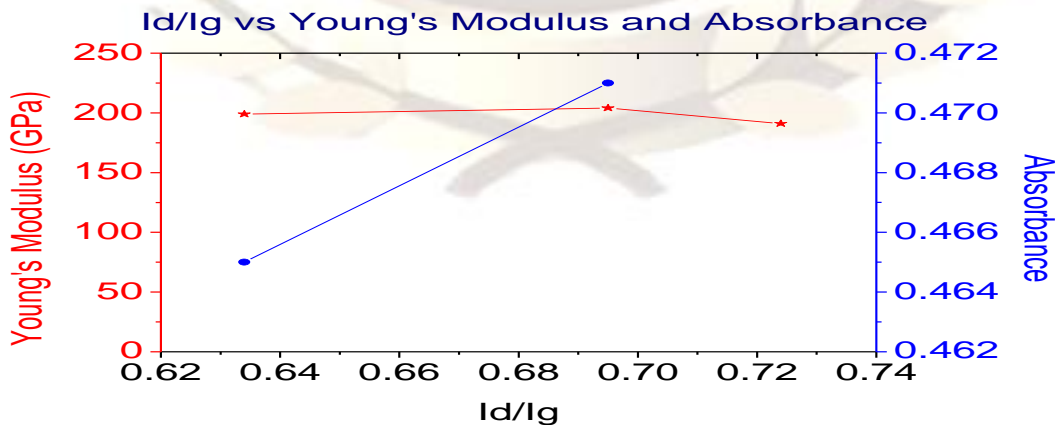


Figure 10: The I_d/I_g ratio of sp³ and sp² shows the dependence with the Young's modulus and absorbance.

In the present study the bipolar pulsed bias source used for substrate and inductively coupled plasma source for generating the plasma. By controlling the bias voltage (+ve bias fixed at 30V and -ve bias varied from 60 to 120V at 10 KHz frequency) applied to the substrate without altering the plasma power or electrode geometry, DLC films deposited under different ion fluxes and ion energies. This leads to study and understand the effect of ion bombardment parameters on the film morphology and film properties. The hardness and Young's modulus increases with applied bias, the roughness, on the other hand, decreases i.e. the film becomes smoother with increase of bias implying that ion bombardment promotes uniform film growth. The decrease of roughness at higher biases may be due to increased ion bombardment energy which promote diffusion of adsorbing reactive species on the growth surface and result in denser film. [13] Also, the sp^3/sp^2 ratio given by the I_d/I_g ratio decreases with increase of bias. As in Fig.10, IR absorbance increases, I_d/I_g ratio also increases. This is due to differences in the sp^3 to sp^2 bonding which is altered by the ion bombardment. [12, 21-24] The higher hardness at higher bias voltages is due to the very dense film. [13, 25]

4. Conclusion

Plasma enhanced chemical vapor deposition (PECVD) technique was used for depositing diamond-like-carbon (DLC) coatings on p type silicon in inductively coupled RF plasma at different bipolar pulsed bias (+ve bias fixed at 30V and -ve bias changed from 60V to 120V at 10 KHz frequency) conditions. The films were characterized for surface morphology, hardness and Young's modulus. DLC films deposited with 75:25 gas compositions, gave following interesting results with the conclusion:

Roughness measurements of the DLC coatings show the films are very smooth with a roughness of around (RMS) 2.10 nm. The roughness decreases with increase of bias voltage.

Analysis of Raman spectra for sp^3 and sp^2 ratio shows I_d/I_g values from 0.5 to 0.8 can be obtained under different deposition conditions. Also, I_d/I_g decreases with bias keeping other parameters constant.

Nanohardness of the DLC film is in the range of (13 GPa to 25 GPa) and shows dependence on the bias; it increases with the increase of bias. Young's modulus also shows similar results with increasing bias.

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