

Optical and mechanical properties of diamond like carbon films deposited by microwave ECR plasma CVD

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Abstract. Diamond like carbon (DLC) films were deposited on Si (111) substrates by microwave electron cyclotron resonance (ECR) plasma chemical vapour deposition (CVD) process using plasma of argon and methane gases. During deposition, a d.c. self-bias was applied to the substrates by application of 13.56 MHz rf power. DLC films deposited at three different bias voltages (–60 V, –100 V and –150 V) were characterized by FTIR, Raman spectroscopy and spectroscopic ellipsometry to study the variation in the bonding and optical properties of the deposited coatings with process parameters. The mechanical properties such as hardness and elastic modulus were measured by load depth sensing indentation technique. The DLC film deposited at –100 V bias exhibit high hardness (~19 GPa), high elastic modulus (~160 GPa) and high refractive index (~2.16–2.26) as compared to films deposited at –60 V and –150 V substrate bias. This study clearly shows the significance of substrate bias in controlling the optical and mechanical properties of DLC films.

Keywords. Diamond like carbon; chemical vapour deposition; mechanical properties; Raman spectroscopy.

1. Introduction

Diamond like carbon (DLC) films are being widely studied due to their outstanding properties such as high hardness, wear resistance, low friction coefficient, high electrical resistance, chemical inertness and optical transparency in the infrared region (Groning *et al* 1997; Sanchez *et al* 2000; Cicala *et al* 2004). These films are promising as coatings on tools used in applications that require low friction and high wear resistance and also for photoluminescence and field emission devices. These films can be deposited at room temperature by various physical and chemical vapour deposition (PVD and CVD) methods such as pulsed laser deposition, filtered cathodic vacuum arc deposition and microwave and radio frequency plasma assisted deposition (Lossy *et al* 1995; Kautek *et al* 1996; Musil 1996). Microwave ECR plasma CVD process has inherent advantages due to high degree of ionization of the precursor gases, high density of reactive species and low pressure operation. This results in high growth rates, efficient gas utilization and uniformity in deposition. Further due to the fact that substrates can be independently biased, it is possible to control the flux and energy of ions im-

ping on the substrate surface. This is actually regarded as one of the most important process parameters during DLC deposition (Matsuo and Kiuchi 1983; Grill 1993). The objective of the present study is to deposit DLC coatings on silicon (111) substrates under the influence of different d.c. self bias (developed with the application of RF power to the substrates) and to investigate the effect of this substrate bias level on the structural, optical and mechanical properties of the deposited films.

2. Experimental

The DLC films were deposited on the polished, *p*-type silicon (111) substrates using a 2.45 GHz, 1.5 kW, microwave ECR plasma CVD facility set up in our laboratory. Figure 1 shows the schematics of the experimental system. The ECR plasma is generated in a chamber that is surrounded by two water-cooled electromagnet coils that are powered independently by constant current regulated power supplies. The distance between the coils can be adjusted to generate a desired magnetic field profile in the plasma generation chamber. The current in the top and bottom coil was set at 130 A and 170 A, respectively that generates a magnetic field profile having two ECR zones (one near the quartz isolation window and other near the exit of the ECR plasma generation chamber). This magnetic

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field configuration acts as a magnetic field mirror for electrons in ECR plasma source. The microwave power absorption in the ECR zone is associated with the heating of electron that bounces between the two mirror ends of the ECR zones. This results in increase in the electron energy/temperature that leads to further ionization resulting in high density of electrons for efficient decomposition of the hydrocarbon precursors during deposition. The ECR zone near the quartz window can further be shifted to the quartz window (by tuning the magnetic field profile) for creating energetic ions when required for cleaning of the window. This periodic cleaning of the window is required, as during deposition a carbon film is deposited on the quartz window that reduces the microwave transmission. The microwave hardware consists of a 2.45 GHz magnetron capable of delivering a microwave power of up to 1.5 kW. Microwaves are launched in the wave-guide as TE₁₀ waves. The other components in the microwave transmission line are a three-port circulator with a water cooled dummy load, cross coupler that extracts a signal of the microwave power (forward and reflected) with power indicating meters, three stub tuner, a microwave mode converter TE₁₀ to TM₀₁ and a sliding short circuit. Microwaves enter the ECR plasma generation chamber as TM₀₁ waves. The quartz isolation window separates a plasma generation chamber and the microwave hardware. The divergent magnetic field near the exit of the plasma generation chamber helps in generating large volume plasma in the processing chamber where the substrate is located. The substrate stage is isolated from the grounded chamber walls and is coupled to a 13.56 MHz, 300 W rf power generator through an impedance matching unit built in our laboratory.

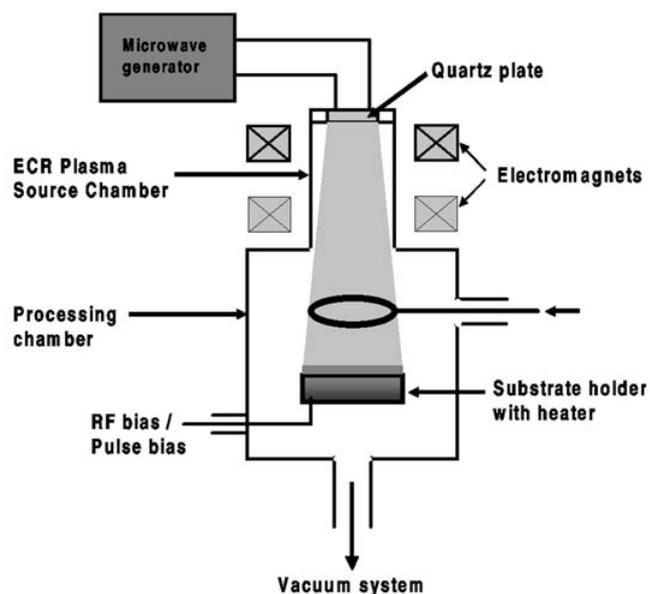


Figure 1. Schematic of the experimental set up of microwave ECR plasma system.

Prior to deposition, Si (111) substrates were ultrasonically cleaned in isopropyl alcohol and kept on a RF electrode. The system was first evacuated to an initial pressure of 1.5×10^{-6} mbar using a turbo molecular pump backed by a rotary pump. After stabilization of the plasma of argon gas, substrates were sputter cleaned to remove the residual contaminant impurities and oxide from the surface by application of RF self bias of -100 V for 10–15 min. Plasma density measurements near the substrate (by Langmuir probe inserted in the plasma) was found to be 1.1 – $1.4 \times 10^{10}/\text{cm}^3$, and also indicated a fairly uniform plasma in the centre of the chamber over an area of ~ 20 cm diameter. Methane as a reactant gas was then introduced into the chamber via a gas shower ring positioned 50 mm above the substrate. The final operating pressure was 5.5×10^{-4} mbar. The depositions were carried out at three levels of substrate bias (-60 V, -100 V and -150 V) for a time duration of 45 min–1 h.

Deposited coatings were characterized using a CCD based Raman spectrometer having argon ion laser of excitation wavelength, 532 nm. The infrared spectra of the coatings were recorded in the range 400 – 4000 cm^{-1} using a Bomem FTIR with a resolution of ~ 4 cm^{-1} . Ellipsometric measurements were carried out with a phase modulated spectroscopic unit (model UVSELTM 460 ISA JOBIN–YVON, SPEX) in the range 350 – 1200 nm. The mechanical properties (hardness and Young's modulus) of the films were measured using a nanoindenter (CSM Instruments). Berkovich three-sided pyramidal diamond indenter with a nominal angle equal to 65.3° was used for these measurements. All tests were performed in clean environment at ambient temperature.

3. Results and discussion

The DLC films deposited by microwave ECR plasma CVD process were visually smooth and flat. A typical SEM image taken on a film deposited at -150 V bias is shown in figure 2. For all films no visible grain features and

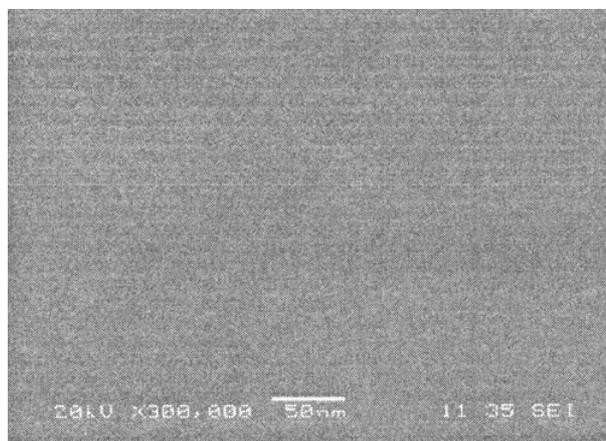


Figure 2. SEM image on film deposited at -150 V bias.

pores could be observed under SEM. The coatings were scratch proof and strongly adherent to substrates. The electrical resistivity of the deposited films was $>200 \text{ M}\Omega$.

The thickness of the deposited films as measured by ellipsometry were $0.315 \mu\text{m}$ (-60 V bias, 1 h deposition), $0.248 \mu\text{m}$ (-100 V bias, 45 min deposition) and $0.679 \mu\text{m}$ (-150 V bias, 1 h deposition). The increase in the thickness of the coating with bias voltage is attributed to the increase in the number of radicals which participate in the reaction. This results in enhanced ionization and dissociation of precursor gas due to increased electron energy in the plasma with increase in the bias voltage. The films deposited at -100 V bias also showed a high residual stress in the coatings, as repeated attempts to deposit coatings thicker than the ones reported failed. Films deposited for longer duration of time ($>45 \text{ min}$) pilled off the substrate base.

A typical loading–unloading curve (for a film deposited at -100 V bias) for a final load of 10 mN is shown in figure 3. Hardness and elastic modulus of the films were estimated from these loading–unloading curves using the Oliver and Pharr method of data analysis (Oliver *et al* 1992). Hardness and elastic modulus of the DLC films were found to be in the range of $\sim 15\text{--}19 \text{ GPa}$ and $\sim 132\text{--}160 \text{ GPa}$, respectively as shown in figure 4. From this figure it is clear that the film deposited at -100 V bias shows maximum hardness and elastic modulus as compared to the films deposited at lower and higher bias voltages, indicating that there is definitely an optimal rf induced d.c. substrate bias at which one can get hard films. It is mentioned here that though in practice the depth of indentation should not exceed 10% of the thickness of the actual coatings during measurement of the hardness of the coatings, here the indentation depth is $\sim 210 \text{ nm}$ which is nearly 85% of the coating thickness. This, therefore, indi-

cates that the measured hardness is not the true hardness of the coatings but a composite hardness (i.e. of the film and the substrate together). The true hardness of the coatings is definitely higher than the values reported here. Nevertheless, the observations reported here do represent a trend in the hardness and elastic modulus values with the applied substrate bias. The high value of hardness reported here for a film deposited at -100 V bias indicate that this film should have higher values of sp^3/sp^2 ratio of the carbon bonding and also higher density.

Refractive index (n) and extinction coefficient (k) variations with the wavelength for DLC films deposited at different bias voltages (-60 V , -100 V and -150 V) are shown in figure 5. The refractive index of these films was found to vary in the range $2.26\text{--}1.82$ with the applied bias as shown in this figure. The refractive index of DLC film deposited at -100 V bias is found to show a very low dispersion compared to the films deposited at -60 V and -150 V bias voltages. The reported value of refractive index for DLC films is in the range $1.8\text{--}2.3$. Dense carbonaceous films have a large refractive index with relatively low dispersion and high amount of hydrogen in the film lowers the refractive index (Sarangi *et al* 2000). For polymer like hydrocarbon films (deposited at low energy), this is reported to be less than 1.8. From the observed data, inference can be drawn that the DLC film deposited at -100 V bias is having high density and is with lesser hydrogen fraction as compared to the films deposited at -60 V and -150 V bias. The value of the refractive index (n) was found to be maximum (~ 2.26 for film deposited at -100 V bias) at $400\text{--}450 \text{ nm}$, while the extinction coefficient (k) attains a value near to zero for all films at 800 nm and beyond, indicating that these films are transparent beyond 800 nm . There is a slight but noticeable

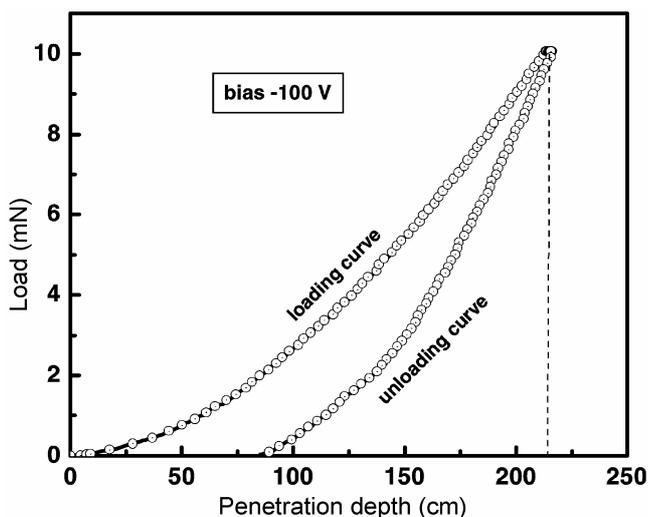


Figure 3. Typical loading–unloading curve of a DLC film deposited at -100 V substrate bias.

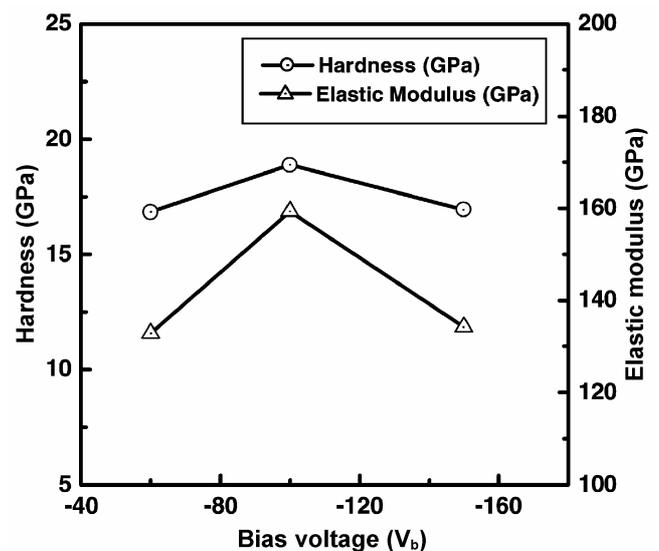
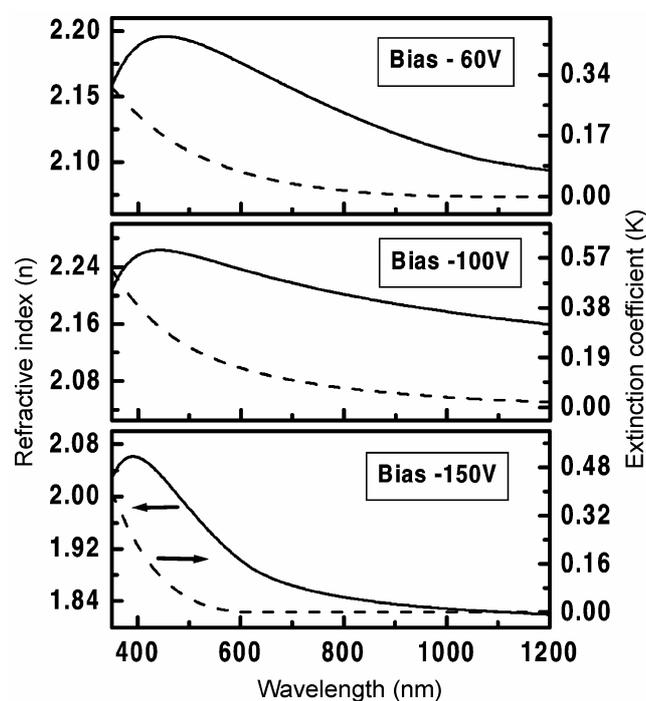


Figure 4. Hardness and Young's modulus of the deposited films as functions of substrate bias.

Table 1. Peak fitting details of IR absorption spectra.

Pk No.	Peak assigned	(-60 V Bias)			(-100 V Bias)			(-150 V Bias)		
		Peak position (cm ⁻¹)	Peak width (cm ⁻¹)	Area (%)	Peak position (cm ⁻¹)	Peak width (cm ⁻¹)	Area (%)	Peak position (cm ⁻¹)	Peak width (cm ⁻¹)	Area (%)
Pk 1	<i>sp</i> ³ -CH ₂ (s)-poly	2850	10	0.7	2847	15	4	2848	10	16
Pk 2	<i>sp</i> ³ -CH ₂ (s)-amor	2850	78	13.3	2850	81	13	-	-	-
Pk 3	<i>sp</i> ³ -CH ₃ (s)	2871	44	9.7	2870	34	5	2862	78	26
Pk 4	<i>sp</i> ³ -CH	2915	6	0.5	2917	12	2.5	2917	11	14
Pk 5	<i>sp</i> ³ -CH ₂ (a)	2918	57	30	2913	62	34	2915	40	39
Pk 6	<i>sp</i> ³ -CH ₃ (a)	2961	67	18	2963	60	14.5	2957	11	3
Pk 7	<i>sp</i> ² -CH (o)	3005	124	27.0	3006	123	28	-	-	-
Average carbon coordination no.		3.698			3.76			3.92		

**Figure 5.** Variation of refractive index (*n*) and extinction coefficient (*k*) with wavelength for DLC films deposited at -60 V, -100 V and -150 V bias.

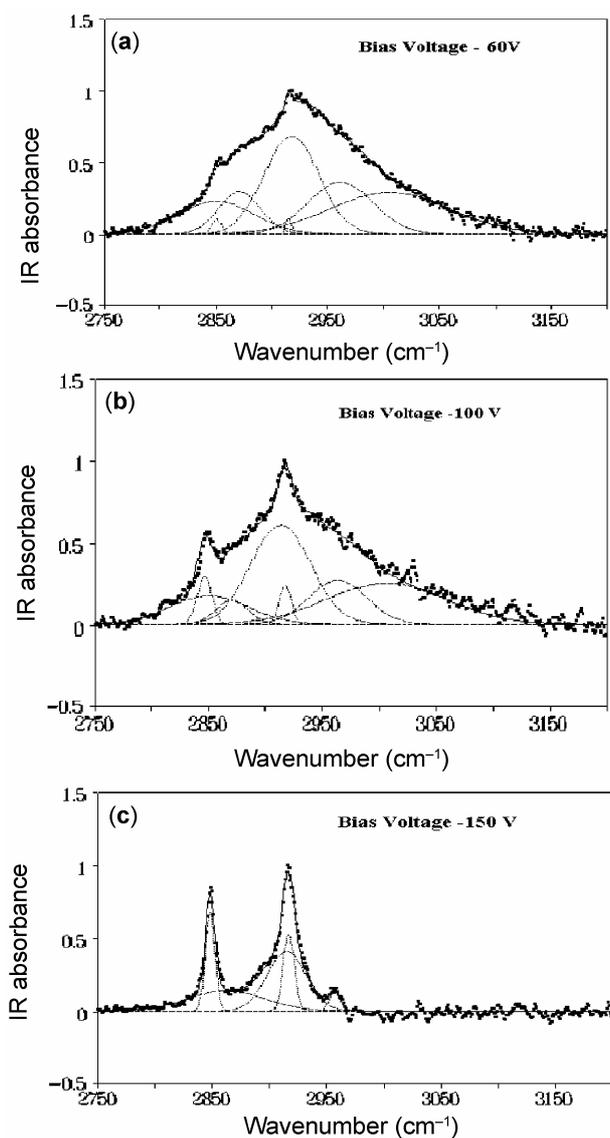
shift in the maximum refractive index peak at different excitation wavelengths in the range 410–500 nm. It is well known that the refractive index of the film is dependent on the density (*sp*³/*sp*² fraction of carbon bonding in the film). The variation in the shift of the maximum of the refractive index peak can, therefore, be associated with the varying ratio of carbon bonding (*sp*³/*sp*² fraction) in the film due to variation in the applied bias voltage.

The infrared spectra of DLC films deposited at different bias voltages (-60 V, -100 V and -150 V) are shown in figures 6a–c. Some sharp IR absorption bands in addition to the broad band that appear in the range 2800–3100 cm⁻¹ are observed. These bands correspond to the

different C–H vibrations corresponding to the *sp*³ and *sp*² clusters present in the films (Dischler *et al* 1983). While the spectra for the film deposited at -60 V and -100 V have been deconvoluted into seven Gaussian peaks, the spectra for film deposited at -150 V have been deconvoluted into five Gaussian peaks. The assignment of these peaks marked pk1 through pk7 is given in table 1. The bands at 2870 cm⁻¹ and 2961 cm⁻¹ are due to symmetric and asymmetric vibrations of *sp*³-CH₃, while bands at 2850 cm⁻¹ and 2920 cm⁻¹ are due to symmetric and asymmetric vibrations of *sp*³-CH₂. In fact, the *sp*³-CH also has its vibrational frequency in its close vicinity. Thus, a combined band due to asymmetric vibrations of *sp*³-CH₂ and *sp*³-CH appear in the range 2915–2925 cm⁻¹. The bands corresponding to the *sp*²-CH (olefinic) appear at 3000 cm⁻¹. At a bias voltage of -60 V there appears two peaks at 2850 cm⁻¹, one sharp peak having a width of ~10 cm⁻¹ due to the symmetric vibrations of *sp*³-CH₂ and second broad peak having a width of ~78 cm⁻¹. Similarly one sharp and other broad band also appear at ~2915 cm⁻¹. Peak at 2870 cm⁻¹ due to *sp*³-CH₃ (sym) which is found for films deposited at -60 V and -100 V bias, is absent for the film deposited at -150 V substrate bias. In addition, the peak at ~3005 cm⁻¹, related to *sp*²-CH, is also absent in case of film deposited at -150 V bias. The intensity of the sharp peaks is quite low for film deposited at -60 V, which develops in case of film deposited at -100 V and become dominant at -150 V bias value. To the best of our understanding, it appears that some polymeric component having sharp bands along with the diamond like carbon is present in the coatings. The polymeric component is increasing with increase in the substrate bias voltage, attaining a maximum at -150 V. In general, sharp IR bands are observed in case of soft-polymeric DLC films. However, the deposited films are not soft. The average carbon coordination number is determined from the fraction of *sp*³ and *sp*² bonded carbon obtained from the C–H absorption spectra of DLC films (Dischler *et al* 1983). The DLC film deposited at -150 V bias is found to have higher carbon coordination number as compared to the films

Table 2. Peak fitting details of Raman spectra.

Substrate bias voltage (V)	D peak		G peak		I_D/I_G (Integrated intensity ratio)
	Position (cm^{-1})	Width (cm^{-1})	Position (cm^{-1})	Width (cm^{-1})	
-60	1326.85	230.98	1535.46	151.89	0.67
-100	1327.13	219.54	1536.1	153.17	0.60
-150	1375.0	210.85	1587.0	104.11	1.52

**Figure 6.** IR absorption spectra of DLC films deposited at (a) -60 V bias, (b) -100 V bias and (c) -150 V bias.

deposited at -60 V and -100 V bias, which indicates that the sp^3 bonded carbon content in this film should be high (in the absence of polymer component) and in that case this film should have higher hardness as compared to the other films. However, hardness measurements on this film show low hardness value as compared to the film deposited

at -100 V bias. It can, therefore, be inferred from the IR spectra that the polymeric component in the deposited films is increasing with the bias voltage, which leads to an increase in carbon coordination number.

Raman spectra of the films deposited at different substrate bias voltages (-60 V, -100 V and -150 V) are shown in figure 7. The as recorded spectra showed a background signal along with the characteristic Raman features of DLC. Fitting these spectra with a third degree polynomial eliminated background signal. A nearly flat baseline obtained for the corrected spectra indicates a proper background subtraction. Later these spectra were fitted to a sum of two Gaussian peaks, one for D and other for G-band, characteristic of sp^2 bonded carbon clusters. The variation of D and G-band positions along with their peak width and I_D/I_G (integrated intensity ratio) is listed in table 2. Also given in this table is the I_D/I_G (integrated intensity ratio) for the D and G-bands. D-band is found at $\sim 1327 \text{ cm}^{-1}$ in case of films deposited at -60 V and -100 V bias voltages. This is blue shifted by considerable amount, $\sim 48 \text{ cm}^{-1}$, in case of film deposited at -150 V bias. The G-band is similarly found to be at $\sim 1536 \text{ cm}^{-1}$ for film deposited at -60 V and -100 V bias levels, while it is again shifted by considerable amount, $\sim 51 \text{ cm}^{-1}$, for film deposited at -150 V bias. Wide variation in the positions of the D and G bands is found in the literature (D band: $1280\text{--}1400 \text{ cm}^{-1}$ and G band: $1510\text{--}1630 \text{ cm}^{-1}$), depending upon the microstructure of the aromatic clusters (Schwan *et al* 1996). Besides the changes in the position of the D and G bands, it is seen that the width of the D and G band in case of film deposited at -150 V bias is also changing. The width of D-band is $\sim 230 \text{ cm}^{-1}$ and 219 cm^{-1} for films deposited at -60 V and -100 V bias, which decreases to $\sim 211 \text{ cm}^{-1}$ for film deposited at -150 V substrate bias. Width of the G-band for film deposited at -150 V substrate bias is lower by $\sim 49 \text{ cm}^{-1}$ as compared to its value for films deposited at -60 V and -100 V bias. The I_D/I_G ratio for deposited films is also found to vary with bias, being 0.67, 0.60 and 1.52 for depositions carried out with substrate bias values of -60 V, -100 V and -150 V, respectively. The ratio I_D/I_G is closely related to size of sp^2 clusters formed during the film growth and high concentration of sp^2 sites gives a large value of I_D/I_G (Ferrari and Robertson 2000). It can be seen that the I_D/I_G initially decreases with increasing bias voltage and then increases. For the film deposited at a bias of -100 V, the

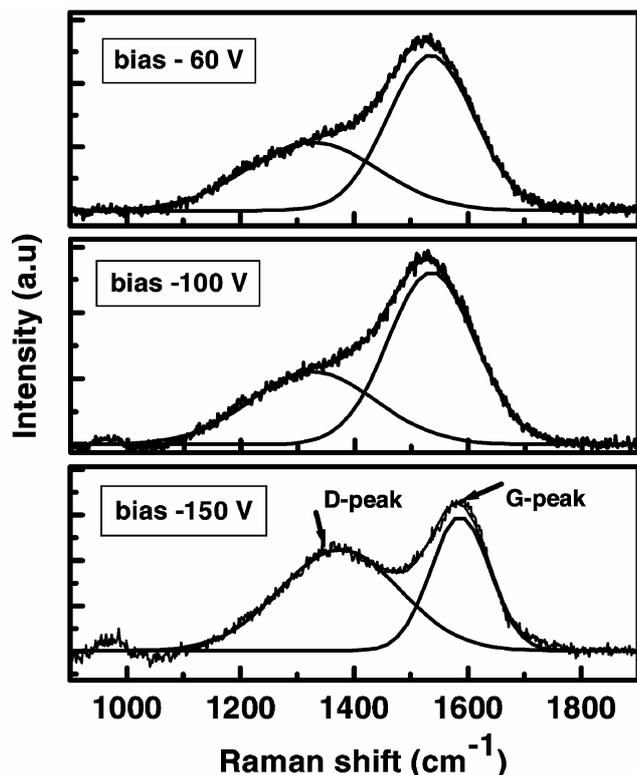


Figure 7. Raman spectra of DLC films (with Gaussian fit of D and G peaks) deposited at -60 V, -100 V and -150 V bias.

width of G peak is high and I_D/I_G is low. This suggests that the size of sp^2 bonded clusters in DLC film deposited at -100 V bias is less as compared to the films deposited at -60 V and -150 V bias. The shift in the positions of D and G peak for film deposited at -100 V bias is towards lower wave number. This coupled with decrease in I_D/I_G is strongly indicative of an increase in the ratio of sp^3 to sp^2 bonded carbon configuration (Ferrari and Robertson 2000). Another measure of disorder is the width of G-peak, which is related to distortions within each sp^2 cluster and is proportional to the stress and sp^3 fraction in the DLC films (Robertson 2003). The maximum in the G-peak width observed in case of film deposited at -100 V bias correlates well with high hardness of the film.

The optical bandgap of these DLC films measured by ellipsometry shows a decrease with the increasing bias (from -60 V to -100 V). The bandgap was 1.16 eV and 0.82 eV, respectively for films deposited at -60 V and -100 V bias. This can be explained on the basis of the fact that optical bandgap is correlated with hydrogen content in the film, with increasing bias voltage the hydrogen content decreases up to certain bias value (-100 V) and so does optical bandgap. It is also possible that increasing substrate bias leads to higher ion bombardment of the deposited film that enhances the damage in the film, thus introducing more gap states that decrease the optical bandgap (Silva 1996). For the film deposited at -150 V

bias, the bandgap is increased to 1.98 eV. This increase in the bandgap may be due to the deposition of more polymeric component in the film.

4. Conclusions

Hard diamond like carbon films have been deposited by microwave ECR plasma CVD using plasma of methane and argon gases. Systematic investigations reported here indicate that the optical, mechanical properties and bonding characteristics of DLC films are strongly dependent on the substrate bias during deposition. The characterization results show that for the DLC film deposited at a substrate bias of -100 V, both hardness and refractive index reach maximum values. The extinction coefficient for all films has a value approaching zero beyond 800 nm indicating that these films are transparent beyond 800 nm. The investigations reported here show the importance of the substrate bias in tuning the properties of the films.

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