Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

3.1 Introduction

DLC films are generally classified as tetrahedral amorphous carbon (ta-C), amorphous carbon (a-C), and their hydrogenated counterparts as ta-C:H, a-C:H. The tetrahedral amorphous carbon (ta-C) films are nothing but the DLC films with higher $sp^3$ bonding (more than 70%). On the other hand, amorphous carbon (a-C) films have less $sp^3$ bonding and their mechanical, electronic, optical properties can be tuned by controlling the $sp^2/sp^3$ ratio. This is one of the important factors behind promoting this material for various technological applications. Additionally, the presence of hydrogen also plays a major role in stabilizing the $sp^3/sp^2$ ratio in amorphous carbon films. Physical and chemical deposition methods allow growth of DLC film with desired $sp^2/sp^3$ bonding state and hydrogen concentration. Various deposition and growth processes were adapted for controlling chemistry and phase fraction of the DLC film. A careful literature survey on DLC films highlighted that ion energy, ion flux density and source gas composition are crucial in controlling the bonding of DLC films. Many studies are focused on the effect of feedstock gas composition in controlling bonding ($sp^2/sp^3$ ratio) as well as hydrogen content on mechanical properties. The Ar and H$_2$ are most commonly used gases for the purpose of dilution in DLC growth. Earlier studies show that dilution with both these gases has significant influence on growth rate, hydrogen content and bonding. It is reported that substrate biasing helps in stabilizing the $sp^3$ bonding and improves the mechanical properties of DLC films. In addition to the structural properties the surface chemistry is also a strong contender for controlling friction behavior of DLC films. DLC films are known for their altering friction behavior with respect to the testing environment. Many studies in recent times proved that the absorbed oxygen plays a crucial role in deciding friction coefficient of DLC films.
Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

This chapter focuses modification of structural and mechanical properties of DLC films via change in gaseous composition and substrate bias parameters (voltage, duty cycle and frequency). Correlation between film density and hydrogen content is established. Extensive analysis on the surface chemistry of DLC films is also carried out. The role of bonding and surface chemistry is described to modify the elastic and tribological properties of DLC films.

3.2. Experimental section

3.2.1 Film growth

The DLC films were deposited in three different set of conditions by varying namely 1) Gas composition, 2) substrate bias voltages and 3) duty cycle and pulsing frequency. Feed stock gas composition variation was studied by changing Ar:CH\textsubscript{4} ratio. The growth was carried out by changing flow rate of one gas at a time. Each time flow rate of either one was varied as 5, 10, 15 and 20 sccm, by keeping flow rate of other gas constantly at 10 sccm. These films are denoted as Ar series (Ar flow rate was variable) and CH\textsubscript{4} series (CH\textsubscript{4} flow rate was variable). In the second set, the substrate bias was varied as -50, -100, -150 and -200 V while keeping other growth parameters constant. These samples were designated as B\textsubscript{1}, B\textsubscript{2}, B\textsubscript{3} and B\textsubscript{4} throughout the thesis. In the third set, the pulse frequency and duty cycle were varied by keeping gas composition and bias voltage constantly. Duty cycles were varied as 50, 70 and 90 % where pulse frequency was set at 10 kHz. On the other hand pulse frequency was varied as 10, 25, 50 and 75 kHz while the duty cycle kept constant at 70%.

3.2.2 Characterization

Topography and film thickness were measured using AFM and FESEM. Chemical structure of these films was analyzed by laser Raman spectroscopy. RBS and ERDA were employed to obtain elemental composition, density and hydrogen content. The tribology studies were
carried out to get the value of friction coefficient and wear rate. AFAM measurements were carried out to analyze the elastic properties of the films.

3.3. Results and discussion

3.3.1 Effect of gas composition

a) Film thickness

![FESEM cross section images of DLC films grown under different gas concentrations](image)

**Figure 3.1** FESEM cross section images of DLC films grown under different gas concentrations, (a-d) Ar series and (e-h) methane series (the numbers in figure indicates the flow rate in sccm)

The cross section FESEM imaging was carried out to obtain the growth rate as a function of source gas composition. Fig. 3.1 (a-h) illustrates the cross section of FESEM images of films corresponds to both Ar and CH₄ series. In the former case where Ar flow rate was varied, upto 15 sccm the film thickness observed to increase and then decrease. Dilution
Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

with Ar gas helps in dissociation of CH$_4$ gas and it increases with the Ar concentration.$^{11,15}$ Dissociation of methane liberates the carbon ions needed for the DLC film growth.

Table 3.1 Film thickness, density and H content of Ar and CH$_4$ series DLC films

<table>
<thead>
<tr>
<th>sample</th>
<th>Film thickness (nm)</th>
<th>Film density (g/cc)</th>
<th>H content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar series</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 sccm</td>
<td>25</td>
<td>1.4</td>
<td>40</td>
</tr>
<tr>
<td>10 sccm</td>
<td>37</td>
<td>1.7</td>
<td>30</td>
</tr>
<tr>
<td>15 sccm</td>
<td>75</td>
<td>2.2</td>
<td>26</td>
</tr>
<tr>
<td>20 sccm</td>
<td>50</td>
<td>1.3</td>
<td>46</td>
</tr>
<tr>
<td>CH$_4$ series</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 sccm</td>
<td>18</td>
<td>1.8</td>
<td>28</td>
</tr>
<tr>
<td>10 sccm</td>
<td>35</td>
<td>1.6</td>
<td>30</td>
</tr>
<tr>
<td>15 sccm</td>
<td>38</td>
<td>1.3</td>
<td>27</td>
</tr>
<tr>
<td>20 sccm</td>
<td>30</td>
<td>1.1</td>
<td>23</td>
</tr>
</tbody>
</table>

The carbon ion concentration goes up with increase in dissociation rate and this leads to higher growth rate. In addition, the energetic Ar$^+$ ions also physically bombard the film surface throughout the growth. This causes re-sputtering of the film due to the heavier mass of Ar$^+$ ions.$^{15,16}$ Increase in Ar concentration reduces concentration of C$^+$ ions due to fixed gas flow.$^{11,16}$ Reduction in C$^+$ ions and physical sputtering by Ar$^+$ reduces film thickness at higher Ar concentration. On the other hand when CH$_4$ flow rate increased up to 10 sccm, the
film thickness observed to increase and decrease thereafter. Upon dissociation, CH$_4$ liberates both C$^+$ and H$^+$ ions. The C$^+$ ions are major constituents for the growth, whereas H$^+$ ions cause chemical etching of DLC films. Increase in CH$_4$ concentration in feed stock gas liberates higher H$^+$ ions upon dissociation. Thus, the reduction in film thickness with increase in CH$_4$ concentration.\textsuperscript{1,15} The values of film thickness for both Ar and CH4 series are given in table 3.1.

b) Raman studies

Laser Raman spectroscopy is used to analyze the chemical structure of the DLC films grown under different gas composition. The broad spectra between 1000 to 1800 cm$^{-1}$ seen in Fig. 3.2 a) (Ar series) and 3.2 b) (CH$_4$ series) are typical signature of DLC films. Two major peaks at around 1300 and 1500 cm$^{-1}$ correspond to D and G peaks of $sp^2$ bonded carbon, respectively. These two peaks are associated to the zone centre vibration modes of A$_{1g}$ and E$_{2g}$, respectively. The Raman spectra belong to Ar 5 sccm in Fig. 3.2 a) does not show any peak and it showed high luminescence back ground which is a usual feature of low density and highly defected DLC films. From Fig. 3.2 a) it is also clear that with increase in Ar content the intensity of the spectra increased upto 15 sccm and reduced thereafter. This is attributed to difference in growth rate as evident from Fig. 3.1. The Fig. 3.2 b) showed an increase in peak intensity upto 10 sccm which gets reduced on further increase in flow. It is also reflected in the growth rate. However, the quality of the DLC films cannot be judged by Raman spectra it requires other information like film density and hydrogen content.
c) Film density and hydrogen content

RBS and ERDA were employed to obtain the film density and hydrogen content. Fig. 3.3 a) and b) depict the film density and hydrogen content of DLC films belonging to Ar and CH$_4$ series, respectively. It is evident from Fig. 3.3a) that the film density increased with Ar concentration up to 15 sccm and reduced thereafter. This is attributed to the Ar$^+$ ion bombardment during the growth.$^{16}$ It also resulted in reduction of hydrogen content by displacing the lighter hydrogen atoms from the DLC network as explained by the sub-implantation growth model.$^1$ However, density is reduced with further increase in Ar content. Because higher Ar ion flux per carbon atom results in higher ion bombardment of film which enhances the $sp^2$ bonding.$^{11}$ Whereas the increase in hydrogen content is because Ar dilution increases dissociation efficiency of CH$_4$ which also leads to higher hydrogen incorporation in the films.$^{15,16}$ On the other hand increase in CH$_4$ content resulted in lower density as well as lesser hydrogen content. As the methane content increases the chances of Ar ion bombardment comes down, thus the reduction in film density with increase in CH$_4$
content. Higher CH$_4$ content gives higher hydrogen species. Higher hydrogen content involves breaking the C-H bonds and formation of H$_2$ which escapes from the film easily. In general, hydrogen saturates the dangling bonds and shields the DLC network from forming $sp^2$ C=C bonding. Removal of hydrogen from DLC networks encourages the $sp^2$ C=C bonding which possess lower film density. This could be the plausible reason for the poor density of films grown under high CH$_4$ content. From the above finding it is evident that the DLC films grown with Ar:CH$_4$ at 15:10 sccm gives dense films and this optimized ratio is maintained for rest of the work in this thesis.

![Figure 3.3](image)

**Figure 3.3** Film density and hydrogen content of DLC films grown under different gas concentration a) Ar and b) CH$_4$ series

### 3.3.2 Effect of duty cycle and frequency of pulsed DC bias

The study was extended to vary the duty cycle and pulse frequency to get DLC films with improved density.

**a) Film density and hydrogen content**

The variation in film density and hydrogen content of DLC films vs duty cycle pulse frequency is shown in Fig. 3.4 (a and b). It is evident that film density initially increased with the duty cycle and reduced thereafter. At lower duty cycles the pulse off time is around
half the deposition time during which the Ar\textsuperscript{+} ion bombardment is absent. This leads to lower ion fluxes.\textsuperscript{18} But, still the growth continues by the neutral hydrocarbon species sticking on the film surface resulting in lower film density. Since the Ar\textsuperscript{+} ion bombardment is crucial to improve DLC film density its absence results in poor density.\textsuperscript{1} As the duty cycle increases, the time for Ar\textsuperscript{+} ion bombardment increases which further improves the film density. Because, pulsing bias helps in increases the ion current and density, it also increases with the duty cycle and frequency.\textsuperscript{19}

Figure 3.4 Variations in film density and hydrogen content of DLC films grown as a function of a) duty cycle and b) pulsing frequency of pulse bias

However, at higher duty cycles the film density is decreased. This is due to charge accumulation at the film surface because of the insulating nature of DLC structure. It in-turn repulses the Ar\textsuperscript{+} ions and avoids the ion bombardment, thus the reduction in film density. Whereas, hydrogen content continuously increased with duty cycle. At higher duty cycles, the growth rate was higher. This was related to increase in ion flux/ density which result incorporation of hydrogen into the film.

However, the film density increased with pulse frequency upto 50 kHz and then reduced thereafter. This is due to increase in flipping rate of polarity with pulsing frequency. This
avoids buildup of surface charge and results in higher Ar\textsuperscript{+} ion bombardment. Moreover, the increase in pulsing frequency also increases the ion current and density at the substrate which improves the film density.\textsuperscript{19, 20} However, at very high pulsing frequency the sluggish movement of heavy Ar\textsuperscript{+} ion reduces ion bombardment thus reduction in film density at higher frequency.\textsuperscript{19} On the other hand, the hydrogen content is found to be continuously reduced. The plausible reasons are the reduction in growth rate and increase in Ar\textsuperscript{+} ion bombardment. Higher Ar\textsuperscript{+} ion bombardment can easily displace the lighter hydrogen atom from the DLC network. However, complete removal of hydrogen content is difficult due to high affinity of the carbon atoms towards hydrogen.

b) Elastic properties

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{elastic_modulus.png}
\caption{Elastic modulus of DLC films grown as a function of a) duty cycle and b) frequency of pulse bias}
\end{figure}

Elastic modulus of DLC films were calculated using contact resonance frequency (CRF) spectra measured in point spectra mode of AFAM. The CRF values are an averaged value of 5 measurements on each film. Fig. 3.5 (a & b) depict the variation in elastic modulus of DLC films grown as a function of duty cycle and pulse frequency. Elastic modulus increased
with increase in duty cycle. On the other hand elastic modulus increased with pulse frequency up to 50 kHz and then reduced. It is attributed to the variation in film density.

c) Tribological properties

![Figure 3.6](image)

**Figure 3.6** Friction coefficient of DLC films grown as a function of a) duty cycle and b) frequency of pulsing bias

The effect of duty cycle and pulse frequency on friction coefficient is depicted in Fig. 3.6 a) and b), respectively. The friction coefficient reduced with increase in duty cycle. This is attributed to the higher film density at higher duty cycle. On the other hand with increase in frequency the friction coefficient reduced up to 50 kHz and increased up on further increase in pulse frequency. The friction coefficient showed a direct correlation with the film density and it followed similar trend as it is observed in case of elastic properties. A clear interdependence of structural, elastic and tribological properties is observed.

3.3.3 Effect of substrate biasing

It is well established that substrate biasing is a crucial parameter to grow $sp^3$ dominant DLC films. The widely accepted sub implantation growth model of DLC films proved that ion energy around 100 eV is optimum to obtain maximum $sp^3$ content. Various studies already existed on the effect of substrate biasing on the properties of DLC films. However, effect of
bias voltage on elastic properties and tribological properties of DLC films is so far not reported. In this chapter, microscopic evidence of sub-implantation growth model is described. It is linked with structural properties of DLC film as a function of substrate bias to explain the friction behavior.

a) Film thickness

![Figure 3.7: AFM topography of DLC films grown at substrate bias of (a) -50, (b) -100, (c) -150 and (d) -200 V. FESEM cross sectional micrograph are given in inset.](image)

Fig. 3.7 shows topography of films grown at different substrate bias. The inset shows corresponding cross section FESEM images. It is evident from the topography that the films are uniform. The RMS roughness was measured over an area of \(5 \times 5 \, \mu\text{m}^2\) for B1, B2, B3 and B4 films and the values are found to be 0.5, 0.14, 0.25 and 4.5 nm, respectively. The film B2 is found to have the lowest roughness of 0.14 nm. Such a low roughness value is explained using the sub-implantation growth model.\(^1\) Film B4 deposited at higher biasing of -200V
showed coexistence of two different phases over the film surface (Fig. 3.7 d)). Such second phase evolution might be attributed to the high energy ion induced local heating caused by high substrate bias.\textsuperscript{21} The cross sectional FESEM images shown in Fig 3.7 of these films reveal significant reduction in film thickness with increase in substrate bias. Thickness of the films is found to decrease from 850 to 240 nm when the bias was changed from -50 to -200V, respectively. The reduction in the film thickness is due to the re-sputtering of the film with increased biasing.\textsuperscript{22} Further increase in substrate biasing raises the local temperature of the film and thereby enhances the etching of film surface through hydrogen ions.\textsuperscript{21,22}

b) Raman studies

![Raman spectra of DLC films grown as a function of substrate bias](image)

**Figure 3.8** Raman spectra of DLC films grown as a function of substrate bias

The chemical nature of the DLC film was analyzed by Raman spectroscopy. These films possess a broad Raman spectra spread over the range 1000 to 2000 cm\(^{-1}\) as shown in Fig. 3.8. It was further deconvoluted and fitted with three peaks using combination of Gaussian and Lorentzian line profiles. The spectra comprise of major peaks located at 1350 and 1560 cm\(^{-1}\) corresponding to D and G bands, respectively.\textsuperscript{23} The additional peak around 1200 cm\(^{-1}\) corresponds to trans-poly acetylene (TPA).\textsuperscript{24} With increase in biasing, blue shift in G peak
position, noticeable increase in D band intensity and increase in $I_D/I_G$ ratio were observed. Moreover, the reduction in FWHM of G band is observed with increasing bias. Such observations strongly indicate ordering of $sp^2$ clusters in ring/chain and the film undergoes graphitization.\cite{1, 23} A noticeable increase in D band of hydrogenated (h) -DLC films is associated with oxidation of the surface.\cite{8} In addition the reduction in FWHM of G peak confirms the formation of large ring like $sp^2$ structures. Such reduction is aided by the oxidation in h-DLC films.\cite{8} Thus, the second phase seen in the topography of the B$_4$ film in Fig. 3.7 d) is constituted by large aromatic rings of $sp^2$ clusters.

These films are further characterized by RBS and ERDA analysis to obtain film density and hydrogen content, respectively. These values are given in table-3.2. The film density is found to increase from 0.7 to 2.2 g/cc with the bias voltage. In contrast, hydrogen content in the film reduced from 37 to 16 %. This shows that the film B$_1$ is highly hydrogenated (C-H-$sp^3$) and polymer like which results in poor density. The density estimation from RBS and ERDA provide a direct support to Raman observations of increase in $sp^2$ concentration in DLC films. The increase in $sp^2$ content and variation of density in these DLC films as a function of substrate bias can be explained by invoking an established growth mechanism called sub-implantation model.\cite{25} According to the sub-implantation model, the ion energy of C radicals decides the type of C-C bonding in the DLC films. The ion energy mainly depends on the applied substrate bias during growth. At low substrate biases, the C ion energy is lower than the penetration threshold energy (Ep) (~30 eV) and hence, C ions just stay on surface and relax to minimum energy state by forming $sp^2$ bond with glassy structure. However, H is also incorporated in the growing film as the energy required to form C-H bonding is minimum.\cite{1, 26}
Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

Table-3.2: Properties of DLC films grown as a function of substrate biasing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface roughness (nm)</th>
<th>Film thickness (nm)</th>
<th>Film density (g/cc)</th>
<th>H₂ content (%)</th>
<th>Id/IG ratio</th>
<th>G peak position (cm⁻¹)</th>
<th>G peak width (cm⁻¹)</th>
<th>Wear rate (mm³/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>0.5</td>
<td>850</td>
<td>0.7</td>
<td>37</td>
<td>0.357</td>
<td>1530.5</td>
<td>175.6</td>
<td>5.0×10⁻⁶</td>
</tr>
<tr>
<td>B₂</td>
<td>0.14</td>
<td>475</td>
<td>2.2</td>
<td>22</td>
<td>0.404</td>
<td>1541.6</td>
<td>158.8</td>
<td>1.6×10⁻⁷</td>
</tr>
<tr>
<td>B₃</td>
<td>0.25</td>
<td>290</td>
<td>1.8</td>
<td>19</td>
<td>0.55</td>
<td>1555.2</td>
<td>146.7</td>
<td>1.0×10⁻⁶</td>
</tr>
<tr>
<td>B₄</td>
<td>4.5</td>
<td>240</td>
<td>1.5</td>
<td>16</td>
<td>0.764</td>
<td>1579.4</td>
<td>113.3</td>
<td>2.2×10⁻⁶</td>
</tr>
</tbody>
</table>

The H incorporation in the glassy carbon favors C-H sp³ bonding but the film density remains very low.¹ At -50V bias, the C⁺ ions gain enough energy to penetrate into the subsurface and occupies the interstitial sites. During sub-implantation growth process the locally altered bonding around the penetrated atoms reforms itself to become bulk bonding of the film with appropriate hybridization i.e. the atomic hybridization will adjust easily to change according to the local density under high energy ion bombardments.²⁵ Hence, the DLC film becomes sp² dominant if the local density is low and sp³ dominant if the local density is high.²⁵ At -100V bias, a large amount of C⁺ ions enter sub-surface of the growing film since the C⁺ ions have sufficient energy. Since larger C⁺ ions occupy interstitial sites the C-C sp³ bonding is energetically favored and this in-turn increases the film density. In the meantime, H is also removed from the growing film since the C-H bonds get easily broken at high energy ion bombardments. At substrate bias greater than -100V, C ions gain much higher energy and it penetrates deeper into the film. The excess energy of C⁺ ions get dissipated in different processes viz. a) penetration into the subsurface, b) atomic displacements along the penetration track and c) release of phonons which results in thermal...
spikes at sub-pico second time scale.¹ This thermal spike allows the atoms to diffuse back to the surface and relax the density locally to stabilize with \( sp^2 \) bonding.¹, ²⁸, ²⁹ The size of the \( sp^2 \) clusters further increase with bias. Thus, the film density is high at substrate bias of -100 V and it reduces with increase in bias. In addition, the increase in ion energy also causes preferential sputtering of the lighter hydrogen atoms from the DLC films.¹ Thus, reduction in hydrogen content also occurs with increase in substrate bias.¹, ²⁶

c) AFAM analysis

Fig. 3.9 a)-e) illustrates the CRF mapping of DLC films corresponding to (b) B₁, (c) B₂, (d) B₃, and (e) B₄, respectively. The CRF mapping of the B₁ and B₂ films are very smooth with a variation in frequencies from 675 to 680 and 762 to 765 kHz, respectively. This indicates that these films possess homogenous elastic properties. Similarly, the sample B₃ also exhibits a smooth CRF mapping but several isolated nanoclusters of 50 nm diameter with low CRF values are observed over the homogeneous background Fig. 3.9 d). Thus, it is inferred from the CRF mapping that the nanoclustered regions have lower elastic modulus than the matrix. Fig. 3.9 e) shows the AFAM mapping of the sample B₄ which varies from 705 to 750 kHz. As similar to the topography, the CRF mapping is also highly inhomogeneous with mixture of low and high frequency regimes indicating presence of soft and hard modulus phases. Based on the CRF mapping, statistical analysis was carried out to extract the CRF for a particular sample. In order to avoid tip induced error in elastic modulus due to wear, the tip was always scanned over reference silicon before and after AFAM measurements on actual DLC films. Fig. 3.10 shows the variation in elastic modulus (E) of the DLC films as a function bias. The elastic modulus of sample B₁ is found to be 110 GPa which is much lower than the reference Si.
Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

**Figure 3.9** Contact resonance frequency mapping of DLC films grown at different substrate bias of (a) Si (100), b) -50, (c) -100, (d) -150 and (e) -200V, respectively

**Figure 3.10** The calculated elastic modulii of the DLC films grown at different bias

As the bias increases to -100V, E of the sample B2 enhanced to 185 GPa which is higher than the reference Si. However, further increase in substrate bias to -150 and -200V, lead to decrease in E to 145 and 130 GPa, respectively. The variation in elastic modulus with
biasing exhibited the similar trend as observed by the film density. The reduction in elastic modulus is directly correlated to the enhancement of $sp^2$ bonding and lower density observed by Raman spectroscopic analysis and film density, respectively. This study provides a direct microscopic evidence for evolution of soft second phases in DLC matrix under high substrate bias.

d) XPS Analysis

Fig. 3.11 shows the XPS survey and corresponding C1s spectra of DLC films deposited as a function of substrate biasing. The C1s peaks of these films were deconvoluted into five peaks centered at 284.6, 285.5, 286.7, 287.9 and 289.1 eV corresponding to $sp^2$ C=C, $sp^3$ C-C, C=O, C-O and O=C-OH, respectively. Film B1 exhibited high surface charging and to counter the charge, the neutralizer (low energy electron gun/flood gun) was used, which resulted in an additional peak at 283.8 eV shown in Fig. 3.11. The intensity of the chemical shift around 284.6 eV is high for all the films. This implies that the film surfaces are dominated by $sp^2$ bonding. However, with increase in biasing, the intensity of $sp^2$ peak decreases and intensity of $sp^3$ peak increases. It is known that the substrate biasing helps in stabilizing $sp^3$ bonding in DLC film. XPS analysis is surface sensitive; hence the results of surface chemical shift cannot be compared to the bulk property. On the other hand, intensity of the deconvoluted peak corresponding to C=O, C-O and O=C-OH decreased with bias in B1 to B3 film. However, it increased for the film B4, indicating chemical reconstruction of the surface.
Figure 3.11 XPS survey spectra and deconvoluted high resolution C1s spectra of DLC films grown at different substrate bias (peak with symbol ‘*’ denotes charging in B₁ sample)
Detailed analysis of C/O ratio of the film was obtained from the fitting of the C1s and O1s peaks. From the XPS survey spectra shown in Fig. 3.11, it is clear that C/O ratio reduces with increase in biasing. It is an indication of the increase in oxygen adsorption. Potential energy of $sp^3$ terminated surface is high when it consist dangling bonds. This possesses high polarity as compared to $sp^2$ terminated surface. This is well corroborated with the increase in intensity of C=O, C-O and O=C-OH peaks as shown in C1s spectra of the film (Fig. 3.11). In addition to this, the film B4 possesses a second phase which results in formation of fresh dangling bonds at the edges. This in turn aids further oxygen adsorption. On the other hand, the film B1 also possesses significant amount of adsorbed oxygen. This can be attributed to the presence of defects resulting from the lower film density. A defect laden film is more susceptible to oxygen/moisture adsorption.

![Friction coefficient of DLC films grown at different substrate bias](image)

**Figure 3.12** Friction coefficient of DLC films grown at different substrate bias

The variation of friction coefficient as a function of sliding distance for the film grown at various biasing voltages is shown in Fig. 3.12. It is observed that the friction coefficient abruptly increases within 100 meters of sliding distance for the film deposited at higher bias.
(B₃ and B₄). This is possibly caused due to reduction in film thickness. However, the friction coefficient also relies on $sp^2/sp^3$ bonding fraction and film density. Substrate bias introduces residual stresses into the films which would have caused the early failure in B₃ and B₄. Thus, it is difficult to figure out the exact parameter which causes abrupt change in friction coefficient. The friction coefficient of the film B₄ is found to be high from beginning of the sliding. Adsorbed layer of oxygen impurities is likely to be a contributing factor in further raising the friction coefficient. The high friction behavior prolonged for longer sliding distances, if the quantity of adsorbed oxygen is high. In case of less adsorption, the oxide layer abruptly fails after a few sliding cycles, bringing the ball directly into contact with the film and further sliding continues between them. In ambient conditions, fresh oxygen gets trapped between the deformed surfaces and forms chemically instable C=O bond. It is a self-sustained reaction and continues to exist throughout the sliding. In this case, the friction coefficient initially falls and saturates at a different value. On the other hand, the film B₁ appears to be stable. But, the friction coefficient of the film is higher than films B₂ and B₃. The higher friction coefficient can be related to reduced $sp^2/sp^3$ ratio in the B₁ film. Furthermore, the role of adsorbed oxygen influencing friction and wear behavior cannot be ignored. Oxygen in the film produces structural and chemical defects which deteriorate surface mechanical properties resulting in high friction and wear. Both the films B₁ and B₄ contains larger concentration of adsorbed oxygen on the surface and exhibit higher friction coefficient. Therefore, this aspect confirms the role of adsorbed oxygen in influencing friction coefficient. Furthermore, surface roughness could be one of the most useful reasons to explain the friction behavior. Roughness is highest for B₄ film (4.5 nm) and it leads to high value of friction coefficient from the beginning of sliding cycles.
However, B₂ film is smoothest (rms value 0.14) and showed lowest value of friction coefficient up to the failure point. Early failure of B₂, B₃ and B₄ films in comparison to B₁ is certainly not related to gradual wear, as it is evident from the film density. B₁ is less dense compared to other three films (table -3.2). Residual stresses of film and interface may increase with biasing.³³ Basically, quantification of residual stress in interface is described by film stress. This is evident from the systematic increase in density of film with biasing. Interfacial stress relaxes when tribo stress overcomes the residual stress in interfaces and this may lead to abrupt film failure. For thinner film, the stress in the interface could be higher because the distance between the contact and interface is small. This might be possible reason for early failure of thinner film compare to thicker one. Therefore, both residual stress of the film/interface and film thickness t together caused the film failure.

![FESEM images of wear tracks on DLC films grown at different substrate bias](image)

**Figure 3.13** FESEM images of wear tracks on DLC films grown at different substrate bias

The FESEM images of the wear tracks showed that the film B₁ is completely deformed (Fig. 3.13). As mentioned earlier, the film B₁ is more of polymer like and has low film density.
Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films

This film is poorly adhering to substrate which causes easy deformation and formation of stable and sustainable deformed layer. This is the reason that this film not showed abrupt failure (Fig. 3.12). Except B₂, all other films wear out and depict larger wear track width. The wear rate measurements show that the film B₂ is highly wear resistant and it is attributed to the less adsorbed oxygen and smoother surface. Considering all the three parameters, such as friction coefficient, wear life and wear resistance the film B₂ turns out to be superior compared to others. Therefore, to further improve the friction stability, the film B₂ was selected for nitrogen doping.

3.4 Conclusions

The Ar dilution of feedstock gas resulted in high growth rate and lower hydrogen content in DLC films. It also helped in increasing the film density. On the other hand increase in CH₄ concentration caused reduction in the film density as well as hydrogen content. Both high duty cycle and pulse frequency increased the film density. It is attributed to the Ar⁺ ion bombardment. Substrate bias voltage showed a significant influence on the microstructure and chemical bonding of the DLC films. Higher bias enhanced the \( sp^2 \) C=C bonding and leads to clustering of the graphitic phase. Elastic modulus mapping confirmed the evolution of graphitic second phase. The elastic modulus of the second phase is lower than the matrix. An increase in friction coefficient with increase in biasing was observed. It is correlated with the absorbed oxygen layer on the surface of DLC films. This study brought out the significance of surface chemistry and chemical bonding in deciding the friction coefficient and wear rate.
3.5 References

Chapter 3: Effect of gas composition and pulse DC biasing on structural and mechanical properties of DLC films


