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Synthesis, structure and properties of nanolayered DLC/DLC films

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SYNTHESIS, STRUCTURE AND PROPERTIES OF NANOLAYERED DLC/DLC FILMS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Engineering Science

in

The Interdepartmental Program in Engineering Science

by

Pankaj Gupta
B.E., Panjab University, 2000
May 2003
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ABSTRACT

Diamondlike carbon (DLC) films have been explored extensively in the past due to their highly attractive properties. However, the high level of internal stress developed during growth prevents deposition of thick films. Synthesis of DLC/DLC multilayers (DDM) presents a venue to overcome this drawback. In the present study, DLC films and DDM were deposited on Si substrate using dc plasma of CH$_4$ and Ar gas mixture. FTIR was used to analyze the structure of the DLC films. Mechanical properties of the films were characterized by microhardness testing and nanoindentation. The tribological properties were studied by conducting pin-on-disc experiments in the laboratory environment (relative humidity 40-60%). Optical profilometry was used to analyze Intrinsic stress in the films and the wear profiles. A preliminary study was conducted utilizing different processing parameter (bias voltage, chamber pressure and ratio of Ar to CH$_4$) to select the constituents of the DDM. Subsequently, DDM were synthesized consisting of alternating nanolayers of “soft” (high sp$^2$ content) and “hard” (low sp$^2$ content) DLC by varying: (i) individual layer thickness while keeping the thickness ratio of soft/ hard DLC film, $\lambda = 1$ and; (ii) $\lambda$. The multilayered films found to exhibit low intrinsic stress ranging mostly below the average values of the two individual components. Nanoindentation behavior of DDM was comparable to the parent films and no significant variation was observed in different DDM films. DDM films with $\lambda=1$ exhibited better tribological properties compared to the films with $\lambda$ other than unity. The 50 nm/50 nm DDM film exhibited the best tribological properties. It combined the low friction coefficient of the soft DLC component and low wear rate of the harder DLC component. The stress was found to be the average of the parent DLC films; hence it
possesses the promise to be deposited as a thick coating, while maintaining desirable mechanical and tribological properties.
1. INTRODUCTION

Carbon has proven to be one of the most fascinating elements. On one hand it occurs in the form of diamond having sp³ hybridization providing properties like exceptionally high hardness and thermal conductivity, chemical inertness, optical transparency, wide band gap, low wear rate but high coefficient of friction. The combination of these attractive properties makes diamond useful in many applications such as cutting and grinding tools, heat exchangers, infrared window and high frequency high power electronic devices. On the other hand, graphite, which has sp² hybridization, is soft, has good electrical conductivity and low coefficient of friction but high wear rate, is a well-known solid lubricant. Carbon also occurs in amorphous form like soot, glassy carbon, carbon fibers and evaporated carbon. Diamondlike carbon (DLC), a form of amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H), consists a of network of sp³ and sp² co-ordinations. DLC can be obtained as a thin film at low deposition temperatures on various substrates and has some unique properties. The attractive properties include high hardness, chemical inertness, high thermal conductivity, good electrical and optical properties, biocompatibility and excellent tribological behavior. DLC has attracted a considerable interest as coating material and has been used as antireflective coating, wear resistant coating, corrosion resistant coating for biomedical applications, etc.

DLC films have shown a considerable potential in wear resistant coatings due to their low coefficient of friction and wear resistance. The tribological properties of DLC films have been studied previously [1-6] and Liu and Meletis [7] proposed a “wear-induced graphitization mechanism”. Direct transmission electron microscopy (TEM) evidence of the
wear-induced DLC graphitization has been obtained providing experimental verification of the proposed mechanism. A major drawback of DLC films is that they have high internal compressive stresses. This reduces their adhesion to the substrate and prevents the growth of thick films [8], which are sometimes required for practical wear-layer applications. Previous efforts have attempted to reduce the stress in DLC especially in hydrogen free, high sp<sup>3</sup> bonded form of DLC, also known as tetrahedral amorphous carbon (ta-C), by thermal annealing [9]. The complete stress relief has shown to occur at 600-700 °C with minimal structural modifications [9,10]. The problem with thermal annealing of a-C:H films is that they start graphitizing after 350 °C-400 °C and loose their diamond like properties [11]. The thermal stability of a-C:H has been improved by doping the films with metallic elements (silicon, titanium, tungsten, etc.) [12, 13], or synthesizing multilayers [14].

The magnitude of internal stresses depends upon the ratio of sp<sup>3</sup>/sp<sup>2</sup> in the film, which can be varied by varying deposition parameters. High sp<sup>3</sup> content films have high residual stresses and at the same time, are hard whereas high sp<sup>2</sup> content films have lower residual stresses and are relatively soft. Gioti et al. [15] have reported the reduction of intrinsic stresses in as-deposited a-C films. They have deposited DLC-DLC multilayers of a-C by magnetron sputtering and observed that internal stresses are a function of the ratio of sp<sup>3</sup>/sp<sup>2</sup> content in the film, which can be varied by varying deposition parameters. Further, the multilayers were deposited up to a thickness of 274 nm and had better mechanical properties than the parent a-C films with hardness and elastic modulus of 32 GPa and 260 GPa, respectively [16]. Knoblauch and Hauert [17] have deposited multilayers of a-C:H films by rf plasma deposition and these films exhibited better tribological properties. The wear rate decreased by a factor of ten down to 4x10<sup>-9</sup>mm<sup>3</sup>/N-m compared to the parent DLC
films. There has not been much work reported in the field of DLC multilayers and still there is lack of basic understanding of the reported behavior of DLC multilayers. This is an area of high potential since these multilayers can significantly affect the mechanical and tribological behavior.

In this study, DLC/DLC multilayered films were synthesized by plasma enhanced chemical vapor deposition (PECVD) process using methane as precursor material in presence of Ar. The multilayer films consist of alternate nano-layers of high sp$^3$ and high sp$^2$ DLC films. The thickness of the sp$^3$-rich and sp$^2$-rich nano-layers was varied and the subject of the present work was to study the processing-structure-property relationship of the DLC multilayer in an effort to improve properties and reduce internal stresses allowing deposition of thicker films.
2. OBJECTIVES

The present work is concerned with DLC films and DLC multilayers produced by PECVD.

The objectives of the present research are:

(i) to study the effect of processing parameters on the characteristics and properties of DLC films;

(ii) to study the tribological behavior of multilayered DLC films; and

(iii) to enhance our scientific understanding of the structure-property relationship of multilayered films.
3. LITERATURE REVIEW

3.1 General Review

It has been estimated that approximately one third to one half of world energy resources in present use appears ultimately as friction in one form or other. A significant amount of funds is being invested annually to minimize the loss due to friction. A significant research has been performed on issues of selection of improved bulk materials, utilization of the lubrication techniques and changes in design. It was recognized that in many situations failure originated at surface either by wear, fatigue or corrosion and thus, the area of surface modification by coatings attracted a lot of attention by tribologists and material scientists and is being studied extensively. Bunshah defines hard coatings as “materials with high hardness in the mechanical sense with good tribological properties” [18]. Further, hard materials can be classified as tribologically hard, optically hard, radiation hard and electronically hard.

A review on hard coatings was conducted by Sundgren and Hentzell [19]. Table 3.1 presents the mechanical and thermal properties of some typical hard coatings. It can be seen that all the materials exhibit high hardness and high melting temperatures. Along with these properties, there should be high adhesion between the coating and the substrate, which can otherwise lead to delamination of the coating. The stresses developed in the coating either due to lattice mismatch (intrinsic stresses) or difference in the thermal coefficient of the coating and the substrate (thermal stresses) can also lead to delamination of the coating if adhesion is not high enough. Thus, it is important to gain a fundamental understanding of coating and substrate interactions. All these basic factors should be kept in mind while choosing a coating. At present, there is a tremendous number of hard and protective
coatings, which include metal nitride coatings (TiN, CrN etc.), carbide coatings (SiC, WC, etc.), oxide coatings (Al₂O₃, etc.) and borides.

Table 3.1. Mechanical and thermal properties of some typical hard coatings [19].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (GPa)</th>
<th>Poisson’s ratio</th>
<th>Thermal Expansion Coefficient (10⁻⁶K⁻¹)</th>
<th>Hardness (kg mm⁻²)</th>
<th>Melting or decomposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coatings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>450</td>
<td>0.19</td>
<td>7.4</td>
<td>2900</td>
<td>3067</td>
</tr>
<tr>
<td>HfC</td>
<td>464</td>
<td>0.18</td>
<td>6.6</td>
<td>2700</td>
<td>3928</td>
</tr>
<tr>
<td>TaC</td>
<td>285</td>
<td>0.24</td>
<td>6.3</td>
<td>2500</td>
<td>3983</td>
</tr>
<tr>
<td>WC</td>
<td>695</td>
<td>0.19</td>
<td>4.3</td>
<td>2100</td>
<td>2776</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>370</td>
<td>….</td>
<td>10.3</td>
<td>1300</td>
<td>1810</td>
</tr>
<tr>
<td>TiN</td>
<td>….</td>
<td>….</td>
<td>9.35</td>
<td>2000</td>
<td>2949</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>400</td>
<td>0.23</td>
<td>9.0</td>
<td>2000</td>
<td>2300</td>
</tr>
<tr>
<td>TiB₂</td>
<td>480</td>
<td>….</td>
<td>8.0</td>
<td>3370</td>
<td>2980</td>
</tr>
<tr>
<td>Substrates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94WC-6Co</td>
<td>640</td>
<td>0.26</td>
<td>5.4</td>
<td>1500</td>
<td>….</td>
</tr>
<tr>
<td>High speed steels</td>
<td>250</td>
<td>0.30</td>
<td>12-15</td>
<td>800-1000</td>
<td>….</td>
</tr>
<tr>
<td>Al</td>
<td>70</td>
<td>0.35</td>
<td>23</td>
<td>30</td>
<td>658</td>
</tr>
</tbody>
</table>

Diamond, the hardest material known, had always been a material of interest to tribologists because of its unusual properties. Researchers tried to synthesize diamond at high temperature and pressure but the usefulness of diamond was enhanced when it was discovered that diamond could be grown as thin films at low pressure. Chemical vapor deposition was used to synthesize these films from a mixture of hydrogen and hydrocarbon gas. These films exhibit the good properties of diamond, namely, extremely high hardness and thermal conductivity, high electrical resistivity, chemical inertness, wide optical band gap along with good tribological properties. Diamond films have been applied in ultra hard tools, semiconductor heat sinks, optical applications, computer hard disks, and etc. But,
diamond films have certain limitations [20]: (i) they require high temperature (~900°C) for their deposition, thereby limiting the choice of substrate; (ii) they are polycrystalline in nature and usually have rough faced surface; (iii) it is difficult to deposit them uniformly on a large surface; and (iv) it is difficult to grow large crystallite diamond at reasonable growth rates. So, there is a need for another type of film, which retains most of the properties of diamond and can overcome the aforementioned limitations to a large extent. These films are amorphous in nature and are called “Diamondlike carbon films”.

3.2 Diamondlike Carbon Films

DLC is metastable, amorphous carbon material, which may contain micro-crystalline phase of diamond. These films have aroused a considerable interest as coating material due to their attractive properties and have been applied to many fields. A brief summary of properties and applications of DLC is given in Table 3.2 [21]. DLC films in general, are very smooth and can be deposited at low temperatures.

Various methods used in deposition have led to a wide range of DLC films and as such there is no nomenclature to describe them. But, in general, various forms of DLC can be divided into two broad categories:

(i) DLC containing carbon only is called amorphous carbon or amorphous diamond (i-C, ta-C)

(ii) DLC containing a mixture of hydrogen and carbon is called hydrogenated amorphous carbon (a-C:H).

Certain materials can be added to DLC films to improve their properties such as Si, N, metal atoms, F and they change the notation to Si-C:H, a-C:H-N, Me-C:H and a-C:H-F, respectively.
Table 3.2. Summary of properties and applications of diamondlike carbon films. Text in parenthesis indicates potential applications [21].

<table>
<thead>
<tr>
<th>Property</th>
<th>Type of use</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency in Visible and IR; optical band = 1.0-4.0eV</td>
<td>Optical Coatings</td>
<td>Antireflective coatings and wear resistant coatings for IR optics</td>
</tr>
<tr>
<td>Chemical inertness to acids, alkalis and organic solvents</td>
<td>Chemically passivating coatings</td>
<td>Corrosion protection of magnetic media, biomedical</td>
</tr>
<tr>
<td>High Hardness; H=5-80GPa; low friction coefficient. &lt;0.01-0.7</td>
<td>Tribological, wear resistant coatings</td>
<td>Magnetic hard drives, magnetic tapes, razor blades (bearing, gears)</td>
</tr>
<tr>
<td>Nanosmooth</td>
<td>Very thin coatings &lt; 5nm</td>
<td>Magnetic media</td>
</tr>
<tr>
<td>Wide range of electrical resistivities = 10^2-10^{16}Ω/cm</td>
<td>Insulating coatings</td>
<td>Insulating films</td>
</tr>
<tr>
<td>Low dielectric constants &lt;4</td>
<td>Low-k dielectrics</td>
<td>(Interconnect dielectrics)</td>
</tr>
<tr>
<td></td>
<td>Field emission</td>
<td>(Field emission flat panel displays)</td>
</tr>
</tbody>
</table>

Various methods of preparation have also given different carbon and hydrocarbon films with broad spectrum of properties. They can be considered to have a structure intermediate to those of diamond, graphite and hydrocarbon polymers containing various proportions of sp³ carbon, sp² carbon and hydrogen. Angus and Hayman [22] proposed a valuable means of classifying the various carbon forms and hydrocarbons in terms of their atomic density and hydrogen content as shown in Figure 3.1. It can be seen that the DLC films, a-C:H, have much higher atomic density than conventional polymers. A comparison of basic properties of various amorphous and crystalline forms of carbon to DLC can be seen in Table 3.3 [23].
Figure 3.1 Atom number density vs. atom fraction of hydrogen expressed in gram atom/cm³. Symbols used are, AC- oligomers of acetylene, AD- adamantanes, AL - n-alkanes, AM- amorphous carbon, AR – polynuclear aromatics, DI - diamond and GR – graphite [22].

Table 3.3. Properties of various forms of carbon [23].

<table>
<thead>
<tr>
<th></th>
<th>Density (gm cm⁻³)</th>
<th>Hardness (GPa)</th>
<th>sp³ (%)</th>
<th>H (at%)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>3.515</td>
<td>100</td>
<td>100</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>Graphite</td>
<td>2.267</td>
<td>0</td>
<td></td>
<td>0</td>
<td>-0.04</td>
</tr>
<tr>
<td>Glassy C</td>
<td>1.3-1.55</td>
<td>2-3</td>
<td>~0</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>a-C (evaporated)</td>
<td>1.9-2.0</td>
<td>2-5</td>
<td>1</td>
<td></td>
<td>0.4-0.7</td>
</tr>
<tr>
<td>a-C (MSIB)</td>
<td>3.0</td>
<td>30-130</td>
<td>90±5</td>
<td>&lt;9</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>a-C:H (hard)</td>
<td>1.6-2.2</td>
<td>10-20</td>
<td>30-60</td>
<td>10-40</td>
<td>0.8-1.7</td>
</tr>
<tr>
<td>a-C:H (soft)</td>
<td>0.9-1.6</td>
<td>&lt;5</td>
<td>50-80</td>
<td>40-65</td>
<td>1.6-4</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.92</td>
<td>0.01</td>
<td>100</td>
<td>67</td>
<td>6</td>
</tr>
</tbody>
</table>
3.3 Structure of DLC

It is desirable to have an understanding of detailed bonding and structure of DLC to be able to design its properties. DLC films mainly consist of combination of four-fold coordinated sp\(^3\) sites, as in diamond, and the three-fold coordinated sp\(^2\) sites, as in graphite with some of the bonds terminated by hydrogen. This hybridization is present in short-range order in the films, thereby exhibiting the amorphous nature. However, microcrystalline phases of diamond have been seen in some DLC films especially with lower hydrogen. If the sp\(^3\) bonding is dominant, the films are diamondlike whereas, with a predominant sp\(^3\) bonding, films are graphite-like. The deposition method, hydrogen content and amount of doping determine the amount of sp\(^3\) and sp\(^2\) content in the film. Composition of DLC can be best shown by ternary phase diagram, Figure 3.2, given by Robertson [24] in terms of sp\(^3\) and sp\(^2\) concentration along with hydrogen.

The detailed structure of bonding of DLC is not fully established to date. Various models have been proposed; but none of them is fully accepted. McKenzie et al. [25] proposed a model describing DLC as nano-crystalline two-phase structure consisting of polycyclic aromatic hydrocarbon regions interconnected by tetrahedral carbon. Robertson [26] also modeled the structure of DLC as a network of covalently bonded carbon atoms in different hybridization, with a substantial degree of medium range order on 1 nm scale. Angus and Jansen [27] based their model on theories of random covalent network (RCN) by Phillips [28] and Thorpe [29]. It assumes that RCN is completely constrained when the number of constraints per atom is just equal to the number of mechanical degrees of freedom per atom. They also found that the covalent network consists of sp\(^3\) and sp\(^2\) carbon
sites, and optimal ratio of this coordination is a function of atomic fraction of hydrogen in the film. This model was well supported by the experimental observations. Further, a:C-H can be regarded as three-dimensional array of mostly six membered rings with some five and seven membered rings, which is able to contain 17-61% bound hydrogen. Angus and Wang [30] illustrated such a cross-linked structure shown in Figure 3.3. It can be seen that it has no long-range order.

Tamor and Wu [31] proposed a \textit{defected graphite} (DG) model. The model assumed two dimensional graphitic structure with randomly distributed nonaromatic defects at which the $\pi$-electron density is zero. When the defect density is low, the remaining $\pi$-electrons are delocalized over the entire $sp^2$ network and the structure remains metallic. However, at some
critical density of defects, the region over which the $\pi$-electrons may delocalize becomes disconnected, conduction electrons are confined to an “archipelago” of small aromatic domains, and material becomes insulating. $\pi$-bonded clusters, or graphitic or aromatic domains, are defined as fused clusters of closed sixfold rings of sp$^2$ coordinated carbon.

Most of the models discussed above are based on graphite structure with some distortion or defects. Jager et al. [32] proposed a simple model, which is non-graphitic. It consists of hydrogen distributed sp$^3$ and sp$^2$ carbon network and short chains of CH$_2$ and CH groups separated by a layer of non-hydrogenated sp$^2$ carbons. These chains of CH$_2$ and CH groups were distributed in carbon network with olefinic rather than aromatic carbons. The model is based on the NMR studies of the deposited films and is consistent with the

\[\text{Figure 3.3 A two dimensional representation of diamondlike carbon film structure [30].}\]

\[\bullet, \text{sp}^2 \text{ carbon atom}; \emptyset, \text{sp}^3 \text{ carbon atom}; \bigcirc, \text{hydrogen atom}.\]
qualitative results spatially averaged from neutron-diffraction and spectroscopy data. The model is shown in Figure 3.4.

![Schematic model of the microstructure of a-C:H entirely based on NMR data showing heterogeneity in the structure of nanometer scale](image)

**Figure 3.4** Schematic model of the microstructure of a-C:H entirely based on NMR data showing heterogeneity in the structure of nanometer scale [32].

### 3.4 Deposition Techniques of DLC

Aisenberg and Chabot [33] were the first who successfully deposited DLC film by ion beam deposition. They quenched a beam of C\(^+\) ions, generated by sputtering carbon electrodes, in the presence of Ar to form an amorphous layer having microcrystallites. Spencer *et al.* [34] further confirmed that the films contained a-C and microcrystallites. Whitmell and Williamson [35] were the first to produce hard carbon films from hydrocarbon gas, ethylene-argon mixture, in a d.c. glow discharge. Further, Holland and Ojha [36] used a rf glow discharge system from butane at a pressure of about 0.1 torr. This is the one of the most common techniques used at present to deposit a-C:H.
Many researchers using CVD methods hypothesized that hydrogen is necessary for the formation of sp³ bonds in DLC films. But, PVD methods based on energetic ablation of carbon like pulsed laser deposition (PLD) demonstrated that hydrogen is not necessary for the formation of sp³ bonds. Therefore, deposition methods can be divided into two categories namely CVD using hydrocarbon gases and other PVD methods using solid target material. In general DLC films are formed when carbon or hydrocarbon radicals bombard a substrate with impact energies from 50 eV to several hundred electron volts. The influence of impact energy on the type of film obtained was summarized by Angus et al. [37] shown in Figure 3.5.
DLC films have been prepared by a variety of methods DC or RF methods, sputtering ion beam deposition, PLD, cathodic arc deposition, mass selected ion beam (MSIB) and etc. Some of the techniques are used to deposit ta-C films exclusively and Wei and Narayan [38] gave a good comparison of those techniques. This section will briefly describe the techniques that have been widely employed to synthesize a-C:H films and some of them are shown in Figure 3.6 [39].

3.4.1 Ion Beam Methods

There are different types of ion beam methods as shown in Figures 3.6 (a)-(c) and they either use solid carbon targets or ionized hydrocarbon gases. In ion beam methods, the plasma is not in direct contact with the substrate, rather the precursor ions are extracted from plasma to form an ion beam. The beam can be directed at the substrate to provide the ion bombardment of the growing film. Also, the energy of the ions can be controlled thereby providing good process control. Thus, the ion beam methods can be scaled up for manufacturing. The limitation with these methods is that the hardest films are obtained under conditions of low power and low gas pressure, which reduces the deposition rate.

3.4.2 PECVD Methods

Plasma is a collection of charged and neutral particles moving in random directions that is on the average, electrically neutral. Plasma has been utilized industrially in processing of various materials. Plasma deposition is also called glow discharge technique and the substrate is generally immersed in the plasma (unlike ion beam methods), where the growing film is subjected to interaction with energetic process in the plasma.

Any hydrocarbon with sufficient vapor pressure can in principle be used as source material for PECVD of a-C:H films. Among these are methane, acetylene, benzene, butane,
cyclohexane, ethane, ethylene, hexane, isopropane, pentane, propylene and propane. There have been previous studies on the effect of these chemical precursors on the properties of DLC films. Koidl et al. [40] used nine different precursors and found that properties of DLC films were independent of the precursor if substrate bias was in excess of certain voltage (-100 V in their case). It was proposed that below a certain bias, the fragmentation of the precursor remains incomplete. However, this lower limit of bias voltage depends upon the pressure during deposition. So, it would be appropriate to say that above certain energy of the impinging species, the nature of precursor does not affect the properties of DLC.

The most common methods of PECVD are dc and rf discharge techniques. In dc discharge technique a negative bias is applied to the substrate, which acts as an electrode. The counter electrode can be either the second electrode as shown in Figure 3.6 (e) or the grounded walls of the deposition chamber. This bias voltage ionizes the hydrocarbon precursor producing plasma thereby attracting the ions required for growth of the film. Bias voltage and total pressure of the system are important processing parameters, which help in minimizing the sputtering of atoms from the film surface. Processing pressure generally lies between 10 mtorr-100 mtorr. The substrate must be electrically conductive for deposition of the film by dc glow discharge. Thus, it limits the choice of substrate and restricts the deposition of a-C:H films on insulating substrates.

R.F. glow discharge overcomes the limitation of dc glow discharge method as it can deposit a-C:H films on insulating substrates. The simple apparatus used for deposition by rf technique is shown in Figure 3.6 (d). It uses capacitively coupled parallel plate rf discharge. The rf frequency used in these processes is generally greater than the ion plasma frequency (~2-5 MHz), thus electrons can follow the r.f. voltage but the ion can not. Coupled with this
Figure 3.6 Techniques used for deposition of diamondlike carbon (a) single ion beam sputtering; (b) dual ion beam sputtering; (c) direct ion beam deposition; (d) parallel plate RF PACVD; (e) parallel plate DC PACVD; (f) ECR deposition. (a) and (b) from solid carbon precursor; (c)-(f) from gaseous hydrocarbon precursor [39].
the difference in the electron and ion mobility, produces a negative dc self bias on the powered electrode.

There have been modifications in conventional PECVD processes in order to improve properties of a-C:H films. Weiler et al. [41] developed a Plasma Beam Source technique to deposit highly tetrahedral a-C:H films using acetylene gas. The plasma beam source consisted of a large movable 13.6 MHz rf powered electrode and a small tungsten grid electrode at ground potential. Confinement of plasma by hyperbolic magnetic field along with low processing pressure of $5 \times 10^{-4}$ mbar created highly ionized plasma. Movement of powered electrode in a vertical direction gave flexibility of variation of self-bias without change of pressure or rf power. This technique provided deposited highly tetrahedral form of a-C:H than can be obtained by conventional plasma.

Nonogaki et al. [42] deposited a-C:H films by Sheet-like Plasma CVD by using toluene precursor. The apparatus emitted an electron beam (up to 100 Å) by an arrangement of LaB$_6$ cathode and couple of hollow anode slits. The electron beam produced by introducing Ar gas in cathodes moved in influence of dc-biased anode and axial magnetic field provided by solenoid coils. This electron beam forms sheet-like plasma above the substrate because of two permanent magnets arranged in cusp geometry on both sides of electron beam. DLC was deposited at a rate of 0.69 $\mu$m/min and the hardness of films was high.

Fujimaki et al. [43] developed a novel technique using magnetron plasma in an unbalanced magnetic field in the presence of methane precursor. A strong magnetic field was applied parallel to the electric field of the cathode to extract the plasma along the
magnetic flux that decreases towards the surface. An increase in hardness was observed by increasing the plasma density and saturation ion current density.

Many more novel techniques have been developed, basically increasing the plasma density around the substrate, thereby improving the properties of the obtained a-C:H films.

3.5 Tribological Behavior of DLC

3.5.1 Tribological Properties

Tribology involves the study of friction and wear properties of surfaces, which are in relative motion with one another [44]. Thus, the nature of the two surfaces in contact play the primary role in tribological behavior.

DLC has shown to possess very good tribological properties and its tribological behavior has been studied extensively in our laboratory [1-4, 7] and elsewhere [5, 6, 45-53]. Recently the tribological properties of DLC films have been reviewed by Erdemir and Donnet [54]. Friction and wear of DLC coatings are strongly affected by

1) nature of films: controlled by the deposition process

2) tribological testing conditions:
   a) material parameters: nature of substrate and pin material.
   b) mechanical parameters: type of contact and contact pressure.
   c) kinematic parameters: nature of motion, velocity.
   d) physical parameters: temperature during friction.
   e) chemical parameters: nature of environment (humidity etc).

Thus, a wide range of tribological properties have been reported in literature for DLC films. The hypotheses proposed to justify the exhibited tribological behavior are very specific to
that DLC film synthesized and tested under a specific condition. Therefore, the proposed friction mechanisms more than likely should not be regarded as applicable to all DLC films.

The span range of friction coefficient of DLC films is 0.007-0.4 in vacuum, below $10^{-4}$ Pa, and in ambient air at $20\%<\text{RH}<60\%$ is 0.05-1.00 as compiled by Donnet [55]. Most typical, however, are the ranges 0.007-0.02 in vacuum and 0.05-0.4 in ambient air. The moisture sensitivity of the DLC films is more in cases of hydrogenated DLC films than hydrogen free DLC films. According to Gardos et al. [56], the increase in friction coefficient of hydrogenated DLC films in humid air is due to the increase in van der Waals bond strength of hydrogen bonding to the adsorbed water molecules (~5 kcal/mol) as compared to bonding of hydrocarbons (~2 kcal/mol). However, the inverse humidity sensitivity has also been reported (i.e., decreasing friction coefficient with increasing humidity) [57]. It is believed that the friction of DLC films is controlled by the formation of transfer layers during wear on the sliding couple, which generally have a lubricating effect [1-4]. It was suggested that the decrease in friction coefficient with increasing humidity might be attributed to the graphitic nature of the transfer [3,4] layer resulting in a tribological behavior comparable to that of graphite itself [47], which is known to require presence of absorbable species such as water to provide lubrication. But some studies show that the presence of water inhibits the formation of transfer layer. According to Kokaku and Kitoh [58] the tribo-chemical reactions leading to the oxidation of the DLC surface increase the friction coefficient in presence of moisture. The friction coefficient decreased by etching the oxide layer by Ar ions.

Generally, the wear rates for DLC films are as low as $10^{-6}$ mm$^3$/Nm [4]. Addition of metals or other elements such as silicon into the films can lead to further reduction in wear
rate [59]. Experiments have shown that these elements can improve the adhesion between DLC films and their substrates. The importance of adhesion on wear life of DLC films was further demonstrated by the fact that the wear rate of DLC films against aluminum depends on the deposition temperature which determines the level of residual stress in the films [60]. Other studies have found that the failure of DLC films during friction is due to spalling which is the result of poor adhesion onto the substrates [61].

The precursor gas affects the nature of the DLC films and thus affect the tribological properties. Recently, Erdemir et al. [62] have investigated the effect of methane, ethane, ethylene and acetylene on friction and wear performance of DLC films deposited on AISI H13 steel substrate. They found a close relation between the friction coefficient and source gas composition. Specifically, films grown in gases with higher hydrogen-to-carbon (H/C) ratio showed lower friction coefficients and higher wear rate than films grown with lower hydrogen-to-carbon (H/C) ratio. Hydrogen is a key element in determination of tribological behavior and presence of hydrogen lowers the friction coefficient of DLC films [63]. Erdemir et al. [64] diluted methane plasma with hydrogen and friction coefficient was found to decrease with increase in hydrogen content in methane plasma. Intense hydrogen ion bombardment prevents cross-linking or C=C double bonding in growing DLC films and etches out the graphitic phases [65]. Also, some of the carbon atoms at the surface can be di-hydrated (i.e. two hydrogen atoms bonded to one carbon atom). The presence of di-hydrated carbon atoms on DLC surfaces is expected to provide better shielding or a higher degree of chemical passivation, thus lower friction.

The material of the sliding counterpart in contact with DLC surface has pronounced affect on the tribological properties. Jia et al. [66] studied the tribological behavior by pin on
disk tribometer in 40% humid and dry air using steel; silicon nitride and DLC coated pins. They found friction coefficient ~ 0.05 in all cases but there was a large difference in wear rates. The wear rate of DLC in dry air against steel, silicon nitride and DLC coated pins was $2.5 \times 10^{-8} \text{mm}^3/\text{Nm}$, $6.5 \times 10^{-9} \text{mm}^3/\text{Nm}$ and $5 \times 10^{-9} \text{mm}^3/\text{Nm}$, respectively. But there was no measurable wear of the pins due to formation of transfer layer. However, in humid air DLC transfer layer did not adhere to pins and wear of both steel and silicon nitride pin was larger than observed in dry air. It was proposed that there was an increase in shear strength of transfer layer, thereby reducing the adhesion between the pin and DLC film leading to wear of pins.

### 3.5.2 Wear Mechanisms of DLC Films

Various theories have been proposed to explain the tribological behavior of DLC films. Hirvonen et al. [67] suggested that the low steady-state friction coefficients of DLC films observed at large sliding distance during lifetime tests were related to the formation of a carbon-rich transfer layer on the counter face. In an alternative mechanism, the low friction coefficients of DLC ($\alpha$-C:H) films during sliding were attributed to the two-stage pyrolysis of organic material into graphite [26], which includes carbonization (loss of hydrogen) and polymerization occurring between 400$^\circ$C and 600$^\circ$C. It has also been proposed that the occupation of the dangling bonds on the surface of the DLC films by oxygen and hydrogen reduces the possibility for the formation of bonds between DLC film and its counter face, which creates the low friction force [68]. Support for this mechanism has been provided by tribological experiments carried out between PTFE and DLC films. Finally, chemisorption of hydrogen and/or other chemically active species [55, 69, 70] and formation of a double-layer structure and/or micrographitization [71, 72] on sliding
interfaces have been proposed to explain the frictional behavior of DLC films. Thus, a controversy exists at present and the actual wear mechanism of DLC films is still not well understood.

As mentioned earlier after studying the tribological behavior of DLC films a “wear-induced graphitization” mechanism was recently proposed by Liu and Meletis [7]. The latter mechanism involves mainly two steps. First, flash temperatures produced by friction on local ‘hot spots’ at asperity contacts are causing release of hydrogen atoms and relaxation in the hard DLC structure. This relaxation permits shearing of the local DLC structure under the applied load, completing the transformation from DLC to a low friction defected graphite structure. Thus, low friction graphitic layers are formed between the two surfaces in contact. These hexagonal layers can undergo a large number of sliding events before they are degraded and consumed. Thus, the lifetime of the graphitic layer has a significant influence on the graphitization kinetics and as a consequence the lifetime of the film.

3.6 DLC Multilayers

This section reviews the intrinsic stress developed in the DLC films and their reduction by various methods. Further, the present state of study in the field of DLC multilayers is being reviewed.

DLC films exhibit high intrinsic compressive stresses preventing deposition of thick films, which are required for many tribological applications. Further more, wear resistant high sp³ films possess higher stresses and thus cannot be grown in high thickness since they peel off the substrate. Zelez [73] first reported of low stress (< 0.01 GPa) DLC films using a hybrid process involving reactive bias sputtering of ultra pure carbon targets together with plasma decomposition of normal butane. The films, reported by Zelez, had some superlative
properties but the results were not reproducible. Another effort towards reduction of residual stress includes annealing of DLC films. Grill et al. [74] reported that annealing at 440 °C reduced the stress in their films. On further investigation Grill and Patel [75] found a correlation between the high residual stress and unbound hydrogen in these films. Doping of DLC films has led to some interesting results with respect to reduction in the intrinsic stress. Among various dopants like nitrogen, fluorine, silicon etc., N has been found to be particularly effective in reducing stress in these films. Torng et al. [76] reported that nitrogen incorporation in a-C films produced by sputtering in the argon/ nitrogen plasma helped to overcome delamination problems to a great extent. Franceschini et al. [77] have also reported internal stress reduction by nitrogen incorporated in hard amorphous carbon thin films. Nitrogen admits a co-ordination equal to 3 at most (sp³ hybridized nitrogen). Therefore, the replacement of carbon by nitrogen in a-C:H film implied a reduction of the average co-ordination number and hence degree of over constraining. This change in co-ordination number could be responsible for the internal stress reduction in a a-C:N:H films [77].

Annealing of DLC films above 300 °C induces graphitization of these films as has already been mentioned and results in loss of diamondlike properties. Some of the doping elements affect the properties of DLC films [78]. The intrinsic stresses are affected by the content of sp² and sp³ co-ordinations in the film. Generally, the stresses increase with increase in the sp³ content. The sp³ and sp² content can be modulated by varying the deposition parameters. Therefore, there has been some attention on the synthesis and behavior of DLC multilayered films with alternate layers of low sp³ content and high sp³ content films [15-16, 79-81]. Ager et al. [79] were the first to report such multilayers of soft
and hard DLC films by filtered vacuum arc plasma deposition. The total thickness of the films was 230 nm, 260 nm and 300 nm with 10 %, 50% and 60% soft phase in the multilayers, respectively. The intrinsic stress reduced with increase in soft phase along with the hardness. However, the tribological studies showed that at high loads the lowest wear rate was observed for multilayered films containing 50% of the soft phase. Knoblauch et al. [80] deposited multilayer films by rf PACVD method with soft, hard and graded interface between the parent nanolayers to a total thickness of 170 nm. They found that the friction coefficient decreases with the interface width (i.e., minimum in the film having sharp interface). The increase in hardness with interface width was proposed as a possible reason. Knoblauch and Meyer [17] further studied DLC multilayer films with variation of nanolayers thickness (thickness of the soft and hard layers being equal) from 8 nm to 40 nm to total film thickness of 300 nm. They found that the friction coefficients of the multilayer films were in range of 0.07-0.18 and minimum wear was found in films with layer thickness between 24 nm – 28 nm. Qi et al. [81] have synthesized DLC multilayers by electron cyclotron resonance (ECR) microwave PECVD to a total thickness of 350 nm. They studied the mechanical properties and did not find any significant increase in nanohardness and modulus of the multilayer films compared to the parent films. But the films possessed higher critical load for fracturing. Studies by Goiti et al. [15] showed that the stress in the film is reduced by formation of a-C multilayers. They used magnetron sputtering to deposit 900 Å thick multilayer films. The coherency strains and moduli mismatch of the constituent layers, or presence of a low amount of cross-linked bonds in soft-hard layer interface were possible reason for the reduction in stress [82]. Further, Logothetidis and Charitidis [16] have studied
the elastic properties of the a-C multilayer films and found that the hardness and elastic modulus of the 274 nm thick multilayer films were above 32 GPa and 260 GPa.

It is apparent that in the above studies the thickness of the DLC/DLC multilayered films was relatively small (<0.5 µm). Also, significant improvements in both wear rate and friction coefficient were not reported for the multilayered films compared to their individual components. At the same time these studies present evidence for potential in reducing the stress in the films and improving the mechanical and tribological properties of the DLC films. It is interesting to note that the multilayers films deposited by most groups are in range of 90 nm to 400 nm, which might not be sufficient for some tribological applications. Also, in these studies, the alternating layers were obtained by alternating the bias voltage. Other routes of developing the multilayers have not been investigated. Improvement in mechanical and tribological behavior by such multilayered films may be produced by thicker individual layers and these films may provide a great promise to the tribological applications.
4. Experimental

This chapter gives the details of the plasma reactor used in the present investigation and the experimental details used to deposit the a-C:H films and a-C:H multilayered films. A preliminary investigation was conducted first to study the effect of different processing parameters such as bias voltage, chamber pressure and dilution of precursor gas on properties of DLC films. Property assessment included hardness, intrinsic stress, surface roughness and tribological behavior of these films. Based on their characteristics two of the DLC films were selected to synthesize the DLC/DLC nanocomposites. This chapter also includes all the characterization techniques used to analyze properties of DLC and DLC multilayered films.

4.1 Plasma Enhanced Chemical Vapor Deposition

4.1.1 PECVD System

The a-C:H films and a-C:H multilayers have been synthesized by the d.c. plasma CVD technique. The plasma glow discharge system consists of a cylindrical stainless steel deposition chamber having a diameter about 45 cm and length 56 cm. The substrate holder is a stainless steel rod of 2 cm diameter. A schematic of the deposition chamber is shown in Figure 4.1. A base pressure of ~3x10^{-6} torr was maintained in the deposition chamber with the help of diffusion pump; backed by a mechanical rotary vane pump. The desired processing pressure in the deposition chamber was controlled by a mechanical valve at a specified flow rate of the gases. MKS thermal mass flow controllers were used to control the flow rate of the gases. The inert gas and the reactive hydrocarbon precursor were premixed in a definite ratio and introduced into the deposition chamber from the
sidewall. The plasma was produced by application of dc bias between the substrate and the grounded wall of the deposition chamber.

There is a provision of covering the substrate, to stop the deposition of the film, by a shutter. The deposition chamber also has a provision of carrying out deposition of films by physical vapor deposition with help of magnetron sputter guns an angle of 45°. The films can also be deposited by the ion beam method using a Kaunfman’s ion gun. The hydrocarbon gas can be introduced in the ion gun and the ions bombard the surface of substrate to produce the desired film. There is a unique feature of carrying out deposition by intensified plasma. The tools that help in intensifying the plasma are a tungsten emission filament and auxiliary anode as shown in Figure 4.1. Voltage is applied to the filament to the desired value leading to thermionic emission of electrons. A positive potential is applied to the anode, thereby accelerating electrons. The electrons on their way to the positively charged anode collide with the gas present in the chamber leading to densification or intensification of plasma.

4.1.2 Experimental Procedure For Deposition of a-C:H Films

The a-C:H films were deposited on 5.08 cm diameter Si P (100) wafers. The substrate was ultrasonically cleaned in acetone, and blown dry in air before loading into the deposition chamber. The base pressure in the chamber was ~ 3x10⁻⁶ Torr. Ar was used as the dilution gas and methane was the hydrocarbon precursor. Ar and methane were purged into the chamber a couple of times. Prior to deposition of the film, the substrate was sputtered etched in Ar plasma at bias voltage of –1500 V for 30 minutes.
Figure 4.1 Schematic of the deposition chamber.

The Ar was introduced at a flow rate of 20 sccm and a pressure of 25 mtorr was maintained in the chamber. This helps reduce impurity levels on the surface by the energetic argon ion bombardment. After sputter cleaning, the system was again evacuated to high vacuum. Then, the mixture of Ar and methane gas was introduced in the chamber and the pressure was adjusted to the required level. The ratio of Ar and methane gas was adjusted by controlling flow rate of these gases individually. DC voltage was applied to the substrate after the pressure and flow rate of the gases stabilized and the plasma was
generated. The films were allowed to deposit for 2.5 hours in most of the cases and then the bias voltage was turned off along with the gas supply to the system. The system was evacuated to the base pressure. The film was allowed to cool in inert Ar gas atmosphere. The deposition conditions of a-C:H films are shown in Table 4.1.

a-C:H multilayers (DDM) were synthesized by deposition of alternating layers of DLC 20 and DLC 27. As can be seen from Table 4.1 all the deposition parameters were the same for the two a-C:H films except the flow rate of CH₄:Ar. Table 4.2 shows the parameters for deposition of a-C:H multilayers. The processing steps for synthesis of a-C:H multilayer films were the same as these of a:C-H films, except that each of the DLC 20 and DLC 27 were deposited in sequential alternating nano-layers. DLC 20 was the first layer to be deposited, after that bias voltage was switched off and the flow rates were adjusted according to the conditions of DLC 27 and deposition was conducted for a definite time to obtain the required layer thickness. Then, again the bias voltage was turned off and flow rate adjusted according to the conditions of DLC 20 and deposition was conducted again for the required time. This process was continued until the film with the desired thickness was obtained. The first set of experiments consisted of varying the thickness of the individual layers but keeping the ratio of DLC 20 to DLC 27 thickness to unity, i.e. λ = 1. Another set of experiments included constant thickness of one layer and varying the thickness of other layer to obtain different ratios of thickness of individual layers, i.e. varying λ. The substrate temperature during deposition remained <100°C. A small area on each sample surface was covered, to prevent deposition and used after processing to measure film thickness.
Table 4.1 Deposition Parameters of a-C:H films

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Bias Voltage (V)</th>
<th>Pressure (mtorr)</th>
<th>Flow Rates (CH$_4$:Ar)</th>
<th>Processing Time (Hr)</th>
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</thead>
<tbody>
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<td>-1000</td>
<td>100</td>
<td>8.4:60</td>
<td>1.5</td>
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<td>-1000</td>
<td>100</td>
<td>8.4:0</td>
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<td>2.5</td>
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</table>

Table 4.2 Deposition Parameters of a-C:H multilayer films

<table>
<thead>
<tr>
<th>Film Si$_{r100}$ Specimen Code</th>
<th>Flow rates (CH$_4$:Ar) sp$^2$/sp$^3$</th>
<th>sp$^2$/sp$^3$ Layer Thickness nm/nm ($\lambda$)</th>
</tr>
</thead>
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<tr>
<td>DDM 1</td>
<td>8.4:30/20:4</td>
<td>200/200</td>
</tr>
<tr>
<td>DDM 2</td>
<td>8.4:30/20:4</td>
<td>100/100</td>
</tr>
<tr>
<td>DDM 3</td>
<td>8.4:30/20:4</td>
<td>50/50</td>
</tr>
<tr>
<td>DDM 4</td>
<td>8.4:30/20:4</td>
<td>50/100</td>
</tr>
<tr>
<td>DDM 5</td>
<td>8.4:30/20:4</td>
<td>100/50</td>
</tr>
<tr>
<td>DDM 6</td>
<td>8.4:30/20:4</td>
<td>200/50</td>
</tr>
</tbody>
</table>

Note: All films were deposited at −1000 V bias and 100 mtorr pressure.
4.2 Characterization of a-C:H and a-C:H Multilayered Films

4.2.1 Thickness

A small area of the sample was covered by washers as shown in Figure 4.2 that created a step after deposition, reflecting the film thickness. Two steps on the sides of each specimen were used for measurement of the thickness of the film. The thickness of the film was measured by a WYKO NT 1000 surface optical profilometer. This instrument functions on the principle of interference of light. The deposition rate of a-C:H films was estimated by the ratio of the observed thickness to the total deposition time.

Figure 4.2 Si substrate on stainless steel holder.
4.2.2 Surface Roughness

Surface roughness, $R_a$, was also measured by using the WYKO NT 1000 surface optical profilometer at a magnification of 10X. The phase shift interference (PSI) mode of the profilometer used for the measurement has a vertical resolution of about 3 Å. Surface roughness values represent the average of at least three measurements.

4.2.3 Stress Measurement

Stress measurement studies were also performed by using the WYKO optical profilometer. The instrument was used to measure the radius of curvature of the Si substrate after deposition of the film. The residual stress in the film was estimated by the radius of curvature using Stoney’s equation:

$$\sigma = \frac{1}{6R} \frac{E_s d_s^2}{(1 - \nu_s) d_f}$$

where $E_s$, $d_s$, $\nu_s$ are the elastic modulus, thickness and Poisson’s ratio of substrate, respectively, and $d_f$ is the thickness of the film. The average of at least three measurements was taken for each film.

4.2.4 Structural Characterization

4.2.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to analyze the structure of the films. FTIR spectroscopy was conducted to obtain bonding characteristics and determine $sp^3/sp^2$ ratios. FTIR was performed at the Chemistry department, Louisiana State University, using a Magna-IR™ 750, Nicolet spectrometer. Transmission mode was used to analyze the samples. To eliminate the background of Si wafer, a spectrum was obtained with a blank Si wafer, which was used to deposit the DLC films. This Si
spectrum was subtracted from the spectra obtained from the DLC films. The resulting spectrum of DLC films were deconvoluted in the regions of interest by using GRAMS software.

4.2.4.2 Transmission Electron Microscopy

High-resolution transmission electron microscopy (HRTEM) of DLC-DLC multilayer samples was performed on a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å. Cross sectional slices were obtained by cutting the samples along a direction normal to the coating surface and then gluing, face to face, the two coating surfaces. Cross-sectional specimens for TEM observation were prepared by mechanical grinding, polishing, and dimpling followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691) at 4.5 keV at an angle of 5°.

4.2.5 Hydrogen Analysis

The nuclear reaction analysis (NRA) [83,84] technique was used to analyze the amount of hydrogen in DLC films. The analysis was performed at the Ion Beam Laboratory, SUNY (Albany, NY) using a nitrogen-15 ion ($^{15}$N) beam from an accelerator to react with protons. The following nuclear reaction takes place

$$^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \text{gamma-ray}$$

This reaction has a large cross section at the resonance energy of 6.385 MeV laboratory energy; yielding an alpha particle and a characteristic 4.43 MeV $\gamma$ ray. The sample is bombarded with $^{15}$N with energy at or above the resonant energy and the yield of characteristic 4.43 MeV $\gamma$ ray is measured by NaI scintillation detector. Hydrogen
content at the surface is directly proportional to the $\gamma$ ray yield when bombarded with $^{15}$N at the resonant energy. The NRA technique can also be used to carry out the depth hydrogen profiling of a material. For this, $^{15}$N with energy higher than the resonant energy is bombarded on to the sample. The reactions at the surface are negligible as the energy higher than the resonant energy. As $^{15}$N penetrates the surface, it slows down and its energy reaches resonant energy at a certain depth. Now the yield of $\gamma$ ray is proportional to the hydrogen at that depth. Hence, measuring the $\gamma$ ray yield as a function of energy of beam, the H concentration as a function of depth can be determined.

DLC films were analyzed by increasing the $^{15}$N beam energy from 6.38 MeV to 7 MeV in steps of 100 KeV. The area of sample analyzed was approximately 0.75cm X 0.75 cm. Thus, a good average of the hydrogen analysis from surface was obtained. The result obtained from the accelerator was analyzed using a software and % hydrogen content vs. depth was obtained. The depth of the sample penetrated by the beam is proportional to the density of the film, it does not affect the overall hydrogen content in the film.

4.2.6 Characterization of Mechanical Properties

To qualify the DLC films as protective coatings it is very important to evaluate the hardness of the film. Hardness is also expected to reflect other related properties of the thin films such as porosity, density or surface quality [80]. The hardness of the films was estimated by microhardness and nanoindentation experiments.

4.2.6.1 Microhardness Measurement

Microhardness measurements were conducted using a Zeiss microhardness tester. The load was applied smoothly onto the film using a Knoop diamond indenter under
specific conditions of load for a fixed time. The Knoop indenter is of rhombohedral-shape that is said to restrict the elastic recovery to minimum. The long diameter of the rhombus shaped indent thus obtained was measured and the hardness was calculated using the formula

$$HK = 14229 \frac{P}{l^2}$$

where, \(l\) is the length of the long diagonal of the indent in \(\mu m\) and \(P\) is the load in \(gf\).

Multiple indentations were carried out at two different loads 25 \(gf\) and 10 \(gf\) and at least three indentations were performed at each loading level.

4.2.6.2 Nanoindentation Experiments

Nanoindentation measurements were taken using a Hysitron Triboscope ® instrumented nanoindentation/nanoscratch device incorporated on a Digital Instrument Dimension 3100 atomic force microscope. The Triboscope ® allows AFM imaging of surfaces prior and after indentation. A three-sided, Berkovich-type pyramidal indenter was employed to carry out nanoindentations on the two DLC and various DLC-DLC multilayered films (thickness > 800 nm). The indenter shape function was obtained, assuming an indenter contact depth independent modulus, using fused silica as the calibration specimen. Multiple indentations were carried out at three different loads 3 mN and 6 mN and and 10 nN. At least three indentations were performed at each loading level and the values represent average of the measured data. The hardness, \(H\), and indentation modulus, \(E/(1-\nu^2)\), found to reach approximately constant values at a contact depth between 70 and 100 nm. These values were below 10% of the coating thickness (1.5 \(\mu m\)) and were taken as representative of the coating.
4.2.7 Tribological Characterization

Pin-on-disc experiments (ISC-200 tribometer) were conducted on DLC and DDM films to characterize their tribological behavior. The standard pin-on-disk Tribometer uses a simple load arm with a tangential force sensor mounted close to the contact point so as to reduce error due to arm compliance. A pin or a sphere is loaded onto the test sample with a precisely known weight. The pin is mounted on a stiff lever, designed as a frictionless force transducer. Different loads can be applied on the films through a pin. Pins of different material and size (diameter) can be used.

The pin material used in the present study was Al₂O₃ ball of 9.5 mm diameter. These wear experiments were performed in laboratory air having a relative humidity of 50 ± 10%, at a sliding velocity of 0.1 m.s⁻¹ for a distance of 1000 m under a load of 2.5 N that produced a Hertzian stress of 0.4 GPa. The friction coefficient (µ) was monitored continuously during the experiments with the aid of a linear variable-displacement transducer and recorded on a dedicated, data acquisition computer attached to the tribometer. The wear volume of the films was calculated from the trace of surface profile (average of four traces) taken across the wear track by using the optical profilometer. The wear rates were calculated by using the formula

\[
\text{Wear Rate} = \frac{\text{Wear Volume (mm}^3\text{)}}{[\text{Load (N)} \times \text{Sliding Distance (m)}]} 
\]

The wear rate in the ball was calculated by measurement of the diameter of the wear scar and using the formula:

\[
W_p = \frac{\pi d^4}{64r}
\]

where, \(W_p\) is pin wear volume, \(d\) is average diameter of the scar and \(r\) is pin radius.
5. RESULTS AND DISCUSSION

5.1 Effects of Processing Parameters on Characteristics of DLC

The hardness, surface roughness and internal stress of various deposited DLC films are summarized in Table 5.1. The intrinsic stresses in the film vary from 0.3 – 2.0 GPa. DLC 15, which was deposited using methane only, seemed to have very high stresses and the film flaked off from most of the regions, thereby relieving the stress. The

Table 5.1. Properties of DLC films

<table>
<thead>
<tr>
<th>DLC Film Code</th>
<th>Thickness (nm)</th>
<th>Deposition Rate (nm/min)</th>
<th>$H_k$ (GPa) 25 gf (10 gf)</th>
<th>Surface Roughness $R_a$</th>
<th>Internal Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1000</td>
<td>8.3</td>
<td>26 (43)</td>
<td>14.8</td>
<td>0.9</td>
</tr>
<tr>
<td>*15</td>
<td>2800</td>
<td>31</td>
<td>34.10 (61.96)</td>
<td>DF</td>
<td>DF</td>
</tr>
<tr>
<td>19</td>
<td>2800</td>
<td>18.6</td>
<td>31.28 (51.2)</td>
<td>12</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>1670</td>
<td>11</td>
<td>28.14 (49.50)</td>
<td>18</td>
<td>0.7</td>
</tr>
<tr>
<td>25</td>
<td>1200</td>
<td>8</td>
<td>20.40 (28)</td>
<td>8</td>
<td>3.4</td>
</tr>
<tr>
<td><strong>26</strong></td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
</tr>
<tr>
<td>27</td>
<td>2000</td>
<td>13</td>
<td>38.70 (67.30)</td>
<td>13</td>
<td>1.2</td>
</tr>
<tr>
<td>28</td>
<td>2500</td>
<td>17</td>
<td>20.65 (28.52)</td>
<td>17</td>
<td>0.75</td>
</tr>
<tr>
<td>29</td>
<td>2300</td>
<td>15</td>
<td>34.00 (60.00)</td>
<td>18</td>
<td>1.4</td>
</tr>
<tr>
<td>30</td>
<td>2500</td>
<td>16.5</td>
<td>28.06 (50.65)</td>
<td>25</td>
<td>1.9</td>
</tr>
<tr>
<td>31</td>
<td>2300</td>
<td>15</td>
<td>32.40 (50.00)</td>
<td>11.5</td>
<td>0.94</td>
</tr>
<tr>
<td>32</td>
<td>3000</td>
<td>20</td>
<td>28 (50)</td>
<td>11.1</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*DF – Discontinuous Film
**NF – No Film
stress measurement was not possible in this film, however the hardness value reported is from an island of film, which was still present on the substrate. The DLC films were found to be smooth with $R_a$ values ranging between 8 nm and 25 nm, surface roughness of Si substrate being 7 nm.

The tribological properties of DLC films are summarized in Table 5.2. The steady-state friction coefficient in the films varies in the range 0.06-0.13. The steady-state refers to the friction coefficient after initial break down (after some distance the friction coefficient almost stabilizes to a constant value). Values of friction coefficient reported previously for DLC films tested at ambient conditions (20%-60% relative humidity) generally lay between 0.05-0.4 [42].

![Table 5.2. Tribological Properties of DLC films](image)

<table>
<thead>
<tr>
<th>DLC Film Code</th>
<th>Initial friction coefficient $f_i$</th>
<th>Steady-state friction coefficient $f_{ss}$</th>
<th>Wear rate $\text{mm}^3/Nm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.35</td>
<td>0.09</td>
<td>$14 \times 10^{-7}$</td>
</tr>
<tr>
<td>*15</td>
<td>DF</td>
<td>DF</td>
<td>DF</td>
</tr>
<tr>
<td>19</td>
<td>0.2</td>
<td>0.13</td>
<td>$2.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>0.06</td>
<td>$18 \times 10^{-7}$</td>
</tr>
<tr>
<td>25</td>
<td>0.23</td>
<td>0.12</td>
<td>$6 \times 10^{-7}$</td>
</tr>
<tr>
<td>**26</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
</tr>
<tr>
<td>27</td>
<td>0.25</td>
<td>0.11</td>
<td>$1.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>28</td>
<td>0.2</td>
<td>0.15</td>
<td>$1.35 \times 10^{-7}$</td>
</tr>
<tr>
<td>29</td>
<td>0.18</td>
<td>0.12</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>30</td>
<td>0.25</td>
<td>0.12</td>
<td>$1.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>31</td>
<td>0.25</td>
<td>0.12</td>
<td>$1.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>32</td>
<td>0.2</td>
<td>0.09</td>
<td>$5 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
The present DLC films seem to show low friction coefficient in the testing conditions of ambient air with 40%-60% relative humidity. The wear rate of all the DLC films is in general low and no significant wear was observed in the alumina pin. In most of the DLC films, the friction coefficient is initially high. It gradually drops and stabilizes to a steady value after some time in most of the films, thereby showing the typical tribological behavior of DLC as has been described previously by Liu et al. [2-4]. DLC is thermally unstable after 350 °C and thus there are microstructural changes after such a temperature. It has been reported that graphitization of DLC starts after 350 °C and increases with further increase in temperature. During wear of DLC film, the local temperature, at the asperity contact between the pin and the DLC film, reaches temperatures above 350 °C. This leads to graphitization of DLC in the localized region of the wear track. The process of low shear strength graphitic microstructure formed between two surfaces was termed as “wear induced graphitization” by Liu and Meletis [7]. This proposal was supported by TEM studies and Raman spectra of the debris collected and wear surface, respectively. The transfer layer is lubricious and reduces the friction coefficient between DLC and the pin. The present results are consistent with this mechanism.

This section further discusses the variation of microhardness, stress, friction coefficient and wear rates of a-C:H films as a function of different processing parameters namely bias voltage, processing pressure and dilution of methane with Ar.

5.1.1 Effect of Processing Pressure

Figure 5.1 shows the effect of chamber pressure on properties of the DLC films at a bias voltage -1000 V and CH₄:Ar ratio of 20:4. Film deposition did not take place at a pressure of 25 mtorr. Thereafter, the hardness and the intrinsic stress increase with
Figure 5.1 Effect of processing pressure on (a) mechanical and (b)tribological behavior of a-C:H films deposited at –1000 V bias voltage and CH₄:Ar flow rate of 20:4 sccm.
increasing the processing pressure. Ryu et al. [85] have reported an increase in sp³ content in the film with increase in pressure due to lower impact energy of ions by scattering. This may cause an increase in the hardness of the film with pressure, along with the increase in intrinsic stress. The friction coefficient of the films did not vary significantly. The increase in wear resistance at 100 mtorr is consistent with the observation that the sp³ content increases with increasing pressure. The morphology of wear tracks of films DLC 25 and DLC 32 are shown in the Figures 5.2 (a)-(d). Film DLC 25 was found to be worn out completely at some places and the alumina pin came in contact with the Si substrate, which has a friction coefficient of 0.4. This may have caused the increase in the steady-state friction coefficient of DLC 25. Increase in pressure also caused higher Rₐ.

5.1.2 Effect of Bias Voltage

The effect of bias voltage on properties of a-C:H films is shown in Figure 5.3 at a pressure of 100 mtorr and CH₄:Ar ratio of 20:4. The intrinsic stress in the film increases with increasing the bias voltage. The hardness of the film also increases with increasing the bias voltage, which probably is due to increase in stress in the film. Also, the energy of the ions bombarding the surface of the growing film increases as the bias voltage is increased, thereby affecting this change in the hardness behavior. The friction coefficient was not found to increase substantially as a function of bias voltage in the tested range. The wear rate of all the films is low. The similarity in the wear rate shown by all the films may be due to the similar values of friction coefficient exhibited by the films.
Figure 5.2 Wear tracks in a-C:H films. Wear track depth profile of (a) DLC 25 and (b) DLC 32, and 3-D image of the wear tracks in (c) DLC 25 and (d) DLC 32.
Figure 5.3 Effect of bias voltage on (a) mechanical and (b) tribological behavior of a-C:H at 100 mtorr pressure and CH\(_4\):Ar flow rate of 20:4 sccm.
5.1.3 Effect of Ar Dilution

Methane, the precursor gas, was diluted with Ar and this effect on the properties of DLC films is shown in Figure 5.4. The film deposited with no addition of Ar in the plasma was found to be discontinuous and had flaked off at many places from the substrate. This indicates the intrinsic stress in the film was very high. This stress-relieving phenomenon has been commonly observed in hard coatings when the stresses are high [86-88]. With increase of Ar dilution, hardness exhibits a maximum value at an Ar content of 16.7%. With addition of Ar, plasma density increases because of more ionization of methane gas. But, the Ar ions have a tendency to sputter the surface of the growing film. So a balance between these two phenomena produces an optimum hardness. Maharazi et al. [89] observed similar trends and obtained the optimum properties at Ar percentage of 30%. In the present study the optimum properties were obtained at 16.7% of Ar. They have analyzed that the structure of DLC changes from granular to columnar for Ar (30%), but the average height profile of this columnar structure decreases with further increasing Ar content. This might also lead to the observed properties.

Previous research shows that the plasma chemistry is different in case of films deposited with more dilution of the methane gas than those deposited with less dilution. When the Ar:CH₄ ratio is high the primary species for deposition is C₂ [90] whereas the ratio is low CH₃ is the dominating species [91] leading to deposition of DLC films. This may have also caused the observed response to the dilution of Ar. This behavior is also consistent with the low internal stresses at high dilution of methane gas.

The wear rate of the films deposited in the presence of more Ar is higher than that
Figure 5.4 Effect of Ar dilution on mechanical and tribological behavior of a-C:H films deposited at –1000 V bias voltage and 100 mtorr pressure.
of the films produced with less Ar present. It has been observed that sp$^2$ content in the film increases with more dilution of plasma with Ar [92]. This increase in sp$^2$ content leads to graphitic films that are characterized by lower coefficient of friction but higher wear rate. It is interesting to note that there is no significant difference in the tribological properties of the films deposited in the low Ar plasma (lower than 35% of Ar). On the contrary, the films deposited with high Ar show a significant variation in tribological properties. At an Ar % of 78, the friction coefficient drops to 0.067 and the wear rate increases. This may indicate a substantial increase of sp$^2$ co-ordination the film at that dilution of Ar.

5.2 a-C:H films for formation of multilayers

The objective of the present study is to synthesize DLC multilayers in order to improve mechanical and tribological properties. Two DLC films were selected, for the multilayered films based on the previous results. The rationale behind their selection was to include a component with wear resistance (high hardness) and a component with low friction. Two films were selected, one having high sp$^3$ content (high wear resistance) and one having relatively high sp$^2$ content (low friction). The preliminary study showed that DLC 27 possessed the maximum hardness while DLC 20 exhibited the lowest friction coefficient (but highest wear rate). This difference in hardness and tribological behavior reflects the difference in sp$^3$/sp$^2$ content in the films. Therefore, these films have been analyzed by FTIR and the sp$^3$ and the sp$^2$ contents in the films have been calculated. These results are discussed in this section. Also, hydrogen content analysis on some of the films was performed to have a better understanding of the structure and composition of these DLC films. Hydrogen analysis of a few DLC films deposited at lower pressure and bias voltage were performed to obtain a better understanding of the effect of these
processing parameters. This section also summarizes the mechanical and tribological properties of these two DLC films selected to synthesize the multilayered films.

5.2.1 Structural Characterization of a-C:H films

The FTIR spectra obtained from films DLC 20 and DLC 27 are shown in Figure 5.5. The spectra were used to obtain information about C-H bonding configuration in DLC films and the ratio of sp³/sp² bonding. The spectra contain a broad band in the region 2800-3100 cm⁻¹ and are indicative of relatively high hydrogen content in the films. They are composed of six absorption peaks, which include a number of sp³ and sp² C-H stretching modes as shown in Table 5.3. It has been observed that with increase in dilution of CH₄, the sp² content in the film increases. Similar trends have been observed recently [93, 94]. Teii [94] also observed relative increases in intensity of sp² band at 3000-3150, similar to the present observations.

Table 5.2 shows that DLC 27 has higher sp³ content than DLC 20. The results also suggest that with more dilution of methane the sp³ content decreases. Previous studies show that hydrogen is one of the essential ingredients to stabilize the sp³ content in DLC films. The bombardment of Ar on the growing surface increases with increasing Ar in plasma. This may lead to the sputtering of hydrogen from DLC film, which may lead to the destabilization of the sp³ content and increase of sp² content in DLC 20.

5.2.2 Hydrogen Analysis

Results of NRA are shown in Figure 5.6. For all the DLC films analyzed, hydrogen exhibits an initial increase and then it remains relatively stable with depth. This initial peak is due to the moisture content present on the surface. For this set of samples ¹⁵N beam penetrated about 200 nm to 300nm in the tested energy range of 6.38
Figure 5.5 Deconvolution of C-H stretch region for DLC 20 and DLC 27.

Table 5.3. IR Vibrational Mode Assignments in the C-H Stretch Region for DLC Films.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
<th>Peak Contribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DLC 20</td>
</tr>
<tr>
<td>2860</td>
<td>sp(^3) C-H, C-H(_2), C-H(_3)</td>
<td>23.4</td>
</tr>
<tr>
<td>2900 to 2920</td>
<td>sp(^3) C-H(_2), C-H</td>
<td>35.5</td>
</tr>
<tr>
<td>2945</td>
<td>sp(^2) (olef) C-H(_2)</td>
<td>13.3</td>
</tr>
<tr>
<td>2970</td>
<td>sp(^3) C-H(_3)</td>
<td>2.2</td>
</tr>
<tr>
<td>3000</td>
<td>sp(^2) (olef) C-H</td>
<td>3.8</td>
</tr>
<tr>
<td>3025</td>
<td>sp(^2) (olef) C-H(_2)</td>
<td>21.8</td>
</tr>
<tr>
<td>sp(^3)/sp(^2)</td>
<td></td>
<td>1 (50/50)</td>
</tr>
</tbody>
</table>
MeV to 7 MeV. The depth to which the $^{15}$N beam penetrates the surface is a function of density of the film. It was difficult to have a good estimation of density of DLC films due to its complex structure. So, the depth of hydrogen analysis does not represent the true depth of penetration but gives a fair representation. The fluctuations in the hydrogen content as a function of depth suggests that the hydrogen is not very stable. This is also indicated by the tribological behavior of DLC films. These films undergo a structural change with sliding distance due to localized rise in temperature. Previous research attributes this structural change to loss of hydrogen from those regions.

Table 5.4 summarizes the NRA results. The values shown in the table are the average of the set of values, which were obtained as a function of depth. Film DLC 20 deposited with higher Ar content, has shown to contain more hydrogen as compared to DLC 27. Theye and Paret [95] have stated that the large concentrations of hydrogen in DLC are liable to bond preferentially to $sp^3$ C or $sp^2$ C atoms that can influence film formation. DLC 20 contains more $sp^2$ as shown by FTIR, suggesting that in the present films hydrogen preferentially bonds to the $sp^2$ bonded C atoms.

DLC 28 was observed to contain 47.6 % hydrogen, which was deposited at lower bias voltage than DLC 27 all other conditions being same. This suggests that the hydrogen content in the films increases with decreasing bias voltage. Previous research on hydrogen content in DLC films has also reported the same trend [36, 96]. This has been attributed to the stabilization of $sp^3$ coordinated carbon atom by lowering the ion energy of the bombarding atoms at lower bias voltage. We also observed the increase in hydrogen content by decreasing the processing pressure (DLC 25 contained 45.3 %,
Figure 5.6 Hydrogen analysis of DLC films.

Table 5.4. Hydrogen content of DLC films.

<table>
<thead>
<tr>
<th></th>
<th>DLC 25</th>
<th>DLC 28</th>
<th>DLC 20</th>
<th>DLC 27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Hydrogen Content (at %)</td>
<td>45.3</td>
<td>47.6</td>
<td>40.3</td>
<td>21</td>
</tr>
</tbody>
</table>
which is deposited at 50 mtorr). In both DLC 20 and DLC 25 the methane content in plasma reduced by either reducing the methane to Ar ratio or total pressure of gas. This may have an effect on the ionization of the methane and may be causing the observed variation in hydrogen content.

5.2.3 Summary of Mechanical and Tribological Properties DLC films for synthesis of multilayer films.

This section summarizes the mechanical and tribological properties of the two DLC films that were used to synthesize DLC multilayers.

Figures 5.7(a)-(d) show the hardness, intrinsic stress, wear rate and friction coefficient of the films. The $R_a$ of Si substrate is 7 nm and that of alumina pin is 65 nm. The $R_a$ of DLC 20 and DLC 27 is 17 nm and 13 nm, respectively. Pin holes have been observed in the DLC films, which lead to the observed higher $R_a$ in the films than Si substrate. DLC 27 is smoother than DLC 20; this might be due to the fact that DLC 20 was deposited at higher dilution of Ar. The larger number of Ar ions bombarding the surface of growing film might lead to the increased surface roughness. Microhardness measurements revealed a significantly higher hardness for film DLC 27 compared to DLC 20. This difference is attributed to higher sp$^3$ content in the former film. It is evident that compared to DLC 27, DLC 20 is characterized by lower friction coefficient but higher wear rate due to its higher sp$^2$ content and lower hardness.

Figures 5.8.1 and 5.8.2 show the results of nanoindentation. Film DLC 27 consistently exhibited a higher hardness and reduced modulus as compared to DLC 20. The nanohardness values compare well with those exhibited by previous research for a-C:H films [97, 81].
Figure 5.7 Mechanical and tribological properties of DLC 20 and DLC 27 films; (a) hardness, (b) internal stress, (c) wear rate and (d) friction coefficient.
Figure 5.8.1 Nano indentation of DLC films (a) reduced modulus and nanohardness and (b) ratio of nanohardness to reduced modulus.
Figure 5.8.2 Nano indentation of DLC films (a) contact depth and (b) ratio of nanohardness to reduced modulus.
However, in contrast to microhardness values, the difference in hardness obtained by nanoindentation was small. Hardness values for both films were higher than those of the Si substrate (12.5 GPa). Also, considering the contact depth, Figure 5.8.2 (a) it can be seen that the depth remains below the range of 10-15% of the film thickness and thus the present values should not involve substrate contribution. In view of the above, the reasons for the small hardness difference for the two DLC films obtained by nanoindentation are not clear at present. A plausible explanation may be provided by considering the NRA results. In the first 25 nm of both films there is layer of lower H content due to the interaction of the films with humidity. Thus, this layer counts for a large portion of the probing volume during nanoindentation and results in a similar behavior. It is interesting to note that the difference in hardness increases with load or increasing contact depth. Simply because the surface layer counts for a smaller portion of the probing volume, thus the “internal” film hardness is giving a higher contribution.

The reduced modulus is somewhat lower than values reported in the literature. Also, the observed reduction in modulus with increasing load (contact depth) is not clear at present. The low stress shown by these DLC films may be due to the low reduced modulus of the films leading to deposition of thicker films for tribological applications. The ratio of the nanohardness and reduced modulus (H/E) is called “plasticity index”. It is considered important in evaluating the limit of elastic behavior in a surface contact, necessary for wear resistance of a material [98]. The H/E ratios shown in Figure 5.8.2 by the DLC films are higher than those reported even for the a-C films [98]. This supports the exhibited tribological behavior.
Figures 5.9 shows the friction coefficient variation of the two DLC films and the Si substrate as a function of sliding distance. Both DLC films exhibit much lower and stable friction coefficient within the measured sliding distance as compared to the substrate. Also, the wear rate calculated for Si is orders of magnitude higher than that for the DLC films. The frictional behavior of film DLC 20 compares favorably with typical DLC films. Similarly, the wear rate of film DLC 27 is at the low end of that shown by typical DLC films.

It is interesting to note that after an initial stage (break in) the friction coefficient of DLC 20 suddenly drops and attains the steady state value, whereas DLC 27 shows somewhat different behavior, where the higher friction stage persists for a longer time. The wear mechanism exhibited by the DLC films has been discussed in section 5.1; wear induced graphitization takes place at the contact between pin and DLC film. It has been observed from FTIR experiments that DLC 27 has higher sp$^3$ content than DLC 20. This may cause a slow down in the graphitization kinetics for DLC 27. Figure 5.9 suggests that the graphitization process more than likely stabilizes after 800 m leading to steady state friction coefficient of 0.12.

The morphology of wear tracks of DLC 20 and DLC 27 is shown in Figures 5.10 (a)-(d). Distinct differences in the wear behavior are discerned. The width and depth of the wear track of DLC 20 are significantly larger than those of DLC 27. This is consistent with the lower hardness and wear rate calculations that show more wear in DLC 20. Presence of more sp$^2$ in DLC 20 leads to lower friction coefficient but higher wear in the film. Also, Figure 5.10 (c) suggests that the wear mechanism of DLC 20 involves a layer-
by-layer removal of the film. High graphitic content in this film is expected to result in weakly bonded (van der Waals) hexagonal layers that can be easily removed by the sliding action. On the other hand, wear of DLC 27 seems to involve formation of fine debris, a process that apparently requires more time thus, resulting in higher wear resistance.

![Figure 5.9](image)

*Figure 5.9* Fiction coefficient of DLC films and the Si substrate as a function of sliding distance.
Figure 5.10 Wear track depth profile of (a) DLC 20 and (b) DLC 27, and 3-D image of the wear tracks in (c) DLC 20 and (d) DLC 27.
5.3 Characterization of DLC Multilayers

5.3.1 Structural Characterization of DLC Multilayer by TEM

The TEM and electron diffraction studies were conducted on film DDM 2. Figure 5.11 (a) shows a cross section of the multilayered DLC/DLC film with layered structure. A distinct sharp interface with the Si substrate can be seen in the micrograph along with layer interfaces. The total thickness of the multilayered film measured from the TEM micrograph was found to be 2 µm in agreement with the profilometry measurements. The contrast between the layers is not very distinct as there is not much difference in composition of the parent DLC films. The contrast from the two types of DLC layers arises from difference in bonding and density. However, the periodicity and continuity of the layers can be seen clearly and the layers seem to have the same thickness. This evidence indicates that the process control is retained and changing the ratio of Ar and CH₄ provides a new avenue for depositing the DLC multilayers.

Figure 5.11 (b) is a HRTEM of the cross section of the interface between the film and the Si substrate. There are no discernible defects at the interface and the amorphous nature of film is evident in contrast to the lattice fringes shown for the Si substrate. The films seem to have excellent adhesion. Also, a diffused region can be seen at the interface. Figure 5.12 (a) shows the electron diffraction from the film. The diffuse ring patterns can be clearly seen, that is characteristic of a material with no long range order, at least for the resolution limit of the TEM (0.23 nm). Figure 5.12 (b) shows the diffraction pattern between the film and Si interface. Diffused rings patterns are also seen in this micrograph from amorphous DLC film. The diffraction spots correspond to the planes of Si (100) substrate.
Figure 5.11  TEM images of cross section of DDM 2 showing (a) alternate constituent layers, and (b) high resolution of the film/ Si interface.
Figure 5.12 Electron diffraction pattern obtained for DDM 2 from (a) a constituent parent layer and (b) the interface between the multilayer and the Si substrate. Note that the diffuse rings represent highly disordered structure.
5.3.2 Mechanical and tribological properties of DLC multilayers

The mechanical and tribological properties of all the DLC multilayered films are summarized in Tables 5.5 and 5.6, respectively. The intrinsic stress in the multilayers was observed to be in the range of 0.8 GPa – 1 GPa except for multilayer 1, which exhibits somewhat higher stress of 1.5 GPa. With one exception, stress in the multilayered films, is found to be lower than the average stress (0.97 GPa) of the two parent DLC films, as shown in Figure 5.13. The compressive stresses in the present multilayers are mostly in the lower range of the data reported in the literature, which range from 0.8 – 6 GPa [76] and 5.2 – 2.4 GPa [79]. The low internal stress levels offer the opportunity to deposit films with greater thickness.

The friction coefficient of all multilayers was found to be low, similar to the DLC films and varied from 0.067 to 0.12. It is interesting to note that the wear rate of all multilayers is in general low. DDM 3 was found to have the lowest friction coefficient of 0.067. The wear rate of all the multilayers was found to be comparable to that of the high sp³ content parent DLC film (DLC 27). Thus, the multilayers were found to combine the best from each individual component (low friction coefficient and low wear rate). Knoblauch and Hauert [17] have reported friction coefficient in the range of 0.1-0.18 and a very low wear rate of 4-60 X 10⁻⁹ mm³/Nm. The multilayer films deposited in the present study compare well with the friction coefficient (on the lower side), though the wear rate is somewhat higher. It should be noted that Knoublauch and Hauert used a steel ball as the pin material where in the present study a harder Al₂O₃ ball was used. In addition, their tests were conducted for longer distance (> 4 Km) and in view of the
Table 5.5. Mechanical Properties of DLC Multilayers.

<table>
<thead>
<tr>
<th>Film No</th>
<th>Thickness (nm)</th>
<th>Surface Roughness</th>
<th>Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDM 1</td>
<td>2000</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>DDM 2</td>
<td>2000</td>
<td>24</td>
<td>0.91</td>
</tr>
<tr>
<td>DDM 3</td>
<td>2000</td>
<td>10</td>
<td>0.94</td>
</tr>
<tr>
<td>DDM 4</td>
<td>2000</td>
<td>13</td>
<td>0.9</td>
</tr>
<tr>
<td>DDM 5</td>
<td>2000</td>
<td>11.8</td>
<td>1</td>
</tr>
<tr>
<td>DDM 6</td>
<td>2000</td>
<td>10.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 5.6. Tribological Properties of DLC Multilayers.

<table>
<thead>
<tr>
<th>Film No</th>
<th>Initial friction coefficient. $f_i$</th>
<th>Steady-State friction coefficient. $f_{ss}$</th>
<th>Wear rate mm$^3$/Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDM 1</td>
<td>0.15</td>
<td>0.08</td>
<td>3 X 10$^{-7}$</td>
</tr>
<tr>
<td>DDM 2</td>
<td>0.14</td>
<td>0.08</td>
<td>2 X 10$^{-7}$</td>
</tr>
<tr>
<td>DDM 3</td>
<td>0.22</td>
<td>0.067</td>
<td>2.1 X 10$^{-7}$</td>
</tr>
<tr>
<td>DDM 4</td>
<td>0.18</td>
<td>0.12</td>
<td>2.2 X 10$^{-7}$</td>
</tr>
<tr>
<td>DDM 5</td>
<td>0.16</td>
<td>0.095</td>
<td>1.8 X 10$^{-7}$</td>
</tr>
<tr>
<td>DDM 6</td>
<td>0.17</td>
<td>0.12</td>
<td>2 X 10$^{-7}$</td>
</tr>
</tbody>
</table>
Figure 5.13 Intrinsic stress in DLC multilayered films as compared to the parent films.
higher friction coefficient in the initial stage, a lower wear rate is expected with increasing sliding distance. Further more it was reported that the steel ball formed a wear scar of about 200 µm after sliding for 12.5 m with no significant wear of the DLC film. Thereafter, a thick layer of transfer layer was formed about 3 µm (thicker than the deposited film), leading to low wear of film in this testing condition. It is evident that, wear of steel ball increased the contact surface and reduced the applied contact stress whereas no wear was observed of the Al₂O₃ pin resulting in higher stresses for the entire duration of the test. Also, a contact with lower radius (lower surface) may inhibit transfer layer transformation on the pin surface.

5.3.2.1 Nanoindentation Characterization of DLC Multilayers

Table 5.7 summarizes the results of nanoindentation experiments on DLC multilayered films. The results of the two DLC components are also presented for comparison. Figure 5.14.1 presents the nanohardness and reduced modulus results. Figure 5.14.2 presents the contact depth and plastic resistance parameter H/E ratio as a function of indentation load. Results show some variation in the nanohardness and reduced modulus with increasing load. There was a general upward trend for hardness and downward trend for modulus similar to those observed for the individual DLC films, Figure 5.8.1. Very limited work has been reported in this area has been reported in the literature.

Analysis of the nanoindentation results may be premature at this. A change in indentation load causes a change in contact depth and thus the number of layers penetrated, are also changing for different DLC multilayers. Thus, the nanoindentation behavior is a function
Table 5.7 Nanoindentation properties of DLC and DLC multilayers.

(i) Summary of Nanohardness (GPa) of DLC and DLC multilayered films

<table>
<thead>
<tr>
<th>Load (nN)</th>
<th>DLC 20</th>
<th>DLC 27</th>
<th>DDM1</th>
<th>DDM2</th>
<th>DDM3</th>
<th>DDM4</th>
<th>DDM5</th>
<th>DDM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>16.12</td>
<td>17</td>
<td>17.15</td>
<td>17</td>
<td>17.1</td>
<td>17.7</td>
<td>16.9</td>
<td>17</td>
</tr>
<tr>
<td>10</td>
<td>16.2</td>
<td>17.3</td>
<td>18</td>
<td>17.2</td>
<td>17.3</td>
<td>17.8</td>
<td>17.7</td>
<td>17</td>
</tr>
</tbody>
</table>

(ii) Summary of reduced modulus (GPa) of DLC and DLC multilayered films

<table>
<thead>
<tr>
<th>Load (nN)</th>
<th>DLC 20</th>
<th>DLC 27</th>
<th>DDM1</th>
<th>DDM2</th>
<th>DDM3</th>
<th>DDM4</th>
<th>DDM5</th>
<th>DDM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>114.4</td>
<td>119.85</td>
<td>115.74</td>
<td>122.23</td>
<td>123.1</td>
<td>129.3</td>
<td>127.82</td>
<td>120.27</td>
</tr>
<tr>
<td>6</td>
<td>109.9</td>
<td>112</td>
<td>122.4</td>
<td>117.45</td>
<td>119.8</td>
<td>125.8</td>
<td>116.12</td>
<td>116</td>
</tr>
<tr>
<td>10</td>
<td>104</td>
<td>106.5</td>
<td>112.57</td>
<td>115</td>
<td>117.1</td>
<td>125.8</td>
<td>127.1</td>
<td>113.67</td>
</tr>
</tbody>
</table>

(iii) Summary of H/E ratio of DLC and DLC multilayered films

<table>
<thead>
<tr>
<th>Load (nN)</th>
<th>DLC 20</th>
<th>DLC 27</th>
<th>DDM1</th>
<th>DDM2</th>
<th>DDM3</th>
<th>DDM4</th>
<th>DDM5</th>
<th>DDM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.142</td>
<td>0.13</td>
<td>0.138</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.137</td>
</tr>
<tr>
<td>6</td>
<td>0.147</td>
<td>0.15</td>
<td>0.148</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.13</td>
<td>0.147</td>
</tr>
<tr>
<td>10</td>
<td>0.15</td>
<td>0.16</td>
<td>0.16</td>
<td>0.15</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.15</td>
</tr>
</tbody>
</table>

(iv) Summary of contact depth (nm) of DLC and DLC multilayered films

<table>
<thead>
<tr>
<th>Load (nN)</th>
<th>DLC 20</th>
<th>DLC 27</th>
<th>DDM1</th>
<th>DDM2</th>
<th>DDM3</th>
<th>DDM4</th>
<th>DDM5</th>
<th>DDM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>88.22</td>
<td>86.2</td>
<td>84.47</td>
<td>84.87</td>
<td>85.25</td>
<td>81.9</td>
<td>82.9</td>
<td>85.6</td>
</tr>
<tr>
<td>6</td>
<td>144.5</td>
<td>141.45</td>
<td>139.2</td>
<td>138.8</td>
<td>137.7</td>
<td>133.5</td>
<td>134.6</td>
<td>139.5</td>
</tr>
<tr>
<td>10</td>
<td>203.9</td>
<td>200</td>
<td>193</td>
<td>193</td>
<td>193</td>
<td>185.8</td>
<td>185.3</td>
<td>195.3</td>
</tr>
</tbody>
</table>
Figure 5.14.1 Nanoindentation of DLC multilayered films (a) reduced modulus and nanohardness and (b) ratio of nanohardness to reduced modulus.
Figure 5.14.2 Nanoindentation of DDM multilayered films (a) contact depth and (b) ratio of nanohardness to reduced modulus.
of extent of penetration of alternate hard and soft layers of DLC multilayers. It is interesting to note that nanohardness of the multilayers was higher of that of DLC 20 (low sp³ content) and DLC 27 (especially for low loads). The reason for this behavior is not clear but it may relate to reduction of scale effects at higher loads. Also the reduced modulus of multilayers is higher than the individual components. In comparison with the a-C:H multilayers reported in literature, the deposited multilayers compare well in terms of nanohardness but reduced modulus of present films is low [82, 98]. The contact depth and ratio of H/E increase with increasing indentation load. The H/E ratio of the present multilayered films is higher than those reported in literature [98]. Figure 5.14.2 (b) indicated a general increase in the H/E ratio as the layer thickness is increased (DDM1, DDM2 and DDM3). Also, in case of DDM 5 and DDM 6 there is increase in H/E ratio by increase in thickness of the soft layer from 100nm to 200 nm, respectively. The response of nano composite multilayers is a complex one and is not understood at present.

5.3.2.1 Tribological Characterization of DLC Multilayers

Figure 5.15 shows the variation of friction coefficient as a function of sliding distance of all the DLC multilayered films. It is interesting to note that the friction coefficient suddenly drops from its initial value and then increases slowly before stabilizing to a steady-state friction coefficient. The initial high value of friction coefficient can be related to the asperities present on the surface and formation of low friction layer, but the reason for the slight increase in friction coefficient behavior is not quite clear. This gradually increasing zone of friction coefficient varies with (a) the increase in the layer thickness of the individual layer of low sp³ and low sp² films for \( \lambda = 1 \); and (b) variation of \( \lambda \). The area of contact between the pin and the film is smaller
Figure 5.15 Friction coefficient as a function of sliding distance for DLC multilayer films.
initially and with the increase in sliding distance the wear track widens, which might be causing this increase in friction coefficient. After some time, the area of contact becomes almost constant, thereby stabilizing the friction coefficient. As already has been discussed in section 5.1, there is graphitization of DLC in the zone of wear and a transfer layer is formed between the film and the pin. This transfer layer is being affected by sliding of the alumina pin through alternate soft and hard DLC nanolayers, which is also contributing to this behavior of DLC multilayers.

Knoblauch and Hauert [17] also found similar behavior in some of the multilayered films. It was observed that particles up to 10 µm were detached from the transfer layer (formed on the pin). During the wear process, the particles have to be broken down into smaller parts, hence may cause the unstable friction coefficient response. It was also observed that the presence of fine particles in the wear track of some of the films resulted in steady value of friction coefficient after the running-in period. In the present study, the 50 nm multilayered film (at $\lambda = 1$) does not show any significant gradually increasing zone of the friction coefficient. It may be due to the fine particles present at the wear track as compared to the rest of the multilayered films.

Figure 5.16 (a) presents the tribological behavior of the DLC multilayers as a function of the individual layer thickness, at $\lambda = 1$. The friction coefficient remains low for all films and is slightly increased from 0.067 to 0.08, but there is not much variation in the wear rate. As the layer thickness was further increased from 100 nm to 200 nm, the friction coefficient does not change but the wear rate increases significantly. This suggests that the tribological properties improve with decrease in the layer thickness. Improvement in the properties of the multilayered films with decreasing the single layer
thickness has been observed in different metal/metal, metal/ceramic and ceramic/ceramic systems [99, 100, 101]. This is consistent with the observation that for many nanolayered systems, the resistance to flow increases with decreasing layer thickness [102].

The morphology of wear tracks of multilayered films is shown in Figures 5.17 –5.19. On close examination of the wear tracks, it was found that on average the width of the wear tracks of the multilayer films, with nanolayer thickness of 200 nm, 100 nm and 50 nm, were 174 µm, 136 µm and 125 µm, respectively. The 50 nm multilayer film shows most resistance to flow in transverse direction of applied load during the tribological test. The depth of the wear tracks of the multilayer films, with nanolayer thickness of 200 nm, 100 nm and 50 nm, were 256 nm, 178 nm and 211 nm, respectively. There is no trend in the depth as in the case of the width of wear tracks. But it may be noted that multilayers with 200 nm and 100 nm layer thickness might have slid over the harder nanolayer for most of the time. Whereas the 50 nm layer thickness multilayer film passes through the alternate soft and hard layer just after the drop in initial friction coefficient. This might have affected the behavior of the transfer layer formed on the alumina pin.

The 50 nm multilayered film slides through alternate hard and soft nanolayers having the friction coefficient of 0.11 and 0.067. It is interesting to note that in spite of sliding through the hard/soft nanolayers, the friction coefficient of the multilayer is stable after the initial break in period. This suggests that low friction layer may have enough thickness to form a transfer lubricating layer thus keeping friction coefficient low. This further suggests the synergetic effect of the individual components in the multilayer leading to the observed low friction behavior along with low wear rate. Also, this alternate sliding may lead to the formation of fine particles in the wear track of multilayer
film with 50 nm layer thickness as compared to the wear track of multilayers with 200 nm and 100 nm layer thickness where, large particles of the hard film or the transfer layer might be present [17]. These results suggest that lowering the thickness of the low sp³ content layer even further transfer layer formation may be possible while wear rate can be reduced. This notions seems consistent with the results of Knoblauch and Hauert [17], who tested 12 nm thick individual layers and the wear rate was extremely low.

Figure 5.16 (b) shows the tribological behavior of the DLC multilayers as a function of λ or percentage of sp² layer in the multilayer films. Multilayer film with λ = 1 is the film with nanolayer thickness 50 nm. It is interesting to note that the friction coefficient for the multilayer film with λ = 1 is the lowest in spite of the fact that the film with λ = 2 and λ = 4 have a higher % of sp² layer. In fact, all the films with λ = 1 exhibit friction coefficients lower than the other multilayered films. This emphasizes that the same thickness of the two nanolayers constituents plays a major role in improving the tribological properties of multilayer films. This may also suggest that the synergetic effect is dominant when λ = 1. This effect can be attributed to higher uniformity and thus mechanical response in films with λ=1. Joel et al. [79] have found similar results with a-C multilayers. They reported that the mulilayered films with 50% sp² phase and 50% sp³ phase exhibited better wear properties than other mutilayered films especially when tested at higher loads of 3 N. Figures 5.20 and 5.21 summarize the friction behavior and tribological properties of parent DLC films and DLC multilayers.

Composite a-C:H multilayers have been synthesized by modulating the bias voltage in the previous studies reported in the literature [79-82]. Even the individual constituent elements of the multilayers exhibited lower friction coefficient than the multilayers
deposited in the previous studies, see for example Knoblauch et al. [80]. A different route was explored in present study, the multilayered films have been deposited by variation of the ratio of Ar/CH₄. The goal of the present study was to have DLC multilayers consisting of alternate nanolayers of two DLC films one being hard with low wear rate and the other being relatively soft with low friction coefficient. The multilayers deposited by Knoblauch and Hauert [17] have either low wear rate or low friction coefficient compared to their parent DLC films. In the present study, a combination of both low wear rate and low friction coefficient was achieved especially for the multilayers with λ = 1, having 50 nm individual layer thickness that exhibited the best tribological performance. a-C:H multilayered films reported in literature do not provide any information regarding the stress in their parent films and the multilayers, but the deposited films are not more than 400 nm thick. The multilayers of a-C reported in the literature have residual stresses in the order of 4 GPa – 6 GPa [79]. The present multilayered films have low stress and can be deposited as thick films in with thickness 2 μm or greater while maintaining low friction coefficient and wear rate. Thus, these multilayered films exhibit a great promise in tribological applications.
Figure 5.16 (a) Effect of layer thickness of DDM films for $\lambda = 1$ and (b) effect of increase of $\lambda$. 
Figure 5.17 Wear track depth profile of (a) DDM 1 and (b) DDM 2, and 3-D image of the wear tracks in (c) DDM 1 and (d) DDM 2.
Figure 5.18 Wear tracks of the a-C:H films. Wear track depth profile of (a) DDM 3 and (b) DDM 4, and 3-D image of the wear tracks in (c) DDM 3 and (d) DDM 4.
Figure 5.19 Wear tracks of the a-C:H films. Wear track depth profile of (a) DDM 5 and (b) DDM 6, and 3-D image of the wear tracks in (c) DDM 5 and (d) DDM 6.
Figure 5.20 Wear track of a-C:H films and a:C-H multilayers.
Figure 5.21 Tribological properties of DLC multilayers.
6. CONCLUSIONS

The following conclusions can be drawn from the present study:

1. Variation of PECVD processing parameters was found to produce DLC films with a range of characteristics such as intrinsic hardness, hardness, sp³/sp² content and tribological behavior.

2. Two of the above films with significant difference in hardness and tribological behavior were selected to form DLC/DLC multilayered films.

3. The intrinsic stress in the majority of the multilayered films was below the average intrinsic stress of the parent DLC films.

4. Friction coefficient and wear rate of all multilayered films was within the range of the individual components. The tribological behavior was found to be affected by the constituent nanolayer thickness suggesting a scale effect. Some of the multilayered films showed the synergistic effect in tribological behavior and combined the best properties of the constituent DLC films (low friction coefficient and high wear resistance).

5. 50 nm multilayered film (λ = 1) with significant thickness (2 μm) exhibited the lowest friction coefficient (0.067) of softer DLC film and low wear rate (2.1 X 10⁻⁷ mm³/Nm) of harder DLC film.

6. Multilayered DLC/DLC can be synthesized in high thickness with low stresses and thus alleviating spalling from the substrate, which is a major current problem. At the same time these films are possessing low friction and wear rate and thus present high potential for a number of tribological applications.
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