Characterization and tribological behavior of diamond-like carbon and nitrogen-doped diamond-like carbon thin films

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CHARACTERIZATION AND TRIBOLOGICAL BEHAVIOR OF DIAMOND-LIKE CARBON AND NITROGEN-DOPED DIAMOND-LIKE CARBON THIN 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 Mechanical Engineering in
The Department of Mechanical Engineering

by
Krishna C. Kadiyala
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ABSTRACT

Diamond-like carbon (DLC) films have been extensively studied for more than two decades due to their highly attractive properties. These films exhibit unique mechanical, electrical and tribological behavior and thus, possess great potential for applications in tribology. However, the high level of internal stress developed and low thermal stability are the main drawbacks. Synthesis of nitrogen-doped DLC (N-DLC) offers the possibility of overcoming these drawbacks. In the present study, DLC and N-DLC films (with low N content) were deposited on Si substrates using a hybrid plasma-assisted CVD/PVD process. Film characterization in terms of microstructure, composition and chemical state of components was carried out by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Mechanical properties of the films were characterized by microhardness testing. The tribological properties were studied by conducting pin-on-disc experiments. Surface optical profilometry was used to analyze the wear profiles and calculate the Archard wear rates.

TEM and XPS analysis showed that low amounts of N-doping results in the formation of an amorphous structure with the presence of short-ranged diamond-like structure (sp$^3$). N-doped DLC films were found to possess comparable hardness with that of DLC films. They exhibited friction coefficients as low as 0.04 compared to 0.2 for DLC, but maintained comparable Archard wear rates with DLC of the order of $10^{-7}$ mm$^3$/Nm. The N-DLC film with 0.73 at. % N exhibited the best tribological behavior. The nanosmooth appearance of the surface, ultralow friction coefficients and low Archard wear rates of N-DLC films obtained with low doping of N in the DLC matrix, show promise for applications such as magnetic hard drives and medical implants.
1. INTRODUCTION

The synthesis of new hard coatings for tribological applications is a topic of great technological interest. Carbon, one of the fascinating elements on the planet, exists in various forms and is used in numerous applications. Thus, it has been an object of research since centuries. Carbon exists in various forms, for example, as diamond with sp$^3$ hybridization and as graphite with sp$^2$ hybridization. Carbon also occurs in amorphous form as soot, carbon fiber, glassy carbon, and evaporated carbon. Diamond-like carbon (DLC) consists of a network of sp$^3$ and sp$^2$ coordinates and can exist as amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H). Diamond has high hardness and thermal conductivity, optical transparency, wide band gap, chemical inertness, high friction coefficient and low wear rates. This combination of properties proves it to be useful in many applications such as cutting and grinding tools, heat exchangers, infrared windows and high frequency high power electronic devices. Graphite on the other hand is soft, has good electrical conductivity, low coefficient of friction but high wear rate, and is a well-known solid lubricant.

DLC can be grown as thin films on different substrates and captures desirable properties of both diamond and graphite such as low coefficient of friction and high wear resistance. Some commercial and industrial areas where the new generation DLC protective coatings can be applied are aerospace, automotive, auto racing, cosmetics, bearings, electronics, industrial wear parts, infrared optics, medical/dental implants and instruments, metal working, military, tools/dies/molds and textiles.

DLC films have been used extensively in the past as coatings by modifying the properties of the films which allowed them to vary the behavior of materials in the
aspects of friction, wear, corrosion, biocompatibility, electronics etc. Though they serve in many applications, they have limitations such as low toughness, poor adhesion and high internal stresses which prevent the deposition of thick films and provide an incentive to investigate possible modifications in an effort to alleviate their limitations. Very smooth surfaces are required when DLC films are used as protective coatings for magnetic media, biological implants and microelectronic applications [1, 2]. With the miniaturization of moving or sliding components in many technological devices, such as MEMS and the magnetic hard disk drives, surface forces like friction and adhesion are very important [3]. In particular, the magnetic recording industry has announced that it is crucial to develop very thin (~2 nm) and smooth protective coatings with very low coefficient of friction and extremely good wear resistance, for the next generation of hard disk drives [2-4].

Metal DLC (Me-DLC) and non metal DLC films have been investigated in the past two decades to provide new generation films in an effort to overcome the limitations of DLC films. Various metals and non metals (such as silicon, fluorine and boron) have been doped into the DLC matrix to alter its properties. The study on nitrogen doped diamond-like carbon (a-C:H:N or N-DLC) thin films was primarily driven with the intention to synthesize a new form of carbon nitride phase (cubic beta carbon nitride \( \beta-C_3N_4 \)) predicted theoretically by Liu and Cohen [5]. This phase exhibits extremely low compressibility, super high hardness and bulk modulus that exceed those of natural diamond. Apart from the theory, most of the N-DLC films deposited so far have been proven to be amorphous in nature. The nitrogen incorporation into DLC in higher amounts so far has been found to form N-H, C≡N and C≡N bonds which decrease the
fraction of sp$^3$ carbon bonds, obstruct the carbon-carbon cross links, and form voids in the matrix resulting in softer N-DLC films [6].

The magnitude of internal stresses depends upon the sp$^3$/sp$^2$ ratio in the film and can be varied by altering the deposition parameters. The decrease in the fraction of sp$^3$ carbon bonds in NDLC films aids in improving the thickness by reducing the internal stresses in the film. Hence, the sp$^3$/sp$^2$ hybridization ratio is considered the most important parameter to characterize DLC and N-DLC (CN$_x$) films and is the subject of intense research [7-13].

Low N contents provide extremely high bond dissociation energy for N in gas discharge plasmas. Some NDLC films have shown presence of small crystallites with electron diffraction patterns matching $\beta$−C$_3$N$_4$ [14,15]. Also the friction coefficient and wear rates are lower for low nitrogen containing films [16]. Hence, there is initial evidence that doping low amounts of nitrogen into DLC has the potential to lower the friction coefficient and reduce the wear rate. Also it has been observed that above 400°C graphitization process starts in DLC films by conversion of sp$^3$ carbon bonding to graphitic sp$^2$ bonding [17]. Thus, potential enhancement of the thermal stability of DLC is very important in delaying ‘wear induced graphitization’ as proposed by Liu and Meletis [18] and thus, extending the life time of the film.

As in DLC films, the tribological performance of N-DLC thin films is also expected to depend mostly on both the environmental conditions and the nature of the coating. The coating characteristics are significantly influenced by the deposition technique and the parameters used for deposition. A plasma-enhanced chemical vapor
deposition (PECVD) process has been used in our laboratory to produce high quality DLC films. Such a process has not been used previously to synthesize N-DLC films.

An attempt was made to synthesize low N content DLC films using this hybrid process, study their characteristics, investigate their tribological behavior and explore their potential.
2. OBJECTIVES

The main objective of the present study is to explore synthesis of N-doped DLC films using a PECVD process that proved in the past of producing high quality DLC films. Also, it is intended to develop an understanding of nitrogen effects on the tribological behavior of diamond-like carbon coatings that will allow their optimization and design of new generation coatings for a number of advanced engineering applications.

The specific objectives of this research are to:

(i) Study the effect of processing parameters on the characteristics of DLC and N-DLC films using PECVD;

(ii) Study the mechanical and tribological (wear and friction) behavior of the produced DLC and N-DLC films; and

(iii) Enhance our scientific understanding of the synthesis-structure-property relationships in N-DLC films.
3. LITERATURE REVIEW

3.1 DLC Thin Films

Diamond is a material of interest to scientists due to its variety of properties. Diamond can be synthesized as a thin film, at low pressure. Different deposition techniques have been used to grow diamond films from carbon or a mixture of hydrogen and hydrocarbon precursor gases. Typically these films exhibit high hardness and thermal conductivity, high electrical resistivity, chemical inertness, wide optical band gap, good tribological properties and biocompatibility. There are numerous applications of these films in industry, but they also have their own limitations [19]. They require high temperatures (~850-950°C) to deposit, limiting the choice of substrate; they are characterized by a rough surface due to their polycrystalline nature; it is difficult to deposit them uniformly on large surfaces; and it is difficult to make large crystalline diamond. Hence, there is a need to grow a different kind of film retaining the properties of diamond and exceeding the limitations. These films are popular by the name DLC thin films.

The amorphous hydrogenated carbon (a-C:H) thin films, also called DLC, have been the focus of research for the past two decades due to their attractive combination of properties including chemical inertness, high thermal conductivity, biocompatibility, high hardness, low friction coefficient and wear rate. Typical properties and applications are summarized in the Table 3.1 [1].

Carbon moulds itself into different forms like diamond, graphite, diamond-like carbon, fullerenes, nanotubes etc, with its ability to hybridize into sp³ (tetrahedral), sp²
(trigonal) and sp\(^1\) (linear) coordination’s [20]. The film properties are determined by the relative ratio of the sp\(^2\) and sp\(^3\) carbon hybridization, the sp\(^1\) C hybridization being negligible [21].

DLC can be categorized into different forms based on the content of hydrogen as shown in the ternary phase diagram in Figure 3.1. Films having a high sp\(^3\) content are called tetrahedral ta-C:H or ta-C depending on whether they contain hydrogen or not. Similarly, amorphous films are shown either as a-C:H or a-C.

Table 3.1. Summary of properties and applications of diamond-like carbon thin films. Text in parenthesis indicates potential applications [1].

<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 = 1.0-4.0 eV</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 devices</td>
</tr>
<tr>
<td>High Hardness (5-80 GPa); low friction coefficient &lt;0.01-0.7</td>
<td>Tribological, wear resistant coatings</td>
<td>Magnetic hard drives, magnetic tapes, razor blades (bearings, gears)</td>
</tr>
<tr>
<td>Nano smooth</td>
<td>Very thin coatings &lt; 5 nm</td>
<td>Magnetic media</td>
</tr>
<tr>
<td>Wide range of electrical resistivity = (10^2)-(10^{16}) (\Omega/cm)</td>
<td>Insulating coatings</td>
<td>Insulating films</td>
</tr>
<tr>
<td>Low dielectric constants &lt;4</td>
<td>Low-k dielectrics Field emission</td>
<td>(Interconnect dielectrics) (Field emission flat panel displays)</td>
</tr>
</tbody>
</table>
The properties of DLC films can be altered when certain elements are introduced to DLC, also called doping. Some of the elements which have been selected from the periodic table are Si, N, F and metallic elements to form Si-C:H, a-C:H-N, a-C:H-F and Me-C:H respectively [23]. Typical metallic elements that have been already used as dopants are Co, Cu, Cr, W, Ti, etc. There are several more potential dopants and several of them are under investigation to enhance the properties of DLC.

The method of preparation also has given these films a broad range of properties. Their structure is intermediate to those of diamond, graphite and hydrocarbon polymers containing different ratios of sp\(^3\) carbon, sp\(^2\) carbon and hydrogen. Angus and Hayman [24] proposed a means for differentiating various carbon forms and hydrocarbons with respect to the atomic density and hydrogen content as shown in the Figure 3.2. It depicts that a-C:H films have much higher atomic density than conventional polymers. A
common comparison of properties of crystalline and amorphous form of carbon to DLC can be observed in Table 3.2.

Table 3.2. Properties of various forms of carbon [25].

<table>
<thead>
<tr>
<th>Form</th>
<th>Density (gm cm$^{-3}$)</th>
<th>Hardness (GPa)</th>
<th>sp$^3$ (%)</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></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>
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</table>
3.2. Deposition Techniques for DLC Thin Films

The first DLC film was deposited by Aisenberg and Chabot [24] in 1970 using an ion beam deposition method by quenching a beam of C\(^+\) ions. These C\(^+\) ions were generated by sputtering carbon electrodes to form an amorphous layer having microcrystallites, in a medium of Ar. The most common technique used to deposit DLC films is an rf glow discharge system. Holland and Ojha [27] used this system from a butane carbon precursor at a pressure of 100 mtorr.

The deposition techniques of DLC may be classified as CVD and physical vapor deposition (PVD) processes. The former method uses hydrocarbon gases and the latter uses solid targets as the carbon precursor. The main principle in depositing a DLC film is to allow carbon or hydrocarbon radicals to bombard a substrate at impact energies ranging from 50 eV to several hundred eV.

Today the main processes used to deposit non-hydrogenated DLC films are magnetron sputtering, mass-selected ion beam (MSIB), cathodic vacuum arc and laser plasma. Whatever be the technique applied, the fraction of sp\(^3\) bonding is maximized for ion-dominated processes with ion energies \(~100\) eV [28]. The variation of the film property with impact energies for different carbon precursors to produce C ions is illustrated in the Figure 3.3.

Ion beam methods and PECVD methods are widely used to deposit hydrogenated DLC films. These techniques are more precisely described in the following sections.

3.2.1 Ion Beam Methods

Different kinds of ion beam methods are presently in use depending on the type of film desired. The principle of this technique is that the plasma is not in direct contact with
the substrate, but the precursor ions are extracted from the plasma to form an ion beam. The beam is directed at the substrate for accomplishing the task of ion bombardment of the growing film. These films can be scaled up for manufacturing due to their excellent process control. The deposition rates are too low in these processes to deposit the hardest films, under the conditions of low pressure and low power which limit their applicability. Some of the very different kinds of ion beam deposition techniques are shown in Figure 3.4.

![Diagram showing the influence of impact energy for different carbon precursors to produce C ions.](image)

**Fig 3.3. Influence of impact energy for different carbon precursors to produce C ions [28].**
3.2.2 PECVD Methods

PECVD has become a significant technology to deposit a variety of coatings for different applications in the fields of electronics, tooling, surgical implants and optics. The major advantages of PECVD over other thin film deposition techniques include low deposition temperature, high deposition rate, and good control over stoichiometry, cleanliness and low particulate levels [30].

Plasma is a collage of neutral and charged particles moving randomly in a confined space or electrically neutral. In this glow discharge technique the substrate is completely immersed in the plasma. PECVD, in which any hydrocarbon gas species is used as a precursor, is probably the most popular means to deposit a-C:H films. It has been reported that above certain energy of the impinging species, the type of precursor has no significant impact on the properties of DLC [31].
Figure 3.5. Deposition techniques for diamond-like carbon (a) Parallel plate rf PECVD; (b) Parallel plate DC PECVD. Both the techniques are from gaseous hydrocarbon precursor [29].

In dc PECVD technique, the deposition chamber is configured with cathode and anode plates, with the substrate attached to the cathode to maximize ion bombardment and the anode plate is usually grounded. The anode could be a secondary electrode as shown in the Figure 3.5(b). The bias voltage and the deposition pressure are the important parameters which help in minimizing the sputtering of atoms from the film surface. The bias voltage ionizes the hydrocarbon precursor producing plasma thereby attracting the ions required for the growth of the film. The bias voltage generally varies from -100 V to -1000 V and the processing pressure varies from 10 to 100 mtorr. The main limitation of this technique is that the substrate must be electrically conductive for the film to be deposited, which restricts the choice of the substrate [32].

In rf glow discharge technique, there is no constraint in picking the substrate because it can deposit DLC films on insulating substrates. A common rf glow discharge technique is shown in Figure 3.5(a). It uses capacitively coupled parallel plate rf discharge and the radio frequency used in these processes is generally higher than the ion plasma frequency (ranges from 2-5 MHz). Thus, the electrons can follow the rf voltage
but the ion cannot. The difference in the electron and ion mobility produces a negative dc self bias on the powered electrode.

### 3.3 Influence of Deposition Method on Film Structure, Composition and Properties

The primary need to optimize the production of DLC films is effective process control, mainly the tailoring of adhesion properties. To be used as a tribological coating, DLC films must adhere well to the substrate material, and the adhesive forces must overcome the high internal stresses that would otherwise cause film delamination [33]. Adhesion can be affected by the deposition method, in combination with the nature of the substrate. Whatever the deposition method, DLC films are referred to as nanosmooth because they are generally smooth and averaged to the order of tenths of a nanometer.

All the methods of deposition are characterized by the interaction of energetic species with the surface of the growing film. The growth and properties of the DLC films are affected by the energy of the species impinging on the surface during deposition and by the substrate temperature rising from the energy of the species. Above a temperature (>250°C), a noticeable decrease in the sp³ content and density is generally observed. The structure and composition of the films (H content, C hybridizations, fraction of H bonded to C, nature of bonds, alloying elements) are also strongly influenced by the average impact energy of the particles that impinge on the growing surface and by deposition temperature. Thus, the film properties are greatly influenced by the specific deposition technique and growth conditions. Table 3.3 illustrates the composition, structure and various properties of a-C and a-C:H films. In hydrogenated films, an increase in hydrogen content is usually associated with a decrease in hardness, Young’s modulus, coefficient of friction, compressive stress, thermal stability, density, refractive
index and an increase in band gap and electrical resistivity; when compared to non-hydrogenated films.

In PECVD processing of DLC films, the flux energy defined as the transfer of energy through the gases by convection has been proved experimentally [34] to be very effective in altering the film properties. Very low impact energies lead to the formation of a polymer-like structure because the hydrocarbon precursor is not decomposed sufficiently. The hydrogen content decreases significantly and sp³ carbon-carbon bonding

### Table 3.3. Range of DLC structure, composition and properties [21].

<table>
<thead>
<tr>
<th>Variable</th>
<th>a-C</th>
<th>a-C:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen content, at%</td>
<td>&lt;5</td>
<td>20-60</td>
</tr>
<tr>
<td>sp³, %</td>
<td>5-90</td>
<td>20-65</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1.9-3.0</td>
<td>0.9-2.2</td>
</tr>
<tr>
<td>Thermal stability, ºC</td>
<td>&lt;600</td>
<td>&lt;400</td>
</tr>
<tr>
<td>Optical gap, eV</td>
<td>0.4-1.5</td>
<td>0.8-4.0</td>
</tr>
<tr>
<td>Electrical resistivity, Ω/cm</td>
<td>10²-10¹⁶</td>
<td>---</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>1.8-2.4</td>
<td>---</td>
</tr>
<tr>
<td>Compressive stress, GPa</td>
<td>0.5-5</td>
<td>---</td>
</tr>
<tr>
<td>Hardness, GPa</td>
<td>&lt;80</td>
<td>&lt;60</td>
</tr>
<tr>
<td>Young’s Modulus, GPa</td>
<td>&lt;900</td>
<td>&lt;300</td>
</tr>
</tbody>
</table>
is promoted at intermediate levels of energy. A completely disordered graphite-like structure is reported to form at very high impact energies [35]. So it is very important to control the concentration of the gaseous species, bias voltage utilized and the processing pressures which affect the impact energy in plasma-assisted deposition methods.

The introduction of dopants in DLC generally brings a decrease in compressive stress due to the partial interruptions of the interconnections between the random carbonaceous networks. The specific chemical composition of the modified films strongly influences the surface energy, depending on the nature of the dopant and may modify various physical properties, making some doped DLC films suitable for various applications [36].

3.4 Structure, Bonding Regimes and Properties of DLC Films

Carbon, the main component of DLC films can exist in different allotropic forms such as diamond, graphite, fullerenes, polymers, etc. Diamond has a tetrahedral structure with a three-dimensional network of strong covalent bonds between the carbon atoms. On the other hand, graphite is very soft and thermodynamically stable. It has hexagonal structure and the basal planes in which hexagonal rings are present, are weakly bonded to each other by Van der waals bonds. Lubrication for graphite is provided by these planes sliding with ease on each other.

DLC films consist of a network of four-fold coordinated sp³ hybridized sites, as in diamond, and the three-fold coordinated sp² hybridized sites, as in graphite, with some carbon atoms terminated with hydrogen. A short-range order of this hybridization is observed in DLC films; hence they are amorphous in nature. However, microcrystalline phases of diamond have been seen in some DLC films especially with lower hydrogen.
The DLC films are said to be diamond-like if the sp$^3$ bonding is dominant, and are graphite-like with a predominant sp$^2$ bonding. The hydrogen content, deposition method and amount of doping determine the amount of sp$^3$ and sp$^2$ content in the film. DLC films also can include a network of sp$^1$ sites as in acetylene. The composition of DLC can be best shown by ternary phase diagram shown previously in Figure 3.1.

The bonding and hydrogen incorporation in hard and polymer-like a-C:H films and other relevant properties are included for comparison in Table 3.4. It has been shown that hydrogen in hard DLC is mainly incorporated as monohydride [37] with a typical CH: CH$_2$: CH$_3$ ratio of 60:40:0. In contrast larger hydrogen content in soft, polymer-like films results in a higher relative concentration of di-hydride [32]. It is evident that hard DLC films have higher sp$^3$ content, compared to polymer-like DLC films.

A detailed structure of DLC has not been completely determined till today. Various models have been proposed with ambiguity in each of them. McKenzie et al. [38] proposed a model describing DLC as nano-crystalline two-phase structure consisting of polycyclic aromatic hydrocarbon regions interconnected by tetrahedral carbon. Angus and Jansen [39] based their model on theories of random covalent network (RCN). They have 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. Robertson [40] also modeled the structure of DLC as a network of covalently bonded carbon atoms in different hybridization. Angus and Wang [41] proposed a two dimensional representation of DLC film structure as shown in Figure 3.6.
Figure 3.6. A 2-D representation of diamond-like carbon film structure [41].

Table 3.4. Bonding and hydrogen incorporation in hard and polymer-like a-C:H. Other relevant properties are included for comparison [32].

<table>
<thead>
<tr>
<th>Property</th>
<th>a-C:H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(hard)</td>
</tr>
<tr>
<td>sp(^3) : sp(^2) : sp(^1)</td>
<td>68 : 30 : 2</td>
</tr>
<tr>
<td>CH(_3) : CH(_2) : CH</td>
<td>0 : 40 : 60</td>
</tr>
<tr>
<td>Optical gap (eV)</td>
<td>1.1</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.1</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.9</td>
</tr>
<tr>
<td>[H] total (at. %)</td>
<td>27</td>
</tr>
</tbody>
</table>
3.5 Tribology of DLC Thin Films

Tribology derives from the Greek *tribos* meaning I rub. Formally defined, it is the science and technology of interacting surfaces in relative motion and all practices related thereto. In other words, it is the science of the mechanisms of friction, lubrication and wear of contacting surfaces that are in relative motion.

There has been extensive research in the past two decades in characterizing the tribological behavior of DLC films due to their high wear resistance and very low friction coefficients [18, 21, 29, 33, 42-45]. The wear and friction of DLC films are greatly affected by:

1. Nature of the film (controlled by deposition process)
2. Tribotesting conditions
   (a). Material parameters (nature of the substrate)
   (b). Mechanical parameters (contact pressure, type of contact)
   (c). Kinematic parameters (nature of motion, speed)
   (d). Physical parameters (temperature during friction) and
   (e). Chemical parameters (nature of the environment such as relative humidity etc.)

Thus, a wide range of tribological properties have been reported in the literature for DLC films. The tribological experiments conducted earlier have shown that DLC films are sensitive to the environmental parameters [46].

3.5.1 Wear Mechanism

The friction coefficient of DLC films ranges from < 0.01 to > 0.5, depending on the nature of the DLC film and the nature of tribotesting conditions. The coefficient of
friction of hydrogenated a-C:H films in vacuum typically ranges from 0.007 to 0.02, and in ambient conditions (20% < Relative Humidity < 60%) from 0.1 to 0.4 [47]. Scratchable films with almost no resistance as well as films with very low Archard wear rates (as low as $10^{-8}\text{mm}^3/\text{Nm}$) can be produced.

Hydrogen free films generally exhibit lower friction (<0.15) compared to hydrogenated DLC films. In ta-C films, friction causes a local shear induced graphitization at the microscopic scale and consequently, it is not a surprise to observe a decrease in friction of ta-C films with increasing humidity [48]. On the other hand, friction of a-C:H films increases with humidity [49]. Unlike friction, the performance of wear resistance is complicated. Extremely low wear rates can be achieved for both ta-C as well as a-C:H films. The findings of Grill et al. [50] show that the optimization of the wear resistance of DLC films required strong attention to the control of the deposition procedure.

In inert environments, including dry N and vacuum, friction coefficients can reach either ultralow values (as low as 0.01 or less) or high values (>0.5) [51, 52]. It has been shown that this binary friction behavior, under ultra high vacuum (UHV) conditions during tribological tests, can be controlled by the hydrogen content of the films [53]. Hydrogen concentrations lower than 34% lead to high friction and ultralow friction is achieved with films that contain at least 40 at% H.

Such tribological behavior has been attributed to transfer layer formation at the asperity contact [43]. The transfer layer behavior during wear of DLC is elaborated in the following section.
3.5.2 Role of Transfer Layer Formation in DLC Films

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 has a lubricating effect [42-45]. The very low friction and reasonably long life of DLC films is explained by a transfer buildup followed by an interfilm sliding mechanism in a velocity accommodation mode [21]. Transfer layer formation is associated with significant wear in the initial stages. The interfilm sliding mechanism exists when a transfer layer forms at the contact area, not allowing physical contact between the DLC film and the counter surface of the pin.

The transfer layer is formed by a friction-induced transformation of the top layer of the DLC film and is a low shear strength layer [18]. This transformation may be caused by friction induced annealing by thermal and strain effects generated during sliding [50]. A wear-induced graphitization mechanism has been put forward by Liu and Meletis [18] to account for the transfer layer formation and subsequent tribological behavior. They provided direct TEM evidence showing extensive graphitization in the transfer layers. The composition of the transfer layer can also be affected by the material of the sliding counterpart. The ultra-low wear rates and low friction of DLC can be explained by the low shear strength of the transfer layer.

The Archard wear rates for DLC films in general, are as low as $10^{-8}$ mm$^3$/Nm [45]. Addition of metals or other elements such as silicon into the films can lead to further reduction in wear rate [53]. In addition, experiments have shown that these elements can improve the adhesion between DLC films and their substrates. Thus, adhesion is a very important property of the film for the formation of transfer layers and
the existence of interfilm transfer mechanism to enhance friction and wear properties. 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 [54].

3.6 Applications of DLC

Diamond-like carbon films are suitable for various applications by choosing the right deposition technique and deposition parameters. The unique properties include low friction coefficients and high wear resistance, infrared transparency, chemical inertness, high electrical resistivity, low dielectric coefficient and excellent biocompatibility. The conventional DLC films have been widely used for practical purposes [29, 55].

DLC films are famous in application for wear and corrosion protection of magnetic storage media such as magnetic disks and magnetic heads, and they are nano smooth and very thin (<5 nm) [56]. The coating also extends the life and reliability of the disks by reducing wear and friction. The property of infrared transparency of DLC is used in antireflective and scratch-resistant, wear-protective coating for IR optics made of Ge, ZnS, and ZnSe [57]. The low deposition temperature of DLC permits as a protective wear coating layer on plastic products such as polycarbonate sunglass lenses. The latest Gillette’s Mach 3 Turbo and M3 Power have been reported to use DLC as a protective coating to improve the quality and performance of the blades.

DLC is biocompatible and has been used in biological applications such as heart valves and stents. As these films are impermeable to liquids and chemically inert, they could be used to protect biomedical implants against corrosion. DLC coatings on the components of artificial heart valves and hip joint implants such as stainless steel and Ti alloys, has been found to be totally compatible and improving the performance of these
components. Table 3.1 shows the various wide range applications with each unique property of DLC films.

3.7 Formation of N-DLC by Nitrogen Doping in DLC

Amorphous carbon-based films exhibit a unique combination of properties such as high hardness, high wear resistance and low friction as discussed in the previous sections. Recent investigations in the past decade have been dedicated to the introduction of additional elements, such as silicon, fluorine and various metals, in the carbonaceous network to modify the properties of conventional DLC coatings, in particular the wear and friction behavior under various conditions [23].

The study on nitrogen doped DLC thin films was primarily driven with the intention to synthesize a new form of carbon nitride phase (cubic beta carbon nitride $\beta-C_3N_4$) predicted theoretically by Liu and Cohen [5], that exhibits extremely low compressibility, superhigh hardness and bulk modulus that exceed those of natural diamond. However, almost all the N-DLC films synthesized so far have been amorphous in nature. These amorphous carbon nitride films being softer than diamond still exhibit excellent tribological properties especially when used as a protective coating on computer hard drive systems [58, 59]. One way to deposit these films has been to incorporate nitrogen in the DLC matrix by several methods as proposed by Wan and Egerton [60].

The crystal structure of $\beta-C_3N_4$ is similar to $\beta-Si_3N_4$, where C replaces Si to achieve an atomic bond configuration favoring extreme hardness and bulk modulus. As hardness is inversely proportional to bond length and also to the radii of the bonding atoms, Cohen predicted that such compounds based on C and N, which have very small atomic radii and the strongest bonds, will exhibit the highest hardness. Based on these
theories, many research scientists have tried to synthesize $\beta-C_3N_4$ in both bulk and thin film forms by various methods, with the expectation that it would lead to the future emerging super hard and wear-resistant materials. $\beta-C_3N_4$ provides excellent thermal conductivity and wide bandgap, in addition to its unique mechanical properties [61, 62].

During the past fifteen years, several new methods have been developed to synthesize crystalline $\beta-C_3N_4$ films. In spite of their intense research efforts, successful synthesis of crystalline $\beta-C_3N_4$ has not yet been fully achieved. PVD and CVD methods such as laser ablation, rf and dc magnetron sputtering, ion-beam deposition, ion implantation, plasma arc deposition, UV-assisted chemical synthesis, hot-filament CVD, dc and rf PACVD have produced amorphous carbon nitride films with low N contents(<30%)[21]. One main reason for the low N content is the extremely high bond dissociation energy of N in gas discharge plasmas. Among these films there were reports showing a presence of small crystallites with electron diffraction patterns matching $\beta-C_3N_4$ [14, 15].

It has been reported that the nitrogen incorporation in DLC may form N-H, C=N, C≡N bonds which decrease the fraction of sp$^3$ carbon bonds, obstruct the carbon-carbon cross links, and form voids in the matrix resulting in softer a-C:H:N films [6]. Also the hardness, density and deposition rate of these films decreases owing to the formation of the above bonds, with a decrease in the fraction of C sp$^3$ hybridization. It has been shown that up to 34 at. % of nitrogen can be incorporated in a-C:H:N films, reducing internal stresses in DLC while preserving hardness and wear resistance [16, 63-65]. However, very little work has been performed in this area and is insufficient to develop a clear picture as to how N incorporation affects the structure and properties of DLC. As
mentioned earlier, a significant role in the N-DLC film structure and properties is expected to be played by the particular deposition process used for synthesizing those films.

### 3.7.1 Tribology of N-DLC Films

The tribological performance of N-DLC thin films is expected to depend mostly on both the environmental conditions and the nature of the coating. Though these films are amorphous in nature with unambiguous reports of crystalline C$_3$N$_4$ phase, it has been reported that nitrogen incorporation in the DLC matrix decreases the fraction of C sp$^3$ hybridization to certain extent depending on the content of N in the film [66]. Indeed, the presence of C=N and C≡N bonds has often been detected by techniques such as XPS, infrared or electron energy loss spectroscopies.

The amorphous carbon nitride films produced by various research groups exhibit large variations in mechanical and tribological performance because of a large variation in their microstructure and chemical stoichiometry (C:N ratio). The friction coefficient values range from 0.05 to >0.5 in air, and much higher values were reported in high vacuum and dry environments. Such a large scatter in friction is ascribed to the difference in N content, extent of sp$^3$ and/or sp$^2$ hybridization, deposition methods and conditions, and, the mechanical properties of the film. It has been shown that N-DLC films deposited with more N (>70%) in the sputtering gas exhibit higher friction and wear coefficients than films grown with lower content of nitrogen during deposition [66]. Similar relationships were found between friction and wear properties of N-DLC films, C:N ratio and deposition conditions [67-69]. Zou et al., reported steady-state friction coefficients of 0.08-0.14 for N-DLC films produced by reactively ionized cluster beam technique [70].
N-DLC films deposited by PACVD on Si substrates from CH$_4$ + NH$_3$ mixture exhibited surface roughness increasing with the amount of nitrogen in the film, from 0.12nm at 0 at.% N to 0.26nm at 11 at.% N [65]. The increase in roughness is ascribed to the increase in sp$^2$ carbon bonds and of the number and size of graphitic domains with increasing nitrogen content.

Koskinen et al. reported the tribological properties of N-DLC films deposited by pulsed vacuum arc method on Si and metallic substrates with N concentrations up to 34% [16]. The films exhibited compressive stress much lower than pure DLC, allowing the growth of thicker films with good wear resistance. The pin-on-disk tribology experiments showed a decrease in friction coefficient from 0.4 to 0.1-0.2 in an initial run-in period, then gradually increased to 0.25-0.3 after 100,000 revolutions at 2.2 N normal load on 100 Cr6 ball-bearing steel. It was found that the friction coefficient increased with increasing nitrogen content. The wear rates varied from 0.1 to $0.5 \times 10^{-7}$ mm$^3$/Nm as the nitrogen content increased from 0 to 34 at. %.

The wear rates of carbon nitride coated disks were reported to be 10 times lower than those of disks coated with commercial DLC film of same thickness [58]. Also these films provided 3 to 30 times longer wear life than commercial C coatings. This is one of the important tribological applications now commercially used in the coating of amorphous carbon nitride films on magnetic hard disks as protective coatings.
3.7.2 Significance of Low Nitrogen Content in the Film

One main reason for using low N contents is the extremely high bond dissociation energy of N in gas discharge plasmas. Reports showed a presence of small crystallites with electron diffraction patterns matching $\beta$-C$_3$N$_4$ [14, 15].

The actual behavior of nitrogen is difficult to comprehend because of the presence of both sp$^2$ and sp$^3$ carbon bonding. At low N contents, if N enters the ta-C in a sp$^3$ site, it will act as a substitutional dopant [71]. At higher nitrogen concentrations and above a certain transition temperature fullerene-like carbon films are formed [72, 73]. This transition temperature from diamond-like to graphite-like differs from one deposition method to the other. At lower N contents (at. % <7%) the film resistivity decreases indicating a high graphitic content [74]. Here nitrogen acts as a thermally activated impurity center in graphitic structures and contributes to the electrical conductivity, but at high nitrogen contents the resistivity increases up to 2 times its magnitude inducing a change in the microstructure to pyridine-like structures and nitrile bonds. Thus, at high N content, these bonds break the interconnection of the graphitic structure of the film and reduce the conduction path of the carriers [74].

The saturation and decline of N incorporation at higher pressures might be explained by a reduction of ionization (the prime deposition mechanism of carbon and nitrogen is mainly due to ions) due to recombination processes [75]. Morrison et. al., proposed that high-energy nitrogen species (100 eV) can be implanted into the ta-C matrix, while the low-energy species tend to etch it [76]. At higher pressures there exist more low-energy species, and hence etching of the carbon matrix by nitrogen might be another reason for the decline of nitrogen content with pressure.
Kleinsorge et al. [75] proposed that in a filtered cathodic vacuum arc (FCVA) deposition method, the doping range from 0 to about 0.4% changes the conductivity while the optical gap and $sp^3$ content remain constant. Nitrogen doped regimes from 0.4% - 10% make the existing $sp^2$ sites condense into clusters and reduce the band gap. Nitrogen contents over 10% change the bonding from $sp^3$ to $sp^2$ drastically. Figure 3.7 shows the variation of $sp^3$ content deposited at room temperature as a function of nitrogen content. Hu et al. found a transition from $sp^3$ to $sp^2$ at 12% nitrogen concentration [77]. Similar results have been observed by Davis et al. [78].

![Figure 3.7. $sp^3$ fraction Vs. Nitrogen content for room temperature deposition [75].](image)

The surface roughness tends to be lower with low nitrogen content in the film [65]. Also the friction coefficient and wear rates are lower for low nitrogen content films [16]. Thus, there is evidence suggesting that the use of low nitrogen contents in the film is desirable in terms of tribological as well as mechanical performance. An attempt was made in the present study to incorporate (dope) DLC films with N in low amounts and study the tribological behavior.
3.8 Applications of N-DLC Thin Films

Nitrogen doped DLC films can exhibit comparable tribological properties as that of DLC but may decrease the internal compressive stresses and improve adhesion. Their applications can spread widely when properly synthesized. Carbon nitride films exhibit diamond-like resistivity and thermal conductivity, hence can be used in applications such as thermal management in multichip modules and reduced dimension devices which require insulating materials with high thermal conductivity [79]. N-DLC coatings are environmental friendly and have been used as coatings on disposable electrodes [80]. As far as tribological applications are concerned, these films are currently used as protective coatings in magnetic hard disks and the wear rates were found to be 10 times lower than those of the disks coated with a commercial DLC film of same thickness [58]. Also the films are expected to provide 3-30 times longer wear life than commercial C coatings. Thus, further study of N-DLC may be rewarding in terms of modifying the DLC structure and enhancing film properties.
4. EXPERIMENTAL DESIGN AND PROCEDURES

DLC is typically produced using methane and Ar plasma. A preliminary study was conducted first to investigate the effect of Ar % dilution on DLC characteristics. Based on this study, N\textsubscript{2} was added in the Ar % dilution at CH\textsubscript{4}/Ar ratio that exhibited the best mechanical and tribological behavior. All coatings and plasma treatments were performed in our laboratory utilizing a multi-purpose surface modification system. The capabilities of the Intensified Plasma Assisted Processing (IPAP) system include: intensified plasma nitriding, dual magnetron co-sputter deposition, ion-beam deposition and ion-beam and plasma-assisted deposition. A description of the deposition system, characterization techniques and parameters involved in the characterization of these films are provided in the following sections.

4.1 Synthesis of DLC Films

4.1.1 IPAP System

The IPAP system in our laboratory allows three different modes of operation, such as conventional and intensified plasma assisted processing, ion beam assisted deposition, and magnetron sputter deposition [81]. A schematic of the system is shown in Figure 4.1. The chamber has a height of 0.56 m and a diameter of 0.45 m. The system consists of a base plate connected to the mechanical and diffusion pumps and holding two magnetrons; an ion beam gun and a thickness monitor. The specimen holder is mounted at the top plate. All the remaining ports accommodating electrical and mechanical feedthroughs are in the cylindrical chamber.

Various gases can be introduced into the chamber. The flow rate is controlled individually for each gas by MKS mass-flow meters. Vacuum level in the chamber is
monitored by an absolute digital pressure gauge. In the lower region of the system below the base plate, there are two thermocouple vacuum gauges to monitor pressure in the fore-line to the diffusion pump and the bottom of the chamber. Vacuum in this system is maintained by a diffusion pump backed with a mechanical pump. The baratron vacuum gauge can measure above 1 mtorr. Pressure below this level is monitored by an ionization gauge connected to a Digital Gauge Control.

The plasma in the chamber is generated by application of a dc bias between the substrate and the grounded wall of the chamber. The system is also capable of depositing films by PVD with the aid of two magnetron guns holding target materials at an angle of 45°. A Kaufman’s ion gun is used to deposit films by ion beam method in the system.

![Figure 4.1. Schematic of the IPAP system with triode configuration.](image-url)
The intensification of the plasma in the system is achieved by a thermionic emission filament and a positive electrode. The filament is made from 0.5 mm diameter tungsten wire. An austenitic (non-magnetic) stainless steel plate (8 cm X 6 cm) is used as the positive electrode and is positioned diametrically opposite to the filament. The thermionically emitted electrons from the filament are attracted by the positive bias applied to the positive plate. In their path, electrons interact with gas ions and neutrals present in the plasma, thereby increasing ionization and intensifying the plasma.

4.1.2 Procedure for Deposition of DLC and N-DLC Films

The DLC and N-DLC thin films were deposited on single crystal Si (100) $p$-type wafers. Samples, of 5 cm diameter were ultrasonically cleansed with acetone and dried in air before mounting inside the chamber. The sample was masked at three different positions at the edges to prevent deposition. These masked areas were later used to measure the thickness of the coating. The chamber base pressure was in the order of $10^{-6}$ torr. The deposition chamber was purged twice by letting Ar gas into the chamber. The substrate was sputtered cleaned with Ar at a bias voltage of -1000 V, with the chamber pressure of 100 mtorr and a flow rate of 20 sccm for 20min. This is to remove contamination on the surface of the Si wafer.

DLC film was deposited by using dc plasma (diode configuration) generated between the negatively biased substrate and the grounded chamber, in a discharge composed of CH$_4$ and Ar. Processing pressure and bias voltage resulting in quality DLC films were obtained from previous studies [82]. Hence, all the DLC and N-DLC films were deposited maintaining a processing pressure of 100 mtorr and of -1000 V bias voltage. The impacting energy of species on the surface of the film is the controlling
factor of the sp$^3$ content in the film. Low energy plasma produces a polymeric film whereas very high energy graphitizes the film producing high sp$^2$ content. Intermediate energy has been found to produce high sp$^3$ content [82]. The values for the bias voltage and processing pressure were chosen in such a way to produce intermediate levels of flux energy.

For the deposition of N-DLC films, the substrate was sputter cleaned using the same process as noted earlier for DLC films. The desired amount of N$_2$ gas was introduced into the chamber in addition to Ar and CH$_4$ while maintaining the same chamber pressure. The temperature in the chamber remained $<100^\circ$C during film deposition.

The deposition conditions of the DLC and N-DLC films are shown in Tables 4.1 and 4.2 respectively. The ratio of Ar: CH$_4$ was varied in order to explore a wide variety of DLC films pertaining to mechanical as well as tribological properties. The results of the preliminary experiments showed that DLC films deposited with Ar: CH$_4$ ratio of 4:1 showed prominent mechanical and tribological behavior. Thus, the (Ar + N$_2$): CH$_4$ ratio was chosen such that the CH$_4$ content remained constant at 20%. Three different NDLC films were deposited with N concentrations of 5%, 10% and 15% and the (Ar + N$_2$) content at 80% such that (Ar + N$_2$): CH$_4$ ratio is (75+5):20, (70+10):20 and (65+15):20.
Table 4.1. Deposition parameters for DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Bias voltage (V)</th>
<th>Pressure (mtorr)</th>
<th>Flow Rates ((\text{CH}_4 : \text{Ar})) in sccm</th>
<th>Ar % Dilution</th>
<th>Processing Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC2</td>
<td>-1000</td>
<td>100</td>
<td>20:4</td>
<td>16.66</td>
<td>2.5</td>
</tr>
<tr>
<td>DLC3</td>
<td>-1000</td>
<td>100</td>
<td>20:10</td>
<td>33.33</td>
<td>2.5</td>
</tr>
<tr>
<td>DLC4</td>
<td>-1000</td>
<td>100</td>
<td>20:20</td>
<td>50</td>
<td>2.5</td>
</tr>
<tr>
<td>DLC5</td>
<td>-1000</td>
<td>100</td>
<td>20:30</td>
<td>60</td>
<td>2.5</td>
</tr>
<tr>
<td>DLC6</td>
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<td>100</td>
<td>20:47</td>
<td>70</td>
<td>1.5</td>
</tr>
<tr>
<td>DLC7</td>
<td>-1000</td>
<td>100</td>
<td>15:60</td>
<td>80</td>
<td>1.5</td>
</tr>
<tr>
<td>DLC9</td>
<td>-1000</td>
<td>100*</td>
<td>15:40</td>
<td>72.7</td>
<td>1.5</td>
</tr>
<tr>
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<td>-1000</td>
<td>100</td>
<td>5:45</td>
<td>90</td>
<td>6.0</td>
</tr>
</tbody>
</table>

*Films deposited at 20 mtorr for first 10min and then 100 mtorr for the rest

Table 4.2. Deposition parameters for N-DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Bias voltage (V)</th>
<th>Pressure (mtorr)</th>
<th>Flow Rates ((\text{CH}_4: \text{Ar}:\text{N})) in sccm</th>
<th>Processing Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDLC1</td>
<td>-1000</td>
<td>100</td>
<td>20:75:5</td>
<td>1.5</td>
</tr>
<tr>
<td>NDLC2</td>
<td>-1000</td>
<td>100</td>
<td>20:70:10</td>
<td>1.5</td>
</tr>
<tr>
<td>NDLC3</td>
<td>-1000</td>
<td>100</td>
<td>20:65:15</td>
<td>1.5</td>
</tr>
</tbody>
</table>
4.2 Characterization of DLC and N-DLC Films

4.2.1 Thickness

The masked sections of the Si wafer were used to measure film thickness. The thickness of the film was measured by a WYKO NT1100 and/or NT3300 surface optical profilometer. This device works on the principle of interference of light. The deposition rate of the films is equal to the ratio of observed thickness to the total deposition time. Figure 4.2 shows the substrate attachment to the holder.

Figure 4.2. (a) Si wafer mounted on the stainless steel holder (b) Si wafer after deposition.

4.2.2 Mechanical Properties

One of the main purposes of the DLC films is to function as a protective coating, and hence hardness of the films becomes vital. Hardness also reflects porosity, density and surface quality of thin films [81]. The hardness of the films was measured by Knoop microhardness measurements.

Micro indentation experiments were conducted by using a Zeiss microhardness tester. The load was applied smoothly on to the Knoop diamond indenter for a fixed time.
and with a fixed load. The rhombohedral shape of the knoop indenter minimizes the elastic recovery. The long axis of the indentation was measured and the hardness was calculated by using the following formula:

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

Here ‘$P$’ is the load in g, and ‘$l$’ is the length of the longer diagonal of the indent on the film in $\mu$m. Hardness measurements were taken at different locations with 10 g and 25 g load. The reported values are the average of at least four measurements.

### 4.2.3 Microstructural and Compositional Characterization

#### 4.2.3.1 Transmission Electron Microscopy (TEM)

The TEM analysis of the produced films was performed using a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å. TEM analysis was conducted in both plan view and cross-sectional modes. Cross-sectional slices were obtained by cutting the samples along a direction normal to the coating surface and then gluing the coated surfaces face to face. Cross-sectional specimens for TEM observations were prepared in stages of mechanical grinding, polishing, and dimpling followed by Ar$^+$ milling using a ‘Gatan Precision Ion Polishing System’ (PIPS$^{TM}$, Model 691) at 4.5 keV, at an angle of 5°. The structure of the films was studied by selected area electron diffraction (SAED) pattern analysis.

#### 4.2.3.2 Scanning Electron Microscopy (SEM)

A Hitachi 4500-II SEM equipped with Energy Dispersive Spectrometry (EDS) detector was used to investigate the surface morphology and composition of the 440C
steel pins used in tribology experiments. The transfer layer present in the steel pins was analyzed by SEM and EDS after the tribology tests.

4.2.3.3 X-ray Photoelectron Spectroscopy (XPS)

Core level XPS stands out as a useful and non destructive tool for investigating the local binding properties of specific atoms. In this technique, the kinetic energy of photo-excited core electrons is determined as a measure of their binding energy. XPS of all the films was performed on an AXIS 165 Kratos analytical system integrated with Auger Electron Spectroscopy (AES). DLC and N-DLC film specimens cut to the required size were mounted on studs and introduced in the chamber under high vacuum. This technique allows analysis of the film characteristics up to a depth of 10 nm from the surface. The surface was first Ar ion sputtered (etched for 2 minutes in four cycles) and the analysis was performed after each step of sputtering to characterize the chemical state of the elements present in the coatings. High resolution (HR) profiles of the peaks were also taken to investigate the chemical state of the carbon atoms.

In order to analyze the chemical state of C in selected DLC films and the chemical state of C and N in NDLC films, deconvolution of the HR peaks was performed in Origin software. The ratio of sp³ and sp² content in DLC and NDLC films was also determined by the known area subjected to analysis. The atomic % of N in the NDLC films was found by using this technique.

4.2.4 Tribological Testing

The tribological behavior of DLC and NDLC films was studied by pin-on-disc experiments using an ISC-200 tribometer. The device uses a simple load arm with a tangential force sensor mounted close to the contact point to reduce error due to arm
compliance. A pin or a sphere is loaded onto the test sample with a known weight. The pin is mounted on a lever, designed as a frictionless force transducer. Pins of different material and size can be used.

The pin material used in the present study was 440C steel ball of 9.5 mm diameter. The wear experiments were performed in laboratory air having a relative humidity of 50 ± 10%, at a sliding velocity of 0.1 m.s⁻¹ and for a distance ranging from 1000-5000 m. In our present wear tests, two different loads (1N and 5N) were chosen to investigate their effect on the tribological behavior of DLC and NDLC films. The friction coefficient (µ) was monitored continuously during the test run by a linear variable-displacement transducer and recorded on a data acquisition computer.

The wear rate was calculated from the trace of the surface profile (average of three to four traces), taken across the wear track by optical profilometry. A surface optical profiler, WYKO NT1100 and/or NT3300, was used for obtaining the wear track profile. The wear volume was measured by multiplying the cross sectional area of the wear track by the length of the wear track. The wear rate of the films was calculated by using the formula:

\[ \text{WEAR RATE} = \text{Wear volume (mm}^3\text{)} / \left[ \text{load (N)} \times \text{total sliding distance (m)} \right] \]

The wear volume of the ball was calculated by measuring the diameter of the wear scar with optimal microscopy and then using the formula:

\[ W_p = \pi d^4 / 64r \]

where \( W_p \) is the pin wear volume, \( d \) is the average diameter of the scar and \( r \) is the pin radius.
4.3 Thermal Stability of N-DLC Films

Akkerman et al. [17], proposed that graphitization of DLC films occurs above 400°C with the liberation of hydrogen and by the gradual conversion of sp\(^3\) carbon bonding to graphitic sp\(^2\) bonding. Thus, thermal stability of DLC as well as N-DLC films is very important to prevent or delay ‘wear-induced graphitization’ [18]. It has also been reported that improvement of thermal stability in DLC films can be obtained through incorporation of Si [83]. In the present study, thermal stability of DLC and N-DLC films was investigated by conducting thermal annealing experiments at temperatures of 300°C, 350°C and 400°C for duration of 30 minutes. Microhardness of DLC and N-DLC coatings was measured following each annealing treatment. Graphitization in DLC as well as N-DLC films is accompanied by a sharp decrease in hardness and thus, is indicative of the transformation of the sp\(^3\) C-C bonding to sp\(^2\) C-C bonding.
5. RESULTS AND DISCUSSION

PART I

5.1 Effect of Ar Plasma Dilution on DLC Characteristics

A preliminary investigation was carried out to determine the processing parameters for producing DLC films that subsequently will be doped with N. Gupta et al. [84], have indicated that a deposition pressure of 100 mtorr and bias voltage of -1000 V can be utilized for depositing hard DLC films with good tribological properties. An investigation was conducted in the present study on the effect of Ar % dilution in the plasma while keeping the bias voltage and pressure constant at -1000 V and 100 mtorr respectively. Based on this study the parameters for synthesizing the best DLC film in terms of CH₄/Ar ratio were chosen to deposit the N-DLC films. The processing parameters involved in the deposition of DLC films and their mechanical and tribological properties are listed in Table 4.1, Table 5.1 and Table 5.2, respectively.

Table 5.1 Mechanical properties of DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Ar % Dilution in Plasma</th>
<th>Thickness (nm)</th>
<th>Deposition Rate (nm/min)</th>
<th>Hardness, Hₓ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 gr</td>
</tr>
<tr>
<td></td>
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<td>25 gr</td>
</tr>
<tr>
<td>DLC2*</td>
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<td>4200</td>
<td>28.0</td>
<td>18.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.85</td>
</tr>
<tr>
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<td>3850</td>
<td>25.6</td>
<td>23.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.92</td>
</tr>
<tr>
<td>DLC4</td>
<td>50</td>
<td>3640</td>
<td>24.3</td>
<td>18.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.43</td>
</tr>
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<td>DLC5</td>
<td>60</td>
<td>3240</td>
<td>21.6</td>
<td>21.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.74</td>
</tr>
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<td>DLC6</td>
<td>70</td>
<td>1600</td>
<td>17.8</td>
<td>27.54</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>20.57</td>
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<td>10.2</td>
<td>29.75</td>
</tr>
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<td></td>
<td></td>
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<td>22.19</td>
</tr>
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<td>13.1</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.45</td>
</tr>
<tr>
<td>DLC12</td>
<td>90</td>
<td>1350</td>
<td>3.7</td>
<td>22.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.66</td>
</tr>
</tbody>
</table>

* Discontinuous film
Table 5.2. Tribological properties of DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Ar % Dilution in plasma (Ar %)</th>
<th>( f_{ss}^{**} ) (Load=1 N)</th>
<th>( f_{ss}^{**} ) (Load=5 N)</th>
<th>Wear rate (mm(^3)/Nm) Load=1 N</th>
<th>Archard wear rate (mm(^3)/Nm) Load=5 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC2*</td>
<td>16.66</td>
<td>0.18</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>DLC3</td>
<td>33.33</td>
<td>0.215</td>
<td>0.125</td>
<td>13.0\times10^{-7}</td>
<td>1.37\times10^{-7}</td>
</tr>
<tr>
<td>DLC4</td>
<td>50</td>
<td>0.19</td>
<td>0.109</td>
<td>2.35\times10^{-7}</td>
<td>1.31\times10^{-7}</td>
</tr>
<tr>
<td>DLC5</td>
<td>60</td>
<td>0.2</td>
<td>0.12</td>
<td>1.96\times10^{-7}</td>
<td>1.46\times10^{-7}</td>
</tr>
<tr>
<td>DLC6</td>
<td>70</td>
<td>0.183</td>
<td>0.105</td>
<td>2.58\times10^{-7}</td>
<td>4.87\times10^{-8}</td>
</tr>
<tr>
<td>DLC7</td>
<td>80</td>
<td>0.144</td>
<td>0.09</td>
<td>1.74\times10^{-7}</td>
<td>8.66\times10^{-8}</td>
</tr>
<tr>
<td>DLC9</td>
<td>72.7</td>
<td>0.164</td>
<td>0.112</td>
<td>2.31\times10^{-7}</td>
<td>1.15\times10^{-7}</td>
</tr>
<tr>
<td>DLC12</td>
<td>90</td>
<td>0.13</td>
<td>0.06</td>
<td>2.14\times10^{-7}</td>
<td>1.6\times10^{-7}</td>
</tr>
</tbody>
</table>

* Discontinuous film  
** Steady-state friction coefficient

The DLC2 film deposited at very low Ar % dilution (16.66% Ar) flaked off at most areas due to high intrinsic stress and poor adhesion to the substrate. The thickness and hardness of that film was however taken at intermittent island spaces where the film was still present.

With increase of Ar % dilution the Ar ions bombard more intensively with the precursor ions and make the plasma denser. The ionization of methane precursor gas aids in relieving stresses and hence, more the Ar content less is the stress in the film. Also the larger number of Ar ions bombarding the surface of growing film might lead to the increased surface roughness at higher % dilution of Ar in the plasma. Too high dilution of Ar is also not desired because the Ar ions are more inclined to sputter the surface of the growing film at higher ionization energies. So, a harmony should exist in the film to
exhibit efficient mechanical and tribological behavior with minimal stresses and having good adhesion to the substrate.

The effect of Ar % dilution on the deposition rate and hardness of DLC films is shown in the Figure 5.1. The microhardness of the DLC films with different Ar plasma dilution ranged from 18-30 GPa for 10 g load and 16-22 GPa for 25 g load.

In the present study the films showed maximum hardness in the range of 70%-80% Ar plasma dilution for both 10 g and 25 g load with no or limited, if any, substrate effects. For example, DLC 12 is thicker than DLC 9. Hardness trend shows an increase with Ar % dilution and at higher dilution, hardness exhibited maximum values in the same range. The decrease in the hardness at 90% Ar in the plasma may be caused due to the sputtering of the growing film. As Ar % dilution increases (since Ar energy is the same under -1000 V) ionization increases along with the number of energetic Ar+/Ar bombarding the substrate. So, as Ar increases the numbers of energetic Ar+/Ar increase. The results show that up to a point the increase in energetic Ar bombardment is beneficial to hardness because the Ar assists in the breaking down of the CH₄ molecules. Beyond a certain point the disproportionally higher number of Ar may cause either graphitization or defect formation in the film reducing its hardness as reviewed in the literature.

A gradual decrease of deposition rate is observed with increasing Ar content, because the methane content decreased. The low-energy species at higher pressures (100 mtorr) and also the etching of the carbon matrix by argon might be another reason for the decline of deposition rates with Ar content in the film [75].
Figure 5.1. Effect of Ar % dilution on deposition rate and hardness of DLC films deposited at 100 mtorr pressure and -1000 V bias voltage.
The variation of steady-state friction coefficient as a function of Ar plasma dilution is shown in the Figure 5.2. The steady-state friction coefficient was measured with two different loads of 1 N and 5 N. The steady-state refers to the friction coefficient after initial breakdown as the friction coefficient stabilizes after certain distance. The steady-state friction coefficient varies in the range 0.06-0.12 for 5 N load and 0.13-0.21 for 1 N load in DLC films. A sliding velocity of 0.1 m.s\(^{-1}\) for a distance of 1500 m under a load of 1 N and 5 N produced a Hertzian stress of 0.25 and 0.43 GPa respectively. The friction coefficient values reported previously for DLC films tested at ambient conditions (20%-60% relative humidity) generally lay in the range of 0.05-0.4 [42, 43, 45], and are in agreement with the present results.

The steady-state friction coefficient decreased gradually with Ar content. Very low coefficient of friction values, as low as 0.06, were observed for DLC 12 at 5 N load. It was difficult to find the friction coefficient and wear rate of the DLC 2 film with 16.66 % Ar as the film flaked off at many areas. The coefficient of friction values of the films tested at 5 N load were lower compared to the values at 1 N. At higher loads (For example, 5 N) the contact area in the asperity increases and hence, the stress decreases followed by a reduction of friction coefficient. This has been observed in numerous previous experiments [42, 43].

The variation of Archard wear rate as a function of Ar plasma dilution is shown in the Figure 5.3. Wear rates as low as \(4.87 \times 10^{-8} \text{mm}^3/\text{N m}\) for DLC 6 were observed at a load of 5 N. With the exception of the films with low Ar all the remaining films showed low wear rates. The variation in the wear rates was minimal with increase in Ar % dilution for almost all the other films at respective loads. The DLC 3 film was tested for a
sliding distance of 1000 m for 1 N load and 1500 m for 5 N. Hence, the film exhibits higher initial wear rate at 1 N load. Also, the reason behind such a variation might be due to inconsistencies in the film structure. For example, the film slightly flaked to cause debris around the edges of the wear track even though it appeared good physically. The film DLC 3 might as well be considered as a transition film to obtain a DLC film with good mechanical and tribological behavior.

The films deposited at higher Ar content (≥50 %) exhibited better mechanical and tribological behavior compared to films deposited at or below 33.33 % Ar in the plasma. Hence, it is evident that the critical Ar content in a DLC film subjected to the present conditions must be greater than 33.33 % in order to exhibit desired mechanical and tribological behavior.

Figure 5.2. Effect of Ar % dilution on steady-state friction coefficient of DLC films deposited at 100 mtorr pressure and -1000 V bias voltage.
5.2 Analysis of DLC Films

Four of the DLC films were selected for further analysis in order to choose the conditions for synthesizing N-DLC films. The rationale behind their selection was to include films at both ends of the Ar plasma dilution (i.e., low and high Ar % dilution) and films exhibiting highest hardness (DLC 6 and 7). These films were analyzed by XPS to determine their sp$^3$ and the sp$^2$ content (Table 5.3). These results along with their mechanical and tribological properties were used to select the conditions for synthesizing N-DLC films.

Figure 5.4 shows typical XPS survey spectra of film DLC 7 as-deposited and after etching for 120 seconds in four cycles of 60 seconds each. It is observed that any traces of impurities such as O or Si were eliminated after etching and an intense C peak was
observed. The HR XPS spectra of C 1s peaks obtained from the aforementioned films DLC 3, DLC 6, DLC 7 and DLC 12 are shown in the Figure 5.5. It is observed that the peaks of films DLC 6, DLC 7 and DLC 12 are similar overall, while the peak of DLC 3 shifted by 0.7 eV to the left. This is probably due to its higher conductivity. Thus, the following discussion is under this assumption. The C 1s peak for DLC films 6, 7 and 12 (higher Ar % dilution) can be deconvoluted into three components with binding energies of 284.3, 284.8 and 286.5 eV corresponding to sp$^2$ C-C and/or C-H, sp$^3$ C-C and/or C-H and C-O bonding respectively [85]. These three films were fitted with the same FWHM (Full Width Half Maximum) values. The pure DLC films deposited earlier in our laboratory by PECVD showed the presence of sp$^3$ and sp$^2$ forms of C at binding energies of 284.3 and 284.8 eV, respectively [84]. The film DLC 3 exhibits a different behavior than DLC may be due to its higher graphitic content (sp$^2$) and was deconvoluted at 283.5, 284.3 and 284.8 eV corresponding to “atomic” C, sp$^2$ (C-C and/or C-H) and sp$^3$ (C-C and/or C-H). Also, it was difficult to fit DLC3 peak into different components at the same FWHM value as that of other DLC films.

The high resolution peaks of C 1s show that with the increase in dilution of Ar %, the sp$^3$ fraction in the film increases as shown in the Figure 5.6. Similar trends have been observed by Teii [89] and Tomasilla et al. [87]. However, considering the hardness it looks like the higher sp$^3$ configurations in DLC 12 are due to C-H sp$^3$. This is consistent also with its somewhat lower friction coefficient. In fact, it has been reported that high hydrogen content in these films can produce ultra low friction coefficients [21]. For DLC films 3, 6 and 7 the increase in Ar$^+$ dilution results in an increase in sp$^3$ content and an increase in hardness which suggests that a C-C sp$^3$ hybridization exists in these films.
Beyond that point (DLC 12), Ar$^+$ dilution seems to favor C-H sp$^3$ thus reducing hardness. This is consistent with the low friction coefficient of this film. The sp$^3$ fractions for the films DLC 6 and DLC 7 are 0.53 and 0.56 respectively, which are comparable.

Figure 5.4. Survey spectrum of as-deposited DLC 7 film and after etching.
Figure 5.5. High resolution C 1s XPS spectra of DLC films.

Table 5.3. C 1s peak assignment and sp$^3$ fraction in DLC films.

<table>
<thead>
<tr>
<th>DLC Film Code</th>
<th>Assignment of BE (eV)</th>
<th>sp$^3$ fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sp$^2$</td>
<td>sp$^3$</td>
</tr>
<tr>
<td>DLC 3</td>
<td>284.3</td>
<td>284.8</td>
</tr>
<tr>
<td>DLC 6</td>
<td>284.3</td>
<td>284.8</td>
</tr>
<tr>
<td>DLC 7</td>
<td>284.3</td>
<td>284.8</td>
</tr>
<tr>
<td>DLC 12</td>
<td>284.3</td>
<td>284.8</td>
</tr>
</tbody>
</table>

( ): The peak shifted by ~ 0.7 eV assuming the film to be highly conductive (more sp$^2$ and atomic C).
Based on previous analysis, films DLC 6 and 7 showed low friction, wear rate and highest hardness. The Ar % dilution in these films ranged from 70-80 %. In order to maintain benefit from this Ar range, the N-DLC films were synthesized by keeping the (Ar+N₂) content to 80%. Since the N content varied from 5-15 %, the Ar varied from 65-75 %. In order to obtain a better understanding of the behavior of films deposited in the 70-80 % Ar range, DLC 6 and 7 were studied in more detail compared to the remaining films. Thus, it was possible to compare them with N-DLC and assess the effect of N.

Figure 5.7 (a) and (b) show the deposition rate and hardness of the DLC films. The film DLC 3 exhibits a very high thickness around 4.2 μm for a deposition time of 2.5 hrs, while DLC 12 has very low thickness around 1.35 μm even for a deposition time of 6 hrs. The films DLC 6 and DLC 7 exhibit moderate thickness around 1.6 μm.

Figure 5.6. Variation of sp³ fraction with Ar % dilution.
and 0.92 $\mu$m respectively when deposited for 2.5 hours. This low deposition rate at high dilution of Ar (films DLC 6, DLC 7 and DLC 12) is accompanied by the etching of the carbon matrix by Ar at high dilution [75]. The deposition rate decrease monotonically with increasing Ar content was also observed in literature [88]. Reports of hardness exhibited a maximum value of 29.75 GPa for DLC 7 at 10 gm load. The increase in hardness is accompanied by the increase in sp$^3$/sp$^2$ ratio from Figures 5.6 and 5.7(b). Similar trends have been observed by Tamor et al. [89]. The film DLC 7 appears to be a good compromise between Ar$^+$ number or energy on CH$_4$ energetic collisions and DLC structure. Hardness values for all the films at different loads were higher than those of the Si substrate (12.5 GPa).

Figures 5.7 (c) and (d) show the Archard wear rate and friction coefficient values of DLC films at loads of 1N and 5N. Ultralow friction coefficient values as low as 0.06 and ultralow wear rates as low as $4.87 \times 10^{-8}$ mm$^3$/Nm at a load of 5 N were observed for the films DLC 12 and DLC 6 respectively in ambient conditions of tribological tests. The low wear rates of DLC 6 and DLC 7 can be attributed to the higher hardness of the films and probably due to higher C-C sp$^3$ content. A decreasing trend in friction coefficient was observed in DLC films with decreasing CH$_4$ content for both 1 N and 5 N loads. It has been evident from literature that the coefficient of friction of hydrogenated a-C:H films in vacuum typically ranges from 0.007 to 0.02, and in ambient conditions (20% < Relative Humidity < 60%) from 0.1 to 0.4 [47]. The current results for all the DLC films dominate this fact by exhibiting friction coefficients ranging from 0.06 to 0.12 at 5 N load and from 0.13 to 0.21 at 1 N load in ambient conditions (RH: 50 ± 10%). These films would have
Figure 5.7. Mechanical and tribological properties of DLC 3, DLC 6, DLC 7 and DLC 12 films; (a) Deposition rate (b) Hardness (at loads of 10 and 25g) (c) Wear rate and (d) Steady-state friction coefficient (at loads of 1N and 5N) [440C steel pin, sliding velocity: 0.1 m s\(^{-1}\), distance: 1500 m].
These films would have shown lower friction coefficient values than observed when the wear tests were conducted in vacuum. Such tribological behavior has been attributed to transfer layer formation at the asperity contact discussed in the next section.

Figures 5.8 (a) and (b) show the steady-state friction coefficient variation of DLC films at 1 N, 5 N loads and the Si substrate as a function of sliding distance in meters. Almost all the DLC films exhibit much lower and stable friction coefficient within the measured sliding distance as compared to the substrate. However, DLC 3 exhibits a different behavior and it might be due to the presence of atomic C and higher amount of sp² content in the film. As mentioned earlier the high wear rate of DLC 3 at 1 N load can be ascribed to the high initial wear of the film, as it was tested for a sliding distance of 1000 m compared to 1500 m for other films.

It is observed that pure Si wafer exhibits a friction coefficient around 0.6, but when deposited with a thin film coat of DLC it exhibits a steady-state friction coefficient less than 0.2 for a load of 1N and less than 0.1 for a load of 5 N. Also, the wear rate calculated for Si is orders of magnitude higher than that for the DLC films. Although the initial friction coefficient values seem to be higher for 1 N load, they tend to be lower for 5 N load. Hence, these films are better off when subjected to higher loads. Also the hertzian stress between the film and the pin for 5 N is only 0.43 GPa compared to 0.25 GPa for 1 N load. This suggests that when the applied load increased to 5 times the value, the hertzian stress in the films increased only by less than twice its value.

The frictional behavior of film DLC 12 and the wear resistance of film DLC 6 are at the low end of that shown by typical DLC films. Similarly, the frictional behavior and wear resistance of all the other DLC films are comparable to typical DLC films.
The wear mechanism exhibited by typical DLC films has been discussed in section 3.5.2; wear-induced-graphitization might have taken place at the contact between the pin and DLC film. It has been observed from XPS experiments that DLC 12 has higher C-H $sp^3$ content than the other films as shown in Figure 5.6. This should cause a slow down in the graphitization kinetics for DLC 12. The wear-induced-graphitization behavior may apply to DLC 12 as it exhibits ultralow friction coefficient of 0.06 for 5 N; 0.13 for 1 N load and also exhibits a wear rate comparable to other films, indicating the scope of transfer layer formation. The high C-H $sp^3$, low friction coefficient in DLC 12 results in a wear rate comparable to DLC 6 and 7.

![Figure 5.8](image)

**Figure 5.8.** (a) Steady-state friction coefficient values of DLC films compared to Si at 1 N load. (b) Steady-state friction coefficient values of DLC films at 5 N load.

The morphology of wear tracks of films DLC 3 and DLC 12 is shown in the Figure 5.9 (a)-(d). Distinct differences in the wear behavior are discerned. The width and depth of the wear tracks of DLC 3 were significantly larger than those of DLC 12. This is consistent with the lower hardness and wear rate values that show more wear in DLC 3.
Presence of more graphitic sp$^2$ and atomic C in DLC 3 leads to a higher wear rate in 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 12 seems to involve formation of a transfer layer, a process that apparently requires more time thus, resulting in higher wear resistance.

Figure 5.9. Wear track depth profiles at 1 N load of (a) DLC 3 and (b) DLC 12, and 3-D image of the wear tracks in (c) DLC 3 and (d) DLC 12.
A similar trend for DLC 12 can be linked to films DLC 6 and DLC 7 as shown in Figure 5.10 (a)-(d), whose wear profiles match closely because of high sp$^3$C bonding in all the three films.

Figure 5.10. Wear track depth profiles at 1 N load of (a) DLC 6 and (b) DLC 7, and 3-D image of the wear tracks in (c) DLC 6 and (d) DLC 7.

The morphology confirms the larger width and depth of the wear track of DLC 3 when compared to DLC 12. Figures 5.11 (a) and (b) show the depth of wear track (nm) and the width of wear track (µm) for DLC films at different loads of 1 N and 5 N. The higher depth of wear tracks in the films DLC 3 and DLC 12 is an indication that these films are softer. Similarly the high width and low depth observed for 5 N in DLC 6 and DLC 7 can be attributed to the high hardness of the films. So, it is desirable to eat away the film surface causing larger widths rather than causing higher depth in the wear track.
It is observed that the depth of wear track for DLC 6 and DLC 7 was less than 200 nm at both 1 N and 5 N. It can be said that at higher dilution of Ar (> 70 %) the maximum depth of wear track that can occur is ~400 nm, under the given set of conditions.

Figure 5.11. (a) Depth of water track in nm. (b) Width of wear track in µm.

5.3 Transfer Layer Behavior in DLC Films

The very low friction and reasonably low wear rates of DLC films at higher dilution of Ar is explained by a transfer buildup followed by an interfilm sliding mechanism also discussed in the section 3.5.2 [21]. A significant wear in the initial states might have created a transfer layer which does not allow further physical contact between the pin and DLC film by interfilm sliding mechanism. SEM micrographs of 440C steel pins subjected to wear tests at 1 N and 5 N loads are shown in the Figures 5.12 (a)-(f). It is observed that uneven spreading of the transition layer occurred in the pin when testing DLC 3 at 1 N due to poor adhesion in the film, but at 5 N the transfer layer covered all of the contact area. The other films DLC 7 and DLC 12 show a transition layer formed at the asperity contact. However, DLC 7 appears as a transition between DLC 3 and DLC 12 in the formation of transfer layer buildup on the pin. This is because the pin of DLC 12 exhibited a denser transfer layer compared to other pins.

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Figure 5.12. SEM micrographs of 440C steel pins used for wear tests on (a) DLC 3 at 1 N load (b) DLC 3 at 5 N load (c) DLC 7 at 1 N load (d) DLC 7 at 5 N load (e) DLC 12 at 1 N load (f) DLC 12 at 5 N load.
The contact diameter of the wear scar for DLC 3 on the 440C steel pin was 260 $\mu$m at 1 N load, whereas for DLC 7 and DLC 12 the diameter of the scar was around 150 $\mu$m. This suggests a higher wear in DLC3 compared to DLC7 and DLC12 for 1 N load. Table 5.4 shows the composition of 440C steel pin at the asperity contact after the wear tests, by characterizing the pins using Electron Discharge Spectrometry (EDS). Normally 440C grade steel composes of 0.95-1.2 % C, 16-18 % Cr and the rest Fe. It shows that very high amount of carbon has accumulated over the steel pin. Also the drastic reduction of Cr % and Fe % in the steel pin from normal is evident that a transfer layer might have been formed on the DLC film leading to such tribological behavior. The higher C % in DLC 12 at both 1 N and 5 N loads is an indication of higher graphitization due to higher C-H sp$^3$ and/or lower H. There might also be a possibility of chromium carbide formation in the transfer layer, resulting in lower friction coefficient and wear rate values. Higher C % values are obtained at 5 N due to the larger contact area compared to 1 N which accumulates more carbon content in the pin. The hertzian stress being higher for 5 N (0.43 GPa) compared to 0.25 GPa in 1N confirms the above statement.

Table 5.4. Composition of 440 C steel pins at the asperity contact with DLC.

<table>
<thead>
<tr>
<th>Specimen used for wear test</th>
<th>C %</th>
<th>Cr %</th>
<th>Fe %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 N</td>
<td>5 N</td>
<td>1 N</td>
</tr>
<tr>
<td>DLC 7</td>
<td>21.84</td>
<td>32.24</td>
<td>14.38</td>
</tr>
<tr>
<td>DLC 12</td>
<td>23.19</td>
<td>60.84</td>
<td>13.76</td>
</tr>
</tbody>
</table>
PART II

5.4 Characterization of N-DLC Films

5.4.1 Film Microstructure

5.4.1.1 Transmission Electron Microscopy Studies

The TEM and electron diffraction studies were conducted on film N-DLC 2. Figures 5.13 (a) and (b) show the plan view TEM images at different magnifications of the N-DLC film with 0.73 at. % N deposited at (Ar+N)/CH\textsubscript{4} ratio of (70+10)/20.

It can be observed that the film appears featureless without diffraction contrast even for high resolution images, indicating the amorphous nature of the deposited film. There were no crystalline phases detected and, as expected, the formation of $\beta-C_3N_4$ does not occur at such lower amounts of N in the DLC matrix. Such morphology is typical of a DLC film [18].

Figure 5.14 shows the Selected Area Electron Diffraction (SAED) pattern of the film N-DLC 2. The SAED pattern reveals two concentric diffuse rings and a halo in the center. The $d$-spacing of the rings was indexed to be 0.207 and 0.12 nm, indicating a short-ranged diamond-like structure (sp\textsuperscript{3}) corresponding to (111\textsubscript{DLC}) and (220\textsubscript{DLC}) respectively. The central halo is produced from the detected hexagonal layers of sp\textsuperscript{2} graphite. Similar results were observed by Liu and Meletis for DLC films produced by PECVD [18]. Also, the diffractions at (111) and (220) correspond to crystal diamond with $d$-spacing of 0.206 nm and 0.126 nm, respectively. It is evident that low amounts of N-doping (10% N in the plasma ~ 0.73 at. % N in the film) in the DLC matrix does not affect the structure of DLC and it maintains the general DLC characteristics.
5.4.1.2 X-ray Photoelectron Spectroscopy Studies

The compositional analysis of all three N-DLC films is shown in the Table 5.5. Attempts to obtain high-resolution N 1s spectra from the N-DLC films were unsuccessful. This is due to the fact that low N content occurred in the films and hence,
the N 1s peaks could not be resolved. Instead, the C 1s core level XPS spectra of the N-DLC films were taken into consideration to determine the sp³ and sp² states in the films.

Figure 5.15 shows the XPS spectra of C 1s peaks for DLC 7 and all three N-DLC films deposited at same CH₄ content in the plasma. For the DLC film, the Ar content in the plasma was 80 % whereas for the N-DLC films 1, 2 and 3 the plasma contained (Ar+N) of (75+5), (70+10) and (65+15) respectively. It is observed that in all the N-DLC films there is a slight broadening of the spectrum towards higher binding energies when compared to that of DLC. This might be due to a very small contribution of sp³ and sp² C-N bonds at high binding energies.

The XPS core level spectra of C 1s obtained from films N-DLC 1, N-DLC 2 and N-DLC 3 are shown in the Figure 5.16. The C 1s peaks were resolved into three components with binding energies located at 284.3 eV (C-C and/or C-H sp²), 284.8 eV (C-C and/or C-H sp³) and 286.5 eV (C-O bonding). The reason to deconvolute the C 1s peaks of N-DLC films at the same binding energies as those of the DLC is because of very low N content in N-DLC films. It has been reported in literature that increase in N concentrations leads to the C 1s peak shift toward higher binding energies, broadening of the spectrum and increase in asymmetry [91]. The deconvolution of DLC 7 and the three N-DLC films shows difference in the C 1s characteristics. Since N content in the film is low (~1.5 %) these changes are not due to the presence of N in the DLC structure. These results suggest that N₂ in the plasma (replacing Ar) modifies the plasma and as a consequence the DLC structure changed slightly. The present results show that N₂ in the plasma increases the sp³ C bonding.
Figure 5.15. Comparison of C 1s HR XPS spectra of DLC 7, N-DLC 1, N-DLC 2 and N-DLC 3 films deposited at the same CH$_4$ content in the plasma.

Figure 5.17 shows a significant increase in the sp$^3$ fraction of C bonding when N$_2$ is used in the plasma. This is in agreement with previous reports that incorporation of low N in DLC films increases the sp$^3$ fraction [75]. Higher amount of N in the film reduces the sp$^3$ fraction. Thus, the present results show that N has an indirect effect. This means that the actual incorporation of low N in the film has insignificant effect but a major effect is produced by N$_2$ incorporation in the plasma.
It should be noted that Ar has high ionization efficiency than nitrogen and the IPAP system is almost as effective as low-energy ion implantation in enhancing nitrogen penetration when ions of similar energies are used [81]. Further more, argon has larger mass than nitrogen. Thus, replacing argon with nitrogen in the plasma is expected to affect the collision process with methane molecules. The results suggest that the incorporation of the lighter energetic nitrogen in the plasma should have a significant effect on the properties of the deposited hydrocarbon species. The results show a higher sp\(^3\) C bonded content in nitrogen containing plasmas. XPS alone cannot discriminate if this sp\(^3\) content is C-C or C-H. Thus, it should be noted that this sp\(^3\) content composes of both sp\(^3\) C-C and C-H bonds.

Figure 5.16. High resolution C1s peaks of N-DLC films.
Table 5.5. Composition and sp$^3$ fraction of N-DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>at. % N</th>
<th>sp$^3$ fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC 7</td>
<td>0</td>
<td>0.56</td>
</tr>
<tr>
<td>N-DLC 1</td>
<td>0.51</td>
<td>0.75</td>
</tr>
<tr>
<td>N-DLC 2</td>
<td>0.73</td>
<td>0.7</td>
</tr>
<tr>
<td>N-DLC 3</td>
<td>1.37</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure 5.17. sp$^3$ fraction vs. Nitrogen content.
5.4.2 Mechanical and Tribological Behavior of N-DLC Films

The mechanical and tribological properties of N-DLC films are summarized in Tables 5.6 and 5.7, respectively. The processing parameters involved in the deposition of N-DLC films are listed in Table 4.2 in section 4.1.2. The hardness values ranged from approximately 28-30 GPa for 10 g load and 20-21 GPa for 25 g load.

Figures 5.18 (a) and (b) show the deposition rate and hardness variation in DLC 6, DLC 7, N-DLC 1, N-DLC 2 and N-DLC 3 films. The two DLC films were plotted along with N-DLC films for comparison. The film DLC 7 had the same methane content in the plasma as that of N-DLC films. The film DLC 6 was selected since it was deposited at 70 % Ar and 30 % CH₄. The N-DLC films were deposited from 65 % Ar to 75 % Ar and this enables a comparison of Ar content. It is observed from Figure 5.18 (a) that replacement of Ar by nitrogen in the plasma reduces the deposition rate.

Table 5.6. Mechanical properties of N-DLC films.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>(Ar+N₂)/CH₄ ratio</th>
<th>Thickness (nm)</th>
<th>Deposition Rate (nm/min)</th>
<th>Hardness Hₓ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 g</td>
<td>25 g</td>
</tr>
<tr>
<td>DLC7</td>
<td>(80+0)/20</td>
<td>920</td>
<td>10.2</td>
<td>29.75</td>
</tr>
<tr>
<td>N-DLC1</td>
<td>(75+5)/20</td>
<td>500</td>
<td>5.5</td>
<td>29.63</td>
</tr>
<tr>
<td>N-DLC2</td>
<td>(70+10)/20</td>
<td>617</td>
<td>6.8</td>
<td>29.32</td>
</tr>
<tr>
<td>N-DLC3</td>
<td>(65+15)/20</td>
<td>733</td>
<td>8.1</td>
<td>28.05</td>
</tr>
</tbody>
</table>
Table 5.7. Tribological properties of N-DLC films for wear length of 1500 m.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Steady-state friction coefficient ($f_{ss}$)</th>
<th>Archard wear rate (mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load=1N</td>
<td>Load=5N</td>
</tr>
<tr>
<td>N-DLC1</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>N-DLC2</td>
<td>0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>N-DLC3</td>
<td>0.12</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure 5.18 (b) shows that the microhardness of all the N-DLC films were similar to that of DLC films deposited at equal percentage of methane in the plasma. A higher sp$^3$ fraction was observed for all N-DLC films. In view of the microhardness results the higher sp$^3$ content is due to higher C-H sp$^3$ that do not contribute to hardness. Thus, the results suggest that both DLC 7 and N-DLC films have similar C-C sp$^3$ fraction (similar hardness) but incorporation of N in the plasma increases the sp$^3$ C-H content.

Figure 5.18. Mechanical Properties of DLC 6, DLC 7, N-DLC 1, N-DLC 2 and N-DLC 3 films; (a) Deposition rate (b) Hardness (at loads of 10 and 25g).
Figures 5.19 (a) and (b) shows the Archard wear rate and friction coefficient values of DLC and N-DLC films. It is observed that the wear rates of N-DLC films were comparable to those of DLC films and they were in the order of $1 \times 10^{-7}$ mm$^3$/Nm. A very high wear rate deviation from the mean value for loads of 1 N in N-DLC films might be due to the lower film thickness and uneven distribution of the load from the device itself. Such a behavior was not noticed for loads of 5 N. Ultralow steady-state friction coefficient values much lower than DLC films were obtained in the range of 0.04-0.06 for all the N-DLC films at a load of 5 N. However, the friction coefficient values at a load of 1 N were comparable to that of DLC films. This might be due to higher sp$^3$ C-H that is in effect at higher loads.
Figure 5.20 compares the friction coefficient values of standard Si wafer, DLC and N-DLC films. All the three N-DLC films exhibited a steady-state friction coefficient value less than 0.06. Reports of friction coefficient values ranging from 0.15 to 0.2 were published in literature and such low friction coefficients at steady-state rarely occur in ambient air [93, 94]. However, the initial friction coefficient values for N-DLC films appear to be slightly higher than DLC films in the first 100-200 meters displacement which caused most of the wear initially. There might be a transfer layer formed at the asperity to delay the graphitization process.
5.4.2.1 Long Duration Tribological Testing

To further study the tribological behavior of N-DLC films, two of the samples were tested in the same conditions for an extended distance. Table 5.8 shows the steady-state friction coefficient values and wear rates of N-DLC 2 and N-DLC 3 at a load of 5 N tested for a longer distance. The N-DLC 2 and N-DLC 3 films exhibited a steady-state friction coefficient of 0.1 and 0.06. The wear rates of these two films was around $1.6 \times 10^{-7}$ mm$^3$/Nm which is comparable to the wear rates obtained when the friction tests were first conducted for 1.5 km. This suggests that a transformation layer has formed near the asperity contact resulting in very low wear rates and friction coefficient as reported earlier [43, 44].

![Friction Coefficient vs. Distance in meters](image)

**Figure 5.21. Friction coefficient vs. Distance in meters.**
Table 5.8. Steady-state friction coefficient and the wear rates of N-DLC films for an extended distance at a load of 5 N.

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>Thickness (nm)</th>
<th>Test Duration (hrs)</th>
<th>Distance (m)</th>
<th>Steady-state friction coefficient ($f_{ss}$)</th>
<th>wear rate $(\text{mm}^3/\text{Nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-DLC2</td>
<td>617</td>
<td>13.9</td>
<td>5000</td>
<td>0.1</td>
<td>$1.6 \times 10^{-7}$</td>
</tr>
<tr>
<td>N-DLC3</td>
<td>733</td>
<td>10.2</td>
<td>3695</td>
<td>0.06</td>
<td>$1.61 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Figure 5.22. Wear track morphology of N-DLC 2 at 5 N (Evidence of Si exposure at the root of the wear track).

Figure 5.21 shows the variation of friction coefficient with sliding distance. It is observed that the initial friction coefficient values for both films were around 0.3 and thereby maintained a steady-state after the first 100 m sliding ($< 0.1$). A slight increase in the friction coefficient of N-DLC 2 around 1100 m might be due to the appearance of Si wafer in some portions of the wear track as shown in the Figure 5.22. Also a slight variation in the friction coefficient of N-DLC 3 around 2800 m is attributed to the same
cause. However, low friction coefficient is still maintained meaning that a transfer layer is still present providing low friction coefficient.

### 5.4.2.2 Wear Morphology

The morphology of wear tracks of N-DLC films for 1 N load is shown in Figures 5.23 (a)-(c). It is observed that the wear profiles of N-DLC films are commensurate with the wear rate values in Table 5.7. It appears that the film N-DLC 1 exhibits slightly higher wear compared to other films. The N-DLC 3 films exhibit higher surface variation (rough) within the wear track and suggests some difference in the wear process. The N-DLC 2 film appears to be having very low depth of wear track and low width. The morphology of N-DLC 2 film appears better when compared to the DLC counterpart (DLC 6).

Figure 5.24 shows the wear track depth profiles of N-DLC 2 and N-DLC 3 when subjected to an extended tribology testing distance at 5 N load. The depth of the wear track was more than the thickness of the N-DLC 2 film. This might be a reason for its high friction coefficient value around 0.1. The morphology of N-DLC 3 showed a very short range layer removal of the film compared to N-DLC 2. The appearance of wear track for the film N-DLC 3 was rough at 1 N and was smooth at 5 N load as shown in the Figures 5.23 and 5.24. This suggests that a higher surface variation exists in N-DLC 3. Overall the film N-DLC 2 appears as a good compromise concerning the tribological behavior.
Figure 5.23. Wear track depth profiles and 3-D images of (a) N-DLC 1 (b) N-DLC 2 and (c) N-DLC 3 at a load of 1 N, for a sliding distance of 1500 m.
5.5 Thermal Stability of DLC and N-DLC Films

Based on previous annealing studies of DLC, the graphitization process starts at about 350°C with liberation of hydrogen and gradual conversion of sp³ bonds into sp² graphitic bonds [17]. Therefore, the thermal stability studies on DLC and N-DLC films were conducted at temperatures ≤ 400°C to analyze the graphitization process.

Thermal annealing experiments were conducted on DLC 9 (72 % Ar in plasma) and N-DLC 2 at different temperatures of 300°C, 350°C and 400°C with 30 minutes duration. DLC 9 and N-DLC 2 films were chosen as they had approximately the same CH₄ content in the films. All samples were placed together in a furnace and were heated slowly at 5°C per minute up to the desired temperature. After the 30 minute annealing treatment, they were furnace cooled before removing them and measuring their hardness. The cooling cycle lasted for about 60 min.

Figure 5.25 presents the thermal stability results of the DLC and N-DLC films in the as-deposited and annealed condition. Both films exhibited almost zero loss of
hardness at a temperature of 300°C. It is observed that there is a sudden drop of microhardness in the range of 300-350°C for N-DLC film indicating onset of graphitization in the film. Similarly, the graphitization in DLC film occurred in the 350-400°C annealing temperature range confining to the thermal stability of a conventional DLC film. So, it seems that the incorporation of N in DLC triggers graphitization earlier than in DLC films. This may be attributed to incorporation of N in the C-C network as lower energy is sufficient for breaking the C-N compared to C-C bonds. This may not be necessarily negative because an earlier graphitization at comparable temperatures achieved at asperities may help the quicker formation of the transfer layer to benefit the wear resistance.

![Graph showing thermal annealing results for DLC and N-DLC films.](image)

**Figure 5.25.** Thermal annealing results for DLC and N-DLC films.
6. CONCLUSIONS

The following conclusions can be drawn from the present study:

1. A preliminary study on the Ar % dilution in the plasma to obtain DLC films was investigated and the characteristics in terms of sp$^3$/sp$^2$ content, mechanical and tribological behavior were found.

2. Based on this study, an attempt was made to develop N-DLC films with low N content and characterized for structure, mechanical and tribological behavior. Thereafter, a comparative study between DLC and N-DLC films was made.

3. The N-DLC films were found to be amorphous and the diffused rings and a halo in the SAED pattern revealed a short-ranged diamond-like structure (sp$^3$) in the film.

4. Overall, the N-DLC films exhibited a higher sp$^3$ (C-H) bonding fraction compared to DLC films.

5. N-DLC films exhibited a hardness range (28-30 GPa for 25 gm load and 20-22 GPa for 10 gm load) similar to that of DLC films deposited with same CH$_4$ content in the plasma.

6. Steady-state friction coefficient values of all the N-DLC films (~ 0.04) were far lower compared to those of DLC films due to higher sp$^3$ (C-H) bonding. The wear rates were comparable to that of DLC (remain in the order of 10$^{-7}$ mm$^3$/Nm). Some of the DLC films at Ar % dilution of 70-80 % exhibited a wear rate in the order of 10$^{-8}$ mm$^3$/Nm. An attempt to understand the transfer layer formation in the asperity contact was accomplished.

7. The N-DLC film with 0.73 at. % N exhibited a friction coefficient of 0.04 and a wear rate of 1.6×10$^{-7}$ mm$^3$/Nm in ambient air; the wear profiles and wear rates of all the N-DLC films suggest that they exhibit the desired tribological behavior comparable to that of DLC films.

8. Thermal stability studies showed that graphitization in DLC films starts by the loss of hydrogen around 350°C while the N-DLC films start to graphitize from 300°C with increase in annealing temperature.

9. There is a great scope for N-DLC films to be synthesized on magnetic hard disks in low amounts of N as they possess lower friction and comparable wear rate to that of DLC films and thus present high potential for a number of other tribological applications and their usage as medical implants.
REFERENCES


VITA

Mr. Krishna Chaitanya Kadiyala was born in the City of Guntur, Andhra Pradesh, India, on 27th December 1980. He got his primary and secondary education from Sai Public School and intermediate education from Nalanda Junior College in Vijayawada. After accomplishing his early studies in Vijayawada, he took the most rigorous competitive entrance examination for engineering in Andhra Pradesh known as EAMCET (Engineering, Agricultural, and Medical Common Entrance Test). After qualifying in this examination he got admitted into the Center for Advanced Study, Department of Mechanical Engineering, K. L. College of Engineering, affiliated to Nagarjuna University. He received his bachelor of technology degree in mechanical engineering from Nagarjuna University, Guntur, India, in May 2002. In fall 2003, he joined Louisiana State University’s materials science program with in mechanical engineering department to pursue a master’s degree. Currently, he is a candidate for the degree of Master of Science in Mechanical Engineering to be awarded at the commencement of August 2006.