SYNTHESIS AND TRIBOLOGICAL PROPERTIES OF DLC FILM BY RF PACVD:

EFFECT OF PROCESSING PARAMETERS

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ABSTRACT

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Diamond-like carbon (DLC) films, have gained grounds in many industries ranging from automobile and oil and gas to electronics and bio fields due to their low friction and wear rate, chemical inertness and high hardness. Radio Frequency (RF) plasma discharge has been widely used to produce amorphous carbon films, because this method can be applied not only for etching but also for deposition on insulators. The advantage of RF plasma discharge is the application for wide area and the stability as compared with direct current (DC) plasma. The properties of DLC films deposited by RF plasma-assisted chemical vapor deposition (PACVD) strongly depend on deposition conditions such as total gas pressure, input power supplied from a generator, gas flow rate and also substrate material.

In the present study, DLC films were synthesized utilizing low power RF PACVD in a CH_4/Ar glow discharge. First, the effect of processing parameters namely: RF power, chamber pressure, gas flow rate and Ar dilution on the DLC film deposition and hardness was studied to identify parameters that produce quality films. Following the initial study, nanoindentation and

tribological experiments were conducted to characterize hardness, friction and wear resistance of the films. Nanoindentation experiments showed that higher hardness can be obtained with a moderate increase in RF power (35 W - 40 W) after which delamination of the film occurs. With decreasing pressure, the hardness of the film increases. This behavior was attributed to higher sp^3 content of the films as the power increases or pressure decreases. Also, it was found that the flow rate and Ar dilution in the range of 17% - 30% Ar has no significant effect on the hardness of the film. Combination of different parameters affect the friction coefficient and wear resistance of the DLC films and three groups of tribological behavior were identified; (i) low friction and low wear resistance, characteristic of films with high graphitic content; (ii) low friction and high wear resistance for films with a good balance of graphite-like and diamond-like content; and (iii) moderate friction (with a coefficient of friction between 0.12 and 0.22) and ultra high wear resistance ($<10^{-8}$ mm^3/Nm). The results show that compared to DC PACVD, low power RF PACVD can produce quality DLC films with comparable if not better tribological behavior. This is attributed to better plasma uniformity produced by RF compared to DC PECVD.

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CHAPTER 1

INTRODUCTION

Nanotechnology has marked the dawn of a new era in respect to unique material properties and has enthralled the world by its wide gamut of applications ranging from electronics and biotechnology to energy and environment. Carbon has drawn the attention of researchers because of its ability to exist in various forms like sp^3 hybridized diamond and sp^2 hybridized graphitic structure. Diamond has high hardness, wide band gap, chemical resistance, and high wear resistance whereas graphite is soft, exhibits high wear rate and good electrical conductivity[1].

Diamonds-like carbons (DLC), a metastable form of amorphous carbon, has drawn attention due to its low friction coefficient and wear rate, chemical inertness and high hardness. It is widely used in automobiles, industrial wear parts like dies and molds, magnetic storage devices and also as a biomedical coating. Moreover, uniform films can be produced which is important for various applications (e.g., resist material for photolithography). The film can be prepared at low temperatures by different techniques using a large variety of precursors. The diversity of methods used for the deposition of DLC films provides the flexibility to tailor their properties according to specific needs and potential applications.

Compared to chemical vapor deposition (CVD) of diamond, deposition of DLC films is easier. Since hydrocarbon gases can be easily decomposed by plasma discharges, plasma CVD is the most common technique for deposition of carbon films. Especially, radio frequency (RF) plasma discharge has been widely used to produce amorphous carbon films, because this method can be applied not only for etching but also for deposition on insulators. The advantage of RF plasma discharge is the application for wide area and the stability as compared with direct current (DC) plasma. The occurrence of the self-bias voltage is originated by the mobility

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difference of ions and electrons at high frequency, and then the positive ions are collected to the powered electrode. However, the properties of DLC films deposited by RF plasma CVD strongly depend on deposition conditions such as total gas pressure, input power supplied from a generator, gas flow rate and also substrate material.

The unique tribological behavior of DLC films may vary a great deal from one type to another. Test conditions and environment can also play a major role in their friction and wear behavior. In particular, the friction values reported for various DLC films span the range 0.001–0.7, which probably represents the widest range of friction among all other materials or coatings[1]. As far as wear performance is concerned, certain DLC films are very soft and easily scratched, while others are extremely hard and resistant to wear. One of the reasons for the observed variation may relate to plasma instabilities during DC processing. It is well known that RF power can alleviate some of these plasma instabilities and result in more stable plasma. The purpose of the present study was to explore the potential of RF power plasma assisted (PA) CVD in producing quality DLC films.

CHAPTER 2

OBJECTIVE

The goal of the present study was to explore the synthesis of DLC films using RF PACVD and compare them with their counterparts produced by DC CVD especially in terms of tribological properties. Within the present objectives was to study the effect of processing parameters during RF deposition on film characteristics and tribological properties.

The following are the specific objectives of this research:

➢ Study the effect of RF power as compared to DC power on the deposition of DLC films.

➢ Investigate the effect of processing parameters on the deposition of DLC films produced by RF-PACVD.

➢ Assess the tribological properties of DLC films produced by RF-PACVD as a function of processing parameters (power, pressure, flow rate and Ar dilution ratio).

CHAPTER 3

LITERATURE REVIEW

3.1 Structure of DLC Film

Carbon is one of the most versatile elements in nature which forms a variety of crystalline and disordered structures. It is able to exist in three hybridizations, sp^3, sp^2 and sp^1. In sp^3 hybridization as in case of diamond, one carbon atom is surrounded by four other carbon atoms forming a tetrahedral directed sp^3 orbital resulting in a strong σ bond to the adjacent atom. In sp^2 hybridization as in the case of graphite, three of the four valence electrons enter trigonally directed sp^2 orbitals, which form σ bonds on a plane. The fourth electron of the sp^2 atoms is in π bond, which forms a weak bond resulting in the sliding of the graphite sheets. A marginal content of sp^1 carbon is reported but can be neglected due to its low abundance[1]. These three forms of carbon are shown schematically in Figure 3.1.
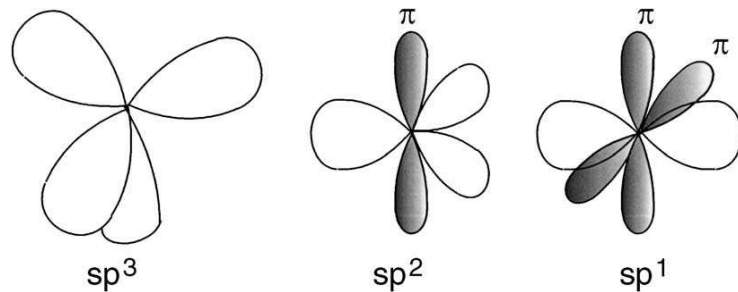
Figure 3.1 The sp^3, sp^2, and sp^1 hybridized carbon bonding[1]

DLC has both sp^2 and sp^3 content and as a result lies between diamond and graphite. The structure of DLC can be best explained by the ternary phase diagram proposed by Jacob and Möller[1] as shown in Figure 3.2.
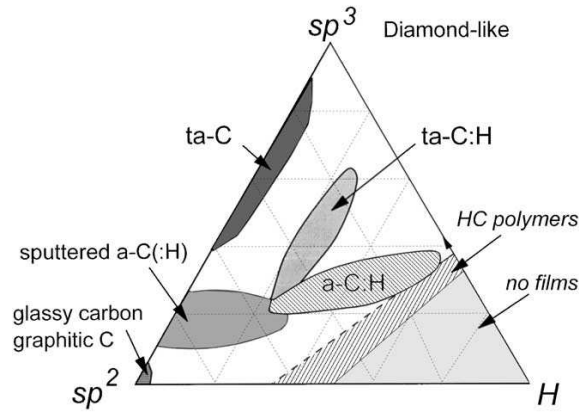
Figure 3.2 Ternary phase diagram of bonding in amorphous carbon-hydrogen alloy[1]

There are many amorphous carbon (a-C) disordered graphitic forms like soot, glassy carbon and evaporated a-C in the left corner of the diagram. The HC polymers form the boundary at the right corner beyond which interconnect C-C network is not possible and it exists only in molecular form. Different deposition methods result in the increase of the sp^3 content in a-C. If the fraction of the sp^3 content increases, then that a-C is denoted as tetrahedral amorphous carbon (ta-C). DLC does not only consist of a-C but it also consists of hydrogenated amorphous carbon (a-C:H). The interior of the ternary diagram shows the presence of a-C:H with less sp^3 bonding and more hydrogen content. Properties of various forms of carbon are shown in Table 3.1.

Table 3.1 Properties of different carbon forms[1]

Carbon Form	% sp^3	Hardness (GPa)	% H	Density (g/cm^3)	Gap (eV)
Diamond	100	100	--	3.5	55
Graphite	0	--	--	2.267	0
a-C (evaporated)	0	3	--	1.9	0.4-0.7
a-c (sputtered)	5	3	--	2.2	0.5
Ta-C	80-88	80	--	3.1	2.5
a-C:H (hard)	40	10-20	30-40	1.6-2.2	1.1-1.7
a-C:H (soft)	60	<10	40-50	1.2-1.6	1.7-4

3.2 Synthesis Techniques

Carbon containing films have been synthesized by a variety of techniques depending on the properties of the film required.

3.2.1 Ion Beam

Aisenberg and Chabot were the first to use this technique for deposition of a-C:H films[2]. In their method, the DLC films were condensed from a beam containing medium energy of around 100 eV carbon or hydrocarbon atoms. It is the impact of these ions on the growing film that induces the sp^3 bonding by a physical process. In a typical ion beam deposition system, carbon ions are produced by the plasma sputtering of a graphite cathode by an ion source as shown in Figure 3.3. An ion beam is then extracted through a grid from the plasma source by a bias voltage. The carbon ions are then accelerated to form the ion beam in the high vacuum chamber. The best deposition process for DLC will provide a carbon flux at about 100 eV per carbon atom with a narrow energy distribution, a single energetic species and a minimum number of non energetic species.

Ion assisted sputtering

substrate

C atom beam

graphite target

ion beam
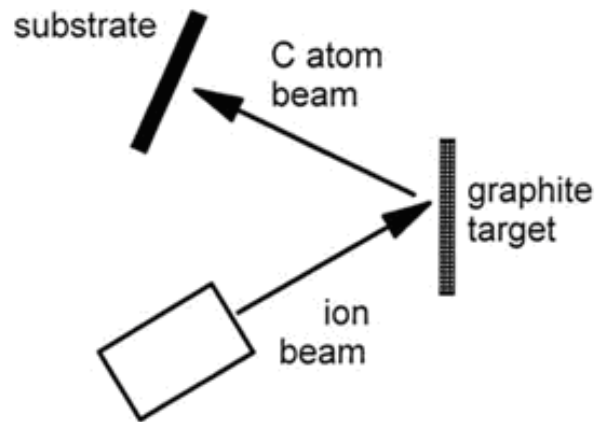
Figure 3.3 Ion assisted Sputtering[1]

3.2.2 Sputtering

Graphite has low sputtering yield due to which magnetron sputtering is often used to increase the deposition rate[1, 3]. Magnets are placed behind the target to cause the electrons to spiral and increase their path length and thus, to increase the degree of ionization in the plasma. The most common gas which is used for sputtering is Ar. As ion bombardment helps the formation of sp^3 bonding, the magnetic field can be configured to pass across to the substrate so this causes the Ar ions to bombard the substrate resulting in the formation of the unbalanced magnetron. Like ion beam deposition, a disadvantage of the sputtering is that it can have relatively low ratio of energetic ions to neutralize so that it does not produce the hardest DLC film.

Other methods for producing the DLC film using graphite or any other hydrocarbon target are cathode arc, mass selected ion beam, pulse laser deposition which are all variations of the sputtering and ion beam having similar principle of deposition forming various types of a-C:H films.

3.2.3 Chemical Vapor Deposition

The most common way to synthesize DLC is either plasma CVD or thermal CVD. In thermal CVD, the substrate is exposed to around 800°C - 900°C in carbonaceous precursor gas environment. DLC is formed on the substrate due to chemical decomposition of the precursor molecule. The other way of DLC deposition is plasma CVD where plasma is used to deposit carbon from a solid state carbon target or from a carbon precursor gas environment.

The method of DLC deposition from gas precursors has gained grounds over the years. In this method, hydrocarbon gases like CH_4, C_2H_4, C_2H_6, etc. are allowed to flow into the vacuum chamber with optimized Ar dilution ratio. This method is very popular for depositing a-C-H films. The major advantages are low deposition temperature, high deposition rate, good quality films and low contamination[1,3].

3.2.3.1 DC biased plasma CVD

In dc biased plasma CVD, normally the chamber acts as the anode and the substrate is the cathode. Figure 3.4 shows that the chamber is normally grounded and a negative bias voltage is applied on the substrate plate.
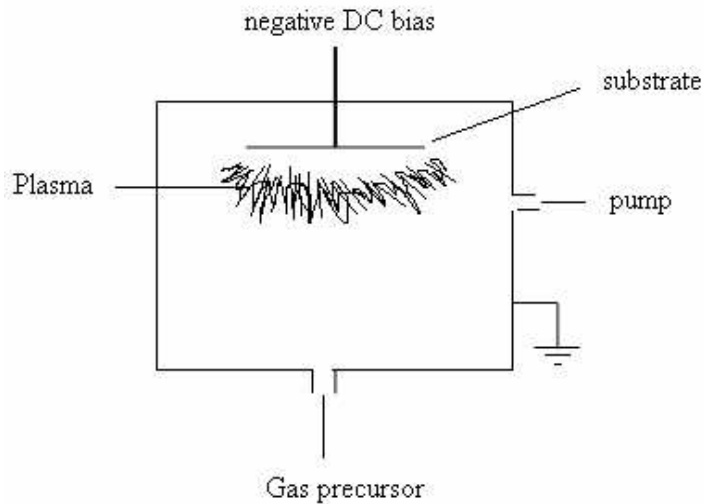
Figure 3.4 DLC deposition by dc biased plasma CVD[4]

Plasma is created by applying a substrate bias voltage ranging typically from -100 V to -1000 V and the chamber pressure is maintained typically from 10 mTorr to 100 mTorr. The bias voltage ionizes the gas precursor molecule and is finally attracted and deposited on the substrate. The applied voltage and gas pressure decide the impinging energy of the ions and thus, regulate the sp^3 /sp^2 ratio in the a-C:H film. The key parameters for obtaining good quality films are the bias voltage, working pressure and the hydrocarbon/Ar ratio in the precursor. The bias voltage and pressure mainly decide the sp^3 /sp^2 ratio and deposition rate of the film respectively. Li *et. al.* for example found that there is no significant change in the deposition rate with the change in the DC bias between 0-400 eV as can be seen in Figure 3.5[6].

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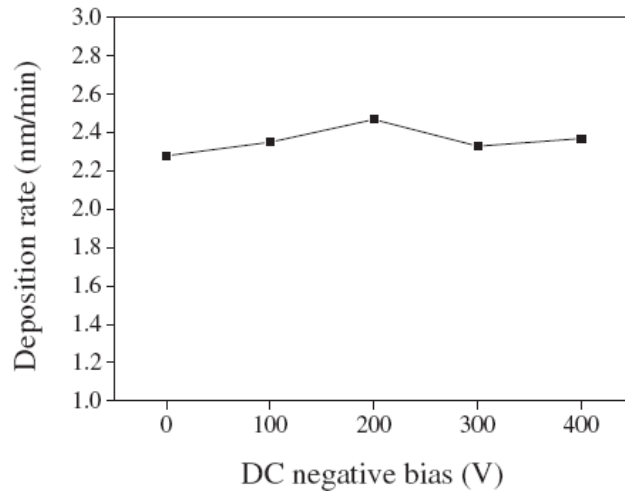
Figure 3.5 Deposition rates of hydrogenated DLC films as functions of DC negative bias[6]

3.2.3.2 RF plasma CVD

The most common technique used to deposit DLC in the laboratory is RF PECVD. Two electrodes are generally used to create RF plasma. The smaller one is generally the substrate and the reactor wall is earthed as shown in Figure 3.6. The RF power produces plasma between the electrodes. There is a sheath formed around the electrodes with an excess of ions. This sheath acts as a diode, so that the electrodes acquire dc self-biased voltage. The dc self biased voltage varies inversely with the electrode area[5] by the formula

$$\frac{V_1}{V_2} = \left(\frac{A_1}{A_2} \right)^2$$

(1)

in which, V is the bias voltage and A is the area. According to the above equation, the smaller electrode will acquire larger bias voltage and become negative with respect to the larger electrode. Thus, the substrate electrode will have a negative sheath voltage which accelerates the positive ions to give the bombardment needed to create sp^3 bonding.
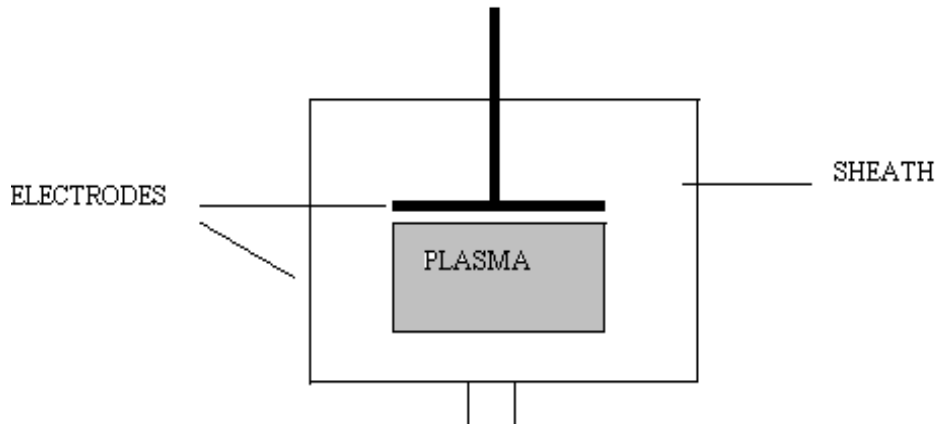
Figure 3.6 Electron and ion distributions which create sheath between neutral plasma and the chamber walls

Li *et. al.* found that RF power has a greater influence on the film deposition rate than the DC bias[6]. Deposition and etching simultaneously occur in the DLC film deposition process. The increase of the RF power at the low region mainly leads to increased gas ionization and hence an increase in the ion flux reaching the substrate surface, subsequently the deposition rate is increased. At a too high RF power, the etching reaction by the hydrogen ions (atoms) and the sputter etching by the argon ions (atoms) on the film surface become more severe and hence lead to a decreased deposition rate.

In contrast to the above, an increase in the DC bias leads not only to directly increased energy of the film forming precursor (ions) but also to increased energy of the argon ions in the plasma impinging on the substrate. In other words, when the deposition rate of the DLC films is increased with increasing DC bias, the etching rate of the film is also raised therewith, and thus the mass deposition rate shows little change with increasing DC bias[7].

3.2.3.3 DC-RF PECVD

In the DC RF PECVD system, the plasma density and the ion energy are separately controlled by RF power and DC bias, respectively. The system consists of two electrodes of different diameter. The larger electrode is given the RF supply to excite the plasma and to control the plasma density. A separate dc power source is given to the small electrode to bias the substrate and control the ion energy. With increasing RF power, the content of the sp^3 bonded carbon in the DLC film increases as well[6]. However, at a higher RF power the film hardness decreases rapidly, suggesting a transformation from a diamond-like structure to graphite-like structure of the DLC films[8].

3.3 Processing Parameters Affecting the Deposition of DLC

Synthesis of DLC films, as seen above can be performed by various methods ranging from ion beam deposition to PECVD. DLC films formed by using gas precursors have major advantages in the quality of the film. Many investigators have carried out studies to determine the parameters affecting the rate of deposition and quality of the film. In most previous studies, only the effect of variation of a single parameter has been investigated[9]. At low impact energies, the hydrocarbon precursor is not sufficiently decomposed and a film with a polymer-like structure is obtained. At intermediate levels of energy, the hydrogen content decreases significantly and sp^3 C–C bonding is promoted. Further increase in impact energy is causing formation of a disordered graphite-like structure. Thus, bias voltage, processing pressure and concentration of gaseous species in the plasma play a critical role since they all affect the average impact energy. Such aspects have been addressed by Meletis and co workers[10] who studied the effect of PECVD processing parameters on the tribological behavior of DLC films.

3.3.1 RF Power

Choi *et. al.* reported on the influence of varying RF power on the DLC films[11]. They found that the deposition rate increased with the increase of the RF power till 100 W as shown in Figure 3.7. It was found that the deposition rate decreases at higher RF power. The increase in the RF power enhances the plasma density resulting in higher deposition rate. At higher power, the plasma sheath increases to a greater extend resulting in enhanced sputtering and a decrease of the deposition rate.
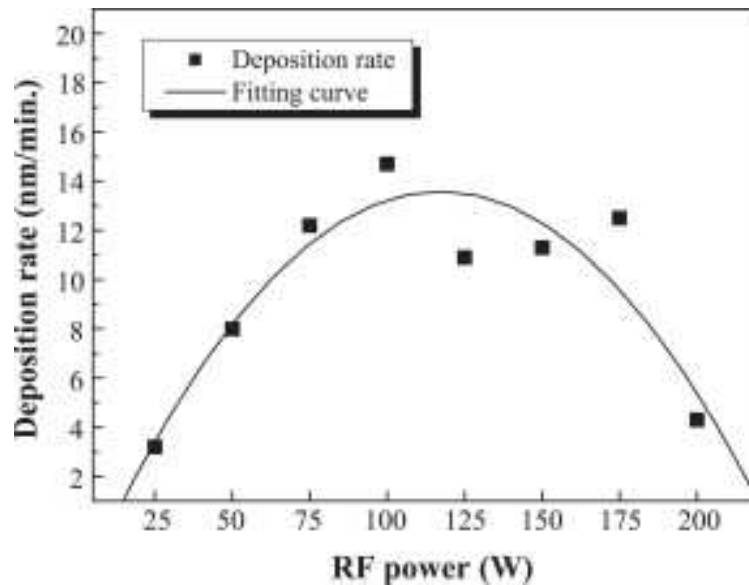
Figure 3.7 Deposition Rate of DLC as function of RF Power[11]

3.3.2 Pressure

The effect of processing pressure on the characteristics of a-C:H films deposited at constant bias voltage and CH_4/Ar were investigated by Meletis and co-worker[10]. It was found that a continuous film was not obtained at low pressures. At higher pressures, the deposition rate increased due to larger hydrocarbon flux reaching the substrate surface. A combination of low pressure that minimizes ion energy loss by collisions in the plasma sheath and a high

applied bias is expected to increase flux energy promoting formation of graphite-like structure. As pressure increases the number of collisions also increases resulting in medium-energy flux promoting sp^3 bonding and lower hydrogen content but also lower deposition rates. It was found that higher sp^3 content is associated with higher hardness, intrinsic stress and relatively higher roughness. Similar trends of higher sp^3 content with increasing pressure due to lower impact energy of ions by scattering were also reported by Ryu *et. al.*[12]
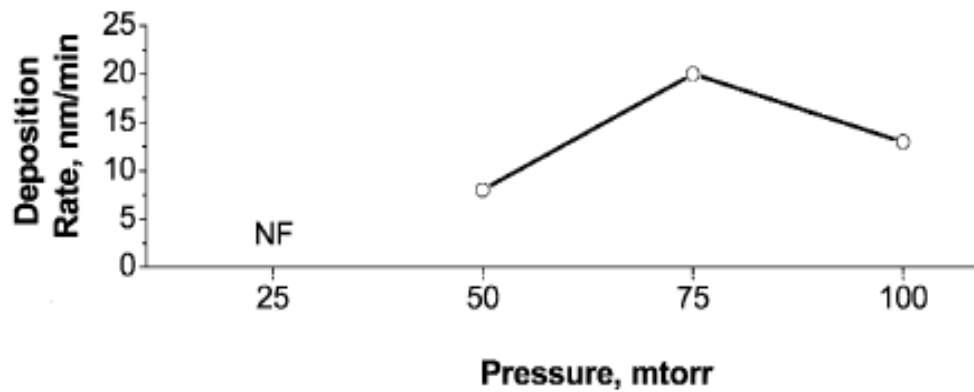
Figure 3.8 Effect of processing Pressure on a-C:H film characteristics (NF-no film)[12]

It is seen in Figure 3.8 that on increasing the pressure, the number of ions generated in the plasma increases resulting in a larger ion flux reaching the substrates. The deposition rate decreases as the pressure increases. Kim *et. al.* concluded that at higher pressures, higher atomic hydrogen concentration is also generated resulting in the etching of the films which can account for a decrease in the deposition rate seen at higher pressure as shown in Figure 3.9[13].
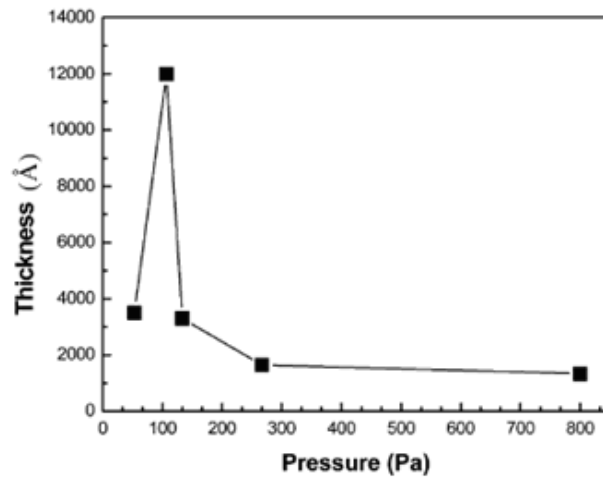
Figure 3.9 Thickness of the films as a function of the Deposition Pressure[13]

3.3.3 Total Gas Flow Rate

Tachibana *et. al.* showed that the gas flow rate is one of the important parameters affecting the properties of the film[14]. The plot shown in Figure 3.10 demonstrates that the deposition rate decreases with the increase in flow rate from 2 sccm to 10 sccm. This can be due to a very high dissociation rate for the low gas flow. They found that this rate is decreasing from about 50% to 25% between 2 and 10 sccm.
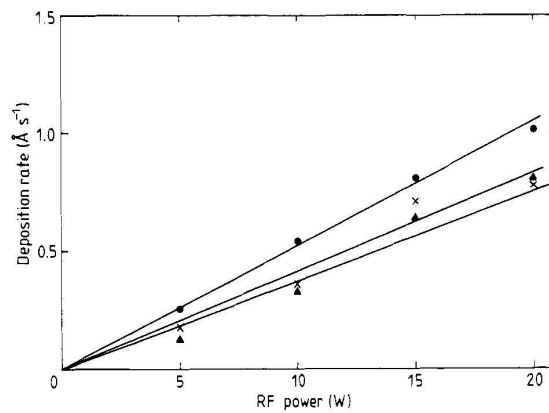
Figure 3.10 Deposition rate of carbon films measured as a function of RF power at gas pressure 0.22 Torr for several values of gas flow rate. (●) 2 sccm, (X) 5 sccm, (▲) 10 sccm[14]

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Keudell *et. al.* predicted that a very high dissociation may accelerate re-etching by atomic hydrogen in the plasma-surface reaction due to the high flow rate in methane[15]. Hytry *et. al.* confirmed the prediction and the theory of dissociation by varying the gas flow rate from 2 sccm to 10 sccm in RF plasma[16]. Chen *et. al.* showed that at higher flow rate (around 300 sccm) the deposition rate is not affected to that much extend, rather the results show that the gas flow rate is an important parameter influencing the nucleation and growth of diamond thin films[17].

3.3.4 CH_4:Ar Ratio

It is well known that the deposition rate of the films depends on the plasma density and the ion energy, and may be considered to be a resulting effect of the balance between deposition and etching[18]. Addition of Ar in the precursor creates the capacitive plasma for dissociating the hydrocarbon gas molecules and enhances the plasma density. This in turn increases the rate of generation of atomic hydrogen and methyl radicals, which results in increased growth rate[18]. However, with the increase of the Ar concentration, the amount of CH_4 gas decreases and above a certain Ar concentration, the CH_4 concentration becomes so low that the etching rate due to Ar becomes more pronounced than the deposition rate from CH_4. As a result, the growth rate drops. This observation for DLC deposition by an Ar diluted CH_4 precursor is similar to that by Sun *et. al.*[19].

Films deposited with no addition of Ar in the plasma have been found to be discontinuous and flake off from the substrate[20]. This indicates that the intrinsic stress in the films is very high. This stress relieving phenomenon has been commonly observed in hard coatings when the stresses are high.

The wear rate of the films deposited in the presence of more Ar is higher than that of the films produced with less Ar present. It has been observed that sp^2 content in the film increases with more dilution of plasma with Ar[21]. This increase in sp^2 content leads to graphitic

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films that are characterized by lower coefficient of friction but higher wear rate. It is interesting to note that there is no significant difference in the tribological properties of the films deposited in the low Ar plasma (lower than 35% of Ar). On the contrary, the films deposited with high Ar show a significant variation in tribological properties. At 78% Ar, the friction coefficient drops to 0.067 and the wear rate increases. This may indicate a substantial increase of sp^2 co-ordination in the film at that dilution of Ar[21].

3.4 Mechanical Properties of DLC films

3.4.1 Hardness

The hardness and elastic modulus are the most commonly measured mechanical properties of amorphous carbon films. This has been possible due to the development of the nanoindentation technique. Nanoindentation is the ideal method for testing DLC films due to its subnanometer depth sensitivity and low load and displacement control. The ability to test the mechanical properties of such thin films without measuring contribution from the underlying substrate is what makes nanoindentation the most accurate method for mechanical property analysis. The importance of nanoindentation is well established. If conventional micro-hardness is used, then these results will be three times higher[24].

The hardness of the DLC films depends on the type of the synthesis process used, i.e., power supply, pressure, flow rate and the ratio of the precursor. The film hardness mainly depends on the ratio of sp^3:sp^2 bonding in the film. As discussed earlier, DLC films consist of sp^3 and sp^2 bonding. If the amount of sp^3 bonding is found to be less than 50% then the film obtained is polymeric type with relatively low hardness. The hardness of DLC film determined by nanoindentation is generally found to be in the range of 10 to 30 GPA[22].

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3.4.2 Friction Coefficient

The friction behavior has been discussed by Voevodin *et. al.*[23]. The diamond surface is normally inert because its broken bonds are generally passivated by C-H bonds. This means that diamond surfaces are hydrophobic, closed shell bond system and they will contact through weak van der Waals forces. Under pressure, the contact will be elastic. As contact shears, it will break weak van der Waals bonds and not the bulk C-C bonds. So, the friction force has adhesive nature rather than abrasive. The DLC behaves in this manner under vacuum or low humidity. Contact with different counter surfaces, produces a transfer layer of DLC on the counter surface. Thus, the contact is between two basically similar hydrophobic DLC layers and so the friction coefficient is low. Anderson *et. al.*[24] suggested that the extremely low friction of DLC can be formed by methane as there are very few dangling C bonds to form residual adhesive contact.

Zhang *et. al.*[25] compared the friction coefficient of films obtained with different bias voltage. They found that the friction coefficient of DLC film decreases with increasing bias voltage.
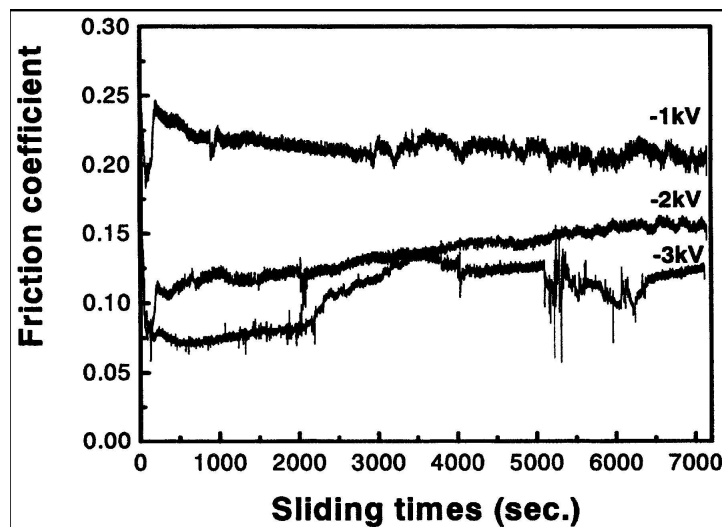
Figure 3.11 Friction Coefficient with varying bias voltage[25]

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3.4.3 Wear Induced Graphitization

Liu and Meletis proposed that during sliding on DLC films, localized graphitization occurs at the contact area resulting in low friction coefficient[26]. DLC is a metastable amorphous film and it can transform to graphite when the energy barrier for transformation of sp^3 to stable sp^2 graphite is overcome. It has been reported that sp^3 C-C domains transform to sp^2 graphite at about 400°C[26]. The heat generated during sliding along with shear forces, provide the energy to the sp^3 carbon structure to graphitize. In addition, it was suggested that shear stresses in the surface layer provide the strain energy for the transformation of DLC to graphite layer after the release of hydrogen[27]. They provided direct TEM evidence for the localized wear induced graphitization by studying the transfer layer forming between the films and counter surface. The transfer layer was mainly composed of defected graphite layers as a result of the wear action.

From the above literature review, it can be seen that depending on the requirement of the film properties, tailoring of the DLC films can be carried out using different deposition techniques. Meletis and co- worker investigated the effect of the processing parameters on DLC produced by DC PECVD. In the present study, the effects of four major processing parameters have been considered which have the main impact on the deposition and tribological properties of DLC films.

The power supply used for the deposition of DLC films has a great effect on the film properties. It was seen that with increasing the RF power supply beyond certain limit the deposition rate decreases due to the increase of the plasma sheath. Moreover, with the increase in the RF power, the friction coefficient decreases. It was found that at lower pressure no film was obtained, but with the increase in the pressure the deposition rate increased due to larger hydrocarbon flux reaching the substrate surface, but the hardness of the film decreases. The higher flow rate results in the decrease on the deposition rate due to a very high dissociation rate for the low gas flow. The ratio of CH_4 to Ar also plays an important role. It was found that Ar in the precursor creates the capacitive plasma for dissociating the hydrocarbon

gas molecules and enhances the plasma density, however with the increase in the Ar content the etching rate increases resulting in the decrease of the growth rate of the film.

All the above mentioned studies with changing in pressure, flow rate and CH_4 to Ar ratio were carried out by using DC or other power sources which have limitation of use with conducting material. The RF power which was used to investigate the properties of the film was way high. The major drawback of high RF power is high emission of radiation which results in heating of body and burning of other internal organs of body. In the present study, the effects of the above mentioned processing parameters using low RF power were considered.

CHAPTER 4

EXPERIMENTAL DESIGN AND PROCEDURE

DLC films were synthesized using a mixture of CH_4 and Ar as the precursor gas in a home built hybrid Physical Vapor Deposition (PVD)/Chemical Vapor Deposition (CVD) system to investigate the effect of processing parameters on the film quality. Subsequently, DLC films were deposited by varying different deposition parameters to investigate their effect on their mechanical and tribological behavior. The details of the deposition system are given below.

4.1 Synthesis of DLC Films

4.1.1 Hybrid plasma CVD and PVD system

Figure 4.1 shows a schematic diagram of the hybrid plasma CVD and PVD system. It is a combination of Magnetron sputtering in the presence of an ionized gas. The chamber of the system is made up of stainless steel with 47 cm (18.38") diameter and 50 cm (19.66") length. It has two Magnetron guns equipped with both DC and RF biasing capabilities. The guns can hold the target of thickness 0.317 cm (0.125"), 0.469 cm (0.185") or 0.635 cm (0.25") and diameter of less than 5.08 cm (2"). Pneumatic shutters shield the targets from the plasma. The gun can be DC biased up to 1 KW (Advanced Energy MDX) and the RF biasing is up to 300 W (AJA 100/300) which is manually matched using a 13.56 Hz generator. The substrate holder has rotating and heating capabilities with an end plate of 15.24 cm (6") in diameter. The substrate can be biased either by the DC on RF (max 50W) power supply. Cooling of magnetron gun as well as substrate holder is performed by using a water chiller. Roughing of the chamber is accomplished using a Trivac B mechanical pump. Low vacuum is achieved using an Ebara FS series 8 cryogenic pump and compressor. There are three pressure measuring gages, thermocouple gage for measuring the pressure in the roughing line (near the mechanical

pump), baratron for measuring the chamber pressure and ion gage for measuring the chamber pressure below 10^{-4} Torr. The gases used as precursor are controlled by mass flow controllers and the read out box. During deposition, very precise control of the pressure is maintained using an automated gate valve in conjunction with a MKS 146C PID controller.
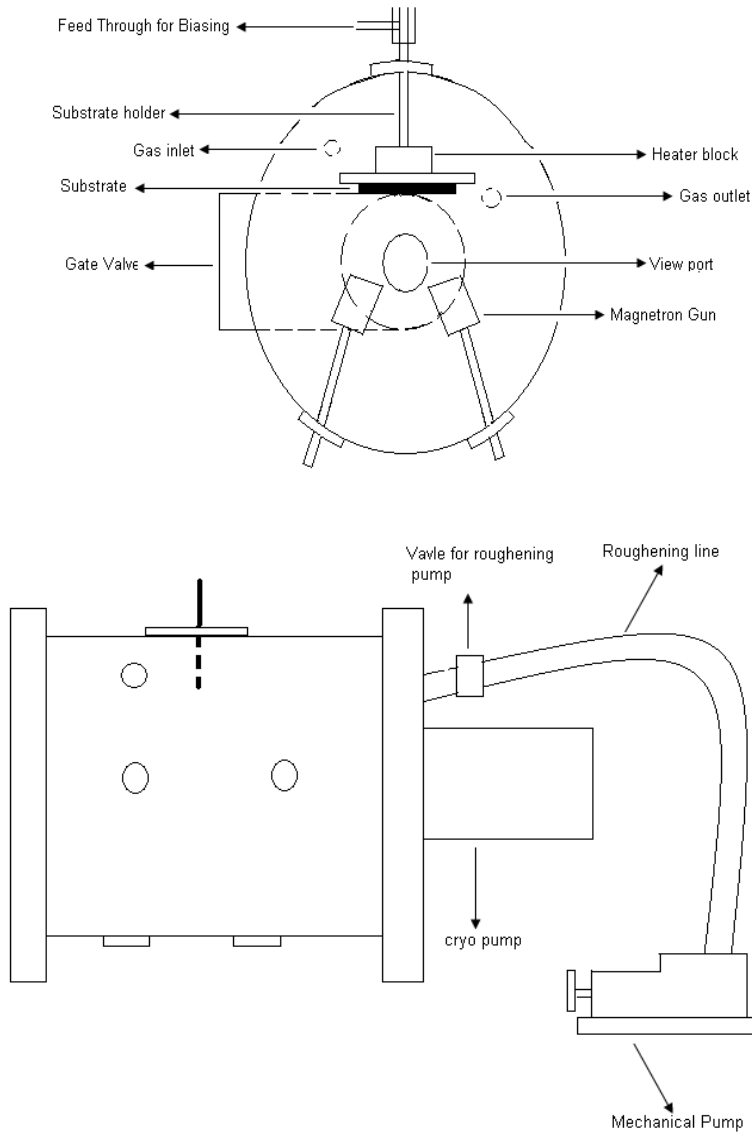
Figure 4.1 (a) Schematic view of hybrid plasma CVD/PVD system. (b) Side view of the hybrid plasma CVD and PVD system

Roughening of the chamber is carried out using the mechanical pump which brings the chamber pressure down to 5 mTorr. The cryogenic pump is pumped down to 10 to 15 mTorr by roughing it with the mechanical pump for partial regeneration which allows the cryogenic pump capable in reaching low temperatures. Once roughening is accomplished, the valve between the chamber and the mechanical pump is closed and the cryogenic pump is brought down to a temperature of 10K. During cooling of the cryogenic pump, the gate valve remained closed to isolate it from the chamber. Once the temperature of 10K is achieved, the gate valve between the cryogenic pump and chamber is opened to lower the pressure inside the chamber down to 10^{-6} Torr.

4.1.2 DLC Deposition by RF Power Supply

DLC films were deposited on square pieces of about 2.5 cm cut from 15.24 cm (6") Si (100) p-type wafers. Prior to deposition, all the wafers were given RCA cleaning treatment. In RCA cleaning, all wafers were first cleaned in mixture of H_2O_2 and HCl for the removal of ionic particles. The wafers were cleaned in HF for removal of oxides (native) and finally they were cleaned in a mixture of H_2O_2 and NH_4OH for removal of organic material. Before loading in the chamber, the wafers were cleaned with acetone and dried with nitrogen. The wafers were masked on two sides for measuring the film thickness by step height analysis. After loading the wafer in the chamber, the pressure was brought down to 5 mTorr using the mechanical pump and then it was exposed to cryopump by opening the gate valve. The base pressure of the chamber was brought to, $< 1 \times 10^{-6}$ mTorr. The chamber was purged with Ar gas five times. During purging and deposition, the substrate was constantly heated at $100^{O}C$. The temperature is maintained by a thermocouple in the heater block. DLC films were deposited by biasing the substrate holder with the RF power supply or negative DC bias. Processing parameters like power, chamber pressure, flow rate and CH_4:Ar ratio was varied in the DLC film deposition experiments.

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4.1.2.1 Variation in Power

The substrate holder can be biased with a RF power supply with maximum capacity of 50 W. Power was varied from 5 W to 45 W by keeping the chamber pressure constant at 100 mTorr. The total flow rate of CH_4 and Ar was kept at 100 sccm with a ratio of 83:17. The ratio values used were selected by considering the previous work by Gupta *et. al.*[9]. The deposition parameters are presented in Table 4.1

Table 4.1 DLC deposition with variation in RF Power

Film Code	RF Power (W)	Time (min)	Pressure (mTorr)	Flow Rate (sccm)	Ratio (CH_4:Ar)
1-a	5	150	100	100	83:17
2-a	10	150	100	100	83:17
3-a	20	150	100	100	83:17
4-a	25	150	100	100	83:17
5-a	35	150	100	100	83:17
6-a	40	150	100	100	83:17
7-a	45	150	100	100	83:17

4.1.2.2 Variation in Pressure

The pressure plays an important role in the deposition by the RF PACVD technique. Significant amount of research has been conducted to verify the importance of the pressure on the deposition rate. Most of the previous experiments were carried out either using DC negative bias or high RF power. So in this work the effect of chamber pressure variation was investigated by conducting low RF power. Table 4.2 shows the different processing conditions used for films deposited different pressure level. The RF power used for this series of depositions was

selected from the outcome of the previous set of experiments conducted at various power levels.

Table 4.2 DLC deposition with variation in Pressure

Film Code	Power (W)	Time (min)	**Pressure (mTorr)**	Flow Rate (sccm)	Ratio (CH_4:Ar)
1-b	35	120	**50**	40	83:17
2-b	35	120	**75**	40	83:17
3-b	35	120	**100**	40	83:17
4-b	35	120	**150**	40	83:17

4.1.2.3 Variation in Total Gas Flow Rate

The total flow rate in the chamber was another of the parameters that was considered for the deposition of DLC films. Table 4.3 shows the different processing parameters used for deposition of films by varying the total flow rate.

Table 4.3 DLC deposition with variation in Total Gas Flow Rate

Film Code	Power (W)	Time (min)	Pressure (mTorr)	**Flow Rate (sccm)**	Ratio (CH_4:Ar)
3-b	35	120	100	**40**	83:17
2-c	35	120	100	**50**	83:17
3-c	35	120	100	**75**	83:17
5-a	35	150	100	**100**	83:17

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4.1.2.4 Variation in CH_4:Ar Ratio

The ratio of the CH_4:Ar ratio has been considered previously by Meletis *et. al.*[10] and by Sun *et. al*[19]. However, the effect of RF power has not being investigated. Table 4.4 shows the variation in the ratio of CH_4:Ar by keeping all the other parameters constant.

Table 4.4 DLC deposition with variation in CH4:Ar Ratio

Film Code	Power (W)	Time (min)	Pressure (mTorr)	Flow Rate (sccm)	Ratio (CH_4:Ar)
3-b	35	120	100	40	83:17
1-d	35	120	100	40	77:23
2-d	35	120	100	40	70:30

<u>4.2 Characterization of DLC</u>

4.2.1 Film Thickness and Deposition Rate

The masked areas of the Si wafers were used to measure the film thickness. The thickness of the film was measured by using a KLA tencor Alpha-Step IQ Profilometer. The step up profilometer uses a stylus as the probe to measure the thickness. As the stylus moves along the masked area the difference in the height is measured. The profilometer was also used to measure film roughness.

4.2.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used to investigate the cross section morphology of the DLC films and observe the substrate/film interface.

4.2.3 Mechanical Properties

Hardness is one of the most important properties for DLC films. These DLC films are mainly known for high hardness and low wear rates. Nanohardness measurements were performed on the DLC films to assess their hardness. Nanoindentation is the most appropriate method for studying mechanical properties at the nanoscale. The technique provides high spatial resolution and real-time load-displacement (into the surface) data while the indentation is in progress. A Berkovich tip was used for measurements. The hardness is given by

$$H = P_{max}/Ar \qquad\qquad (2)$$

Where H is the hardness, P_{max} is the load (10 mN in the present case), Ar is the area of indentation which is a function of height (Ar = f(h)).

The area of the indentation depends on the height and the geometry of the tip. To calibrate the instrument a standard quartz sample with known hardness was used. The

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calibration also determines the area function with respect to the geometry of the tip. The height is kept to 10% of the indentation depth for accuracy of the results.

4.2.4 Tribological characterization of DLC films

The tribological behavior of the DLC films was investigated by conducting pin-on-disc experiments using a tribometer (CSM instruments). A 100Cr6 steel ball of 6mm diameter was used as the pin material for the experiments. A load of 1N was applied for the experiments. The wear tests were performed with a linear velocity of 4 cm/s and for a distance of 1500 meters. The friction coefficient was continuously monitored as a function of sliding distance.

The wear rate was calculated by obtaining the wear track profile under an optical profilometer (Veeco) and four measurements were obtained for each individual wear track. The wear volume was measured by multiplying the average cross sectional area of the wear track by the length of the wear track. The wear rate of the film is given by

Wear Rate = Wear volume (mm^3) / {load (N) x sliding distance (m)} (3)

SEM observations were conducted on the wear tracks to observe wear track morphology and on the pin scar to determine possible transfer layer formation.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Effect of Processing Parameters on Deposition Rate and Hardness of DLC Films

5.1.1 Effect of Power

DLC films were deposited on Si wafers by varying the RF power within the allowable range of the vacuum system. Table 5.1 shows the effect of power on deposition rate and hardness of the DLC films. The films were deposited keeping the pressure at 100 mTorr, flow rate of 100 sccm and CH_4:Ar ratio of 83:17 for 150 minutes. Argon cleaning and activation of surface was conducted for 10 minutes at a substrate biasing of -1000V.

Table 5.1 Effect of Power on DLC Deposition Rate and Hardness

Film Code	Power (W)	Time (min)	Pressure (mTorr)	Flow Rate (sccm)	Ratio (CH_4:Ar)	Thickness (nm)	Deposition Rate (nm/min)	Hardness (GPa)
1-a	5	150	100	100	83:17	350	2.33	2.21
2-a	10	150	100	100	83:17	443.16	2.95	7.85
3-a	20	150	100	100	83:17	851.68	5.68	12.66
4-a	25	150	100	100	83:17	1139.3	7.6	14.16
5-a	35	150	100	100	83:17	1487.14	9.91	14.36
6-a	40	150	100	100	83:17	1589.2	10.59	16.12
7-a	45	150	100	100	83:17	No film	0	--

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It was observed that a deposition rate of about 10 nm/min was obtained at 35 W and 40 W powers. The DLC films deposited at a power above 40 W were not adhesive to the substrate surface. This was attributed to sputtering by the Ar atoms resulting in film delamination. At powers below 35 W, the films were adherent but the deposition rate was relatively low as can be seen in Figure 5.1. It can also be observed in Figure 5.1 that the deposition rate increases linearly with increase in power. Cai *et. al.*[28] reported that the RF power increase enhances the plasma density that in turn results in an increase in the deposition rate.
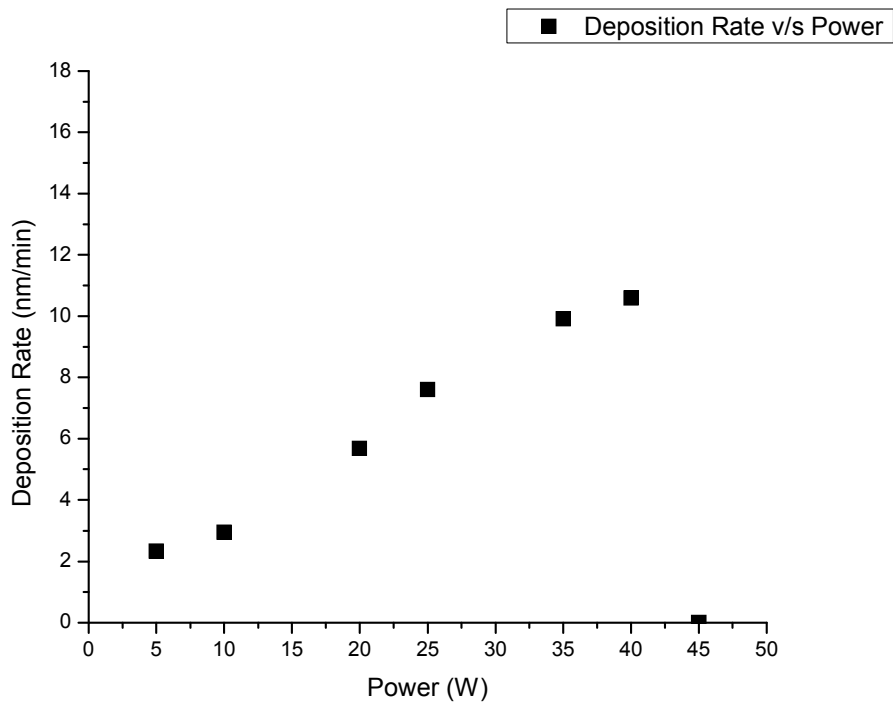

Figure 5.1 Effect of RF Power on Deposition Rate of DLC

Figure 5.2 shows the variation of film hardness obtained from nanoindentation tests with RF power. The hardness of films deposited at low power levels up to 25 W increases linearly with power and reaches a hardness of about 14 GPa. A further increase in power

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causes a moderate increase in hardness reaching a maximum of 16 GPa at 40 W. The film deposited at 45 W (highest power level in the present study) showed delamination. Ravi *et. al.*[29] also observed that the film hardness dramatically increases with rise in power density for value less than 10kW/m^2. This is due to change in the H and sp^3 content in the DLC films. With an increase in power the amount of H content decreases, but the sp^3 content remains at the same levels resulting in an increase of the film hardness. The hardness values above 14 GPa observed in the present study support the above explanation. The delimitation of the film at higher power (45 W) is also consistent with the above rationale. With the increase in hardness, the internal stress of the film increases resulting in highly stressed film which can cause poor adhesion. Based on this hardness response, Films 4-a, 5-a and 6-a showing the highest hardness were selected for tribological testing.
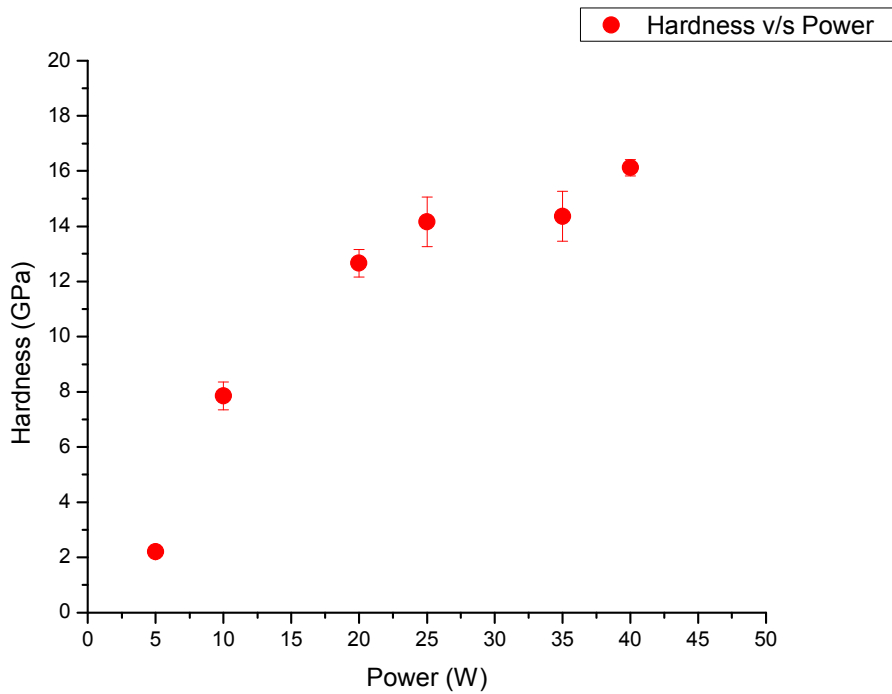

Figure 5.2 Nanoindentation Hardness values as a function of RF Power

5.1.2 Effect of Pressure

DLC films were deposited at various pressure levels ranging from 50 mTorr to 150 mTorr for 120 minutes. All the rest of processing parameters were kept constant; power at 35 W, gas flow rate at 40 sccm and CH_4:Ar ratio at 83:17. Table 5.2 presents the results from this series of experiments. Furthermore, the variation of DLC deposition rate and hardness from nanoindentation experiments versus chamber pressure is shown in Figure 5.3 and 5.4, respectively.

Table 5.2 Effect of Processing Pressure on DLC Deposition Rate and Hardness

Film Code	Power (W)	Time (min)	**Pressure (mTorr)**	Flow rate (sccm)	Ratio $(CH_4$:Ar)	Thickness (nm)	Deposition Rate (nm/min)	Hardness (GPa)
1-b	35	120	**50**	40	83:17	980	8.17	18.14
2-b	35	120	**75**	40	83:17	1350	11.25	16.3
3-b	35	120	**100**	40	83:17	1368	11.4	15.3
4-b	35	120	**150**	40	83:17	1420	11.83	11.6

It was found that under the present processing conditions and up to 75 mTorr, the deposition rate increases with increasing chamber pressure as shown in Figure 5.3. Beyond that pressure, the deposition rate reaches a plateau. According to Ronkainen *et. al*[30]*,* there is a correlation between chamber pressure and growth rate. Higher pressure produces higher growth rate suggesting that the deposition pressure is a controlling factor for the efficiency of deposition process. It can be explained that with the increase in chamber pressure, the number of depositing ions increases resulting in an increase in the deposition rate.
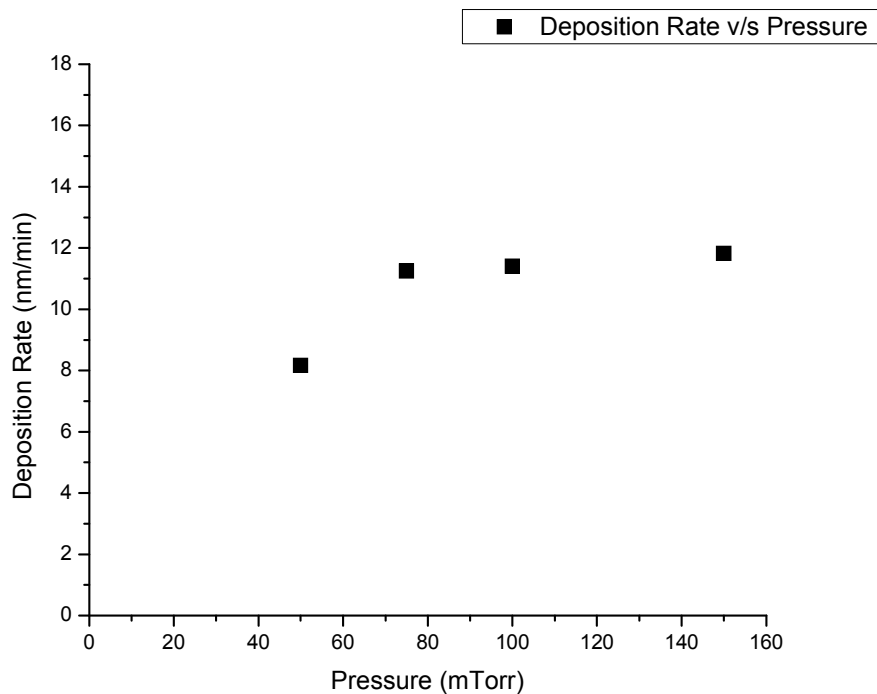
Figure 5.3 Effect of Pressure on Deposition Rate of DLC

Figure 5.4 shows that with an increase in pressure, the hardness of the DLC films decreases. Ronkainen *et. al.*[30] reported that with increasing pressure, the number of ions and energetic neutrals in the plasma increases resulting in an increase in the number of collisions. A larger number of collisions results in a decrease of the energy in ions and neutrals in the plasma. As a result, a smaller number of sp^3 bonds form resulting in the decrease of the hardness. This explanation was confirmed by Hirakuri *et.al.*[7]. Thus, the effect of pressure seems to involve a counter effect between hardness and deposition rate. The film deposited at 50 mTorr exhibited the highest hardness (18 GPa) but at a low deposition rate (about 40% lower than that deposited at 75 mTorr). Based on the present results, the optimum pressure seems to be 75 mTorr. The deposition rate does not increase significantly beyond this pressure level and the film hardness is close to that of the film deposited at 50 mTorr. DLC films deposited at a pressure of 75 mTorr (2-b), 100 mTorr (3-b) and 150 mTorr (4-b) were taken into consideration for further characterization.

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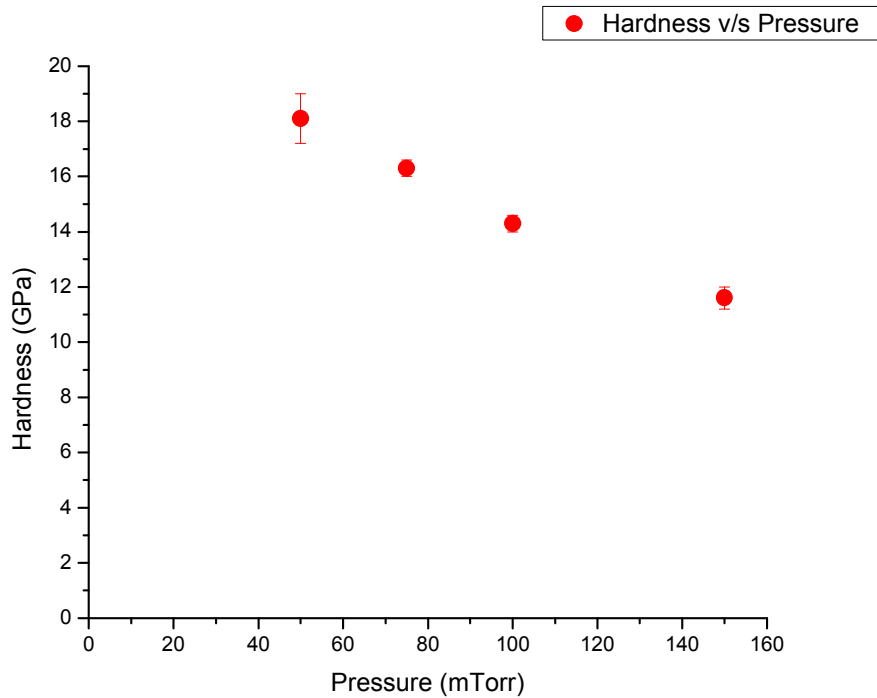
Figure 5.4 Nanoindentation Hardness as a function of Pressure

5.1.3 Effect of Total Gas Flow Rate

There is a considerable effect of gas flow rate at higher power as the flux of carbon carrying radicals' increases with increase in power. Chen *et. al.*[17] varied the flow rate from 30 sccm to 300 sccm at lower power in which they found that the flow rate has negligible effect on the DLC film growth rate. This is consistent with the present results shown in Table 5.3. By varying the flow rate for 40 sccm to 100 sccm while keeping the rest of the processing parameters constant (power at 35 W, pressure at 100 mTorr and CH_4:Ar ratio at 83:17), there is no much change in the deposition rate of the films, Figure 5.5.

Table 5.3 Effect of Total Gas Flow Rate on Deposition Rate and Hardness

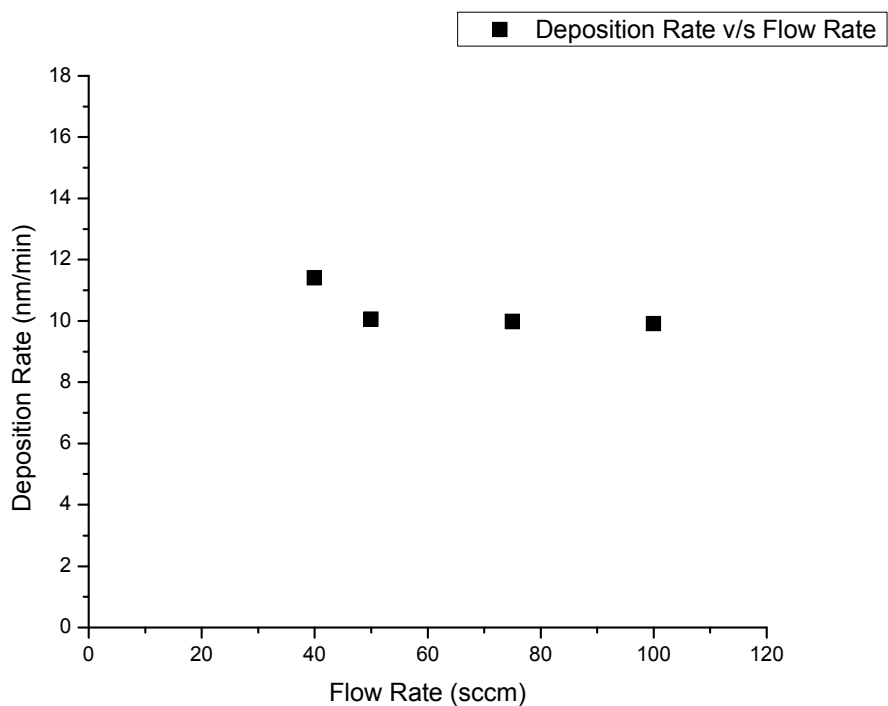| Film Code	Power (W)	Time (min)	Pressure (mTorr)	**Flow rate (sccm)**	Ratio $(CH_4:Ar)$	Thickness (nm)	Deposition Rate (nm/min)	Hardness (GPa)
3-b	35	120	100	**40**	83:17	1,368	11.40	15.30
2-c	35	120	100	**50**	83:17	1,207	10.06	14.48
3-c	35	120	100	**75**	83:17	1,198	9.98	15.31
5-a	35	150	100	**100**	83:17	1,487	9.91	14.36

Figure 5.5 Effect of Total Gas Flow Rate on DLC Deposition Rate

Regarding film hardness, it has been reported that with increase in flow rate the hardness decreases[17]. With a vast increase in the flow rate, the dissociation rate of the gases decreases which results in a higher H_2 content in the film producing lower hardness. The

present results, Figure 5.6, show that with the increase in the flow rate there is no significant variation in hardness since power and pressure are the main governing factor for the formation of sp^3 bonding. Thus, no considerable change occurs in the content of sp^3 resulting in similar hardness values for the present gas flow rate range.
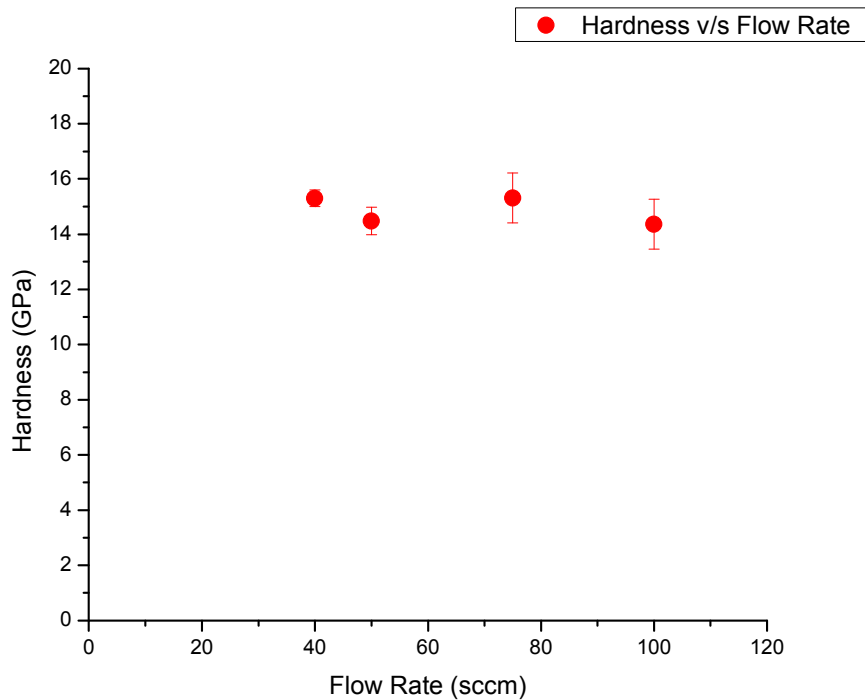
Figure 5.6 Nanoindentation Hardness value as function of Total Gas Flow Rate

5.1.4 Variation in CH$_4$:Ar Ratio

The CH$_4$:Ar ratio plays one of the most important roles in the DLC film deposition. Chakrabati *et. al.*[20] conducted DLC film deposition experiments and found that a CH$_4$:Ar = 77:23 ratio was one of the best ratios. Gupta *et. al.*[10] showed that the best films were observed at the ratio of 83:17. Both studies show that some Ar dilution (around 20%) is required to produce quality DLC films. Considering both reports and to examine the effect of CH$_4$:Ar ratio, DLC films were deposited at various ratios in this rather narrow range while keeping power at 35 W,

pressure at 100 mTorr and flow rate at 40 sccm. Table 5.4 shows the effect of Ar content for that range on film deposition rate and hardness. Figure 5.7 shows that film deposition rate does not vary significantly with Ar% dilution in this range. The slight decrease at higher Ar dilution may be a direct consequence of the sputtering out of the low adhesive carbon atoms on the substrate produced by heavier Ar atoms.

Table 5.4 Effect of CH_4:Ar Ratio on Deposition Rate and Hardness

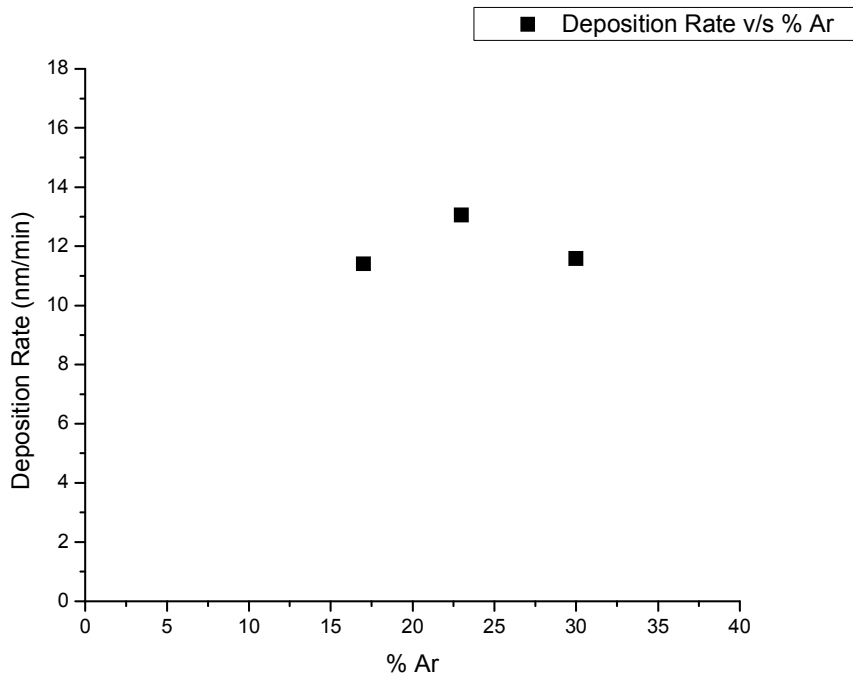| Film Code	Power (W)	Time (min)	Pressure (mTorr)	Flow rate (sccm)	Ratio (CH4:Ar)	Thickness (nm)	Deposition Rate (nm/min)	Hardness (GPa)
3-b	35	120	100	40	83:17	1368	11.4	15.3
1-d	35	120	100	40	77:23	1568	13.06	15.43
2-d	35	120	100	40	70:30	1390	11.58	15.64

Figure 5.7 Effect of CH_4:Ar Ratio on Deposition Rate

The film hardness variation in the selected Ar dilution range is shown in Figure 5.8. There is no much variation in hardness for this range which is in agreement with the previous reports. Indeed, processing in this range provides a good combination of deposition rate and hardness. The slight hardness increase with increased dilution is more or less consistent with the change in the CH_4:Ar ratio. Kim *et. al.*[13] suggested that by adding Ar to dilute the precursor produces a dynamic etching of the sp^2 phase during the deposition of the film resulting in more sp^3 content and thus somewhat higher hardness.
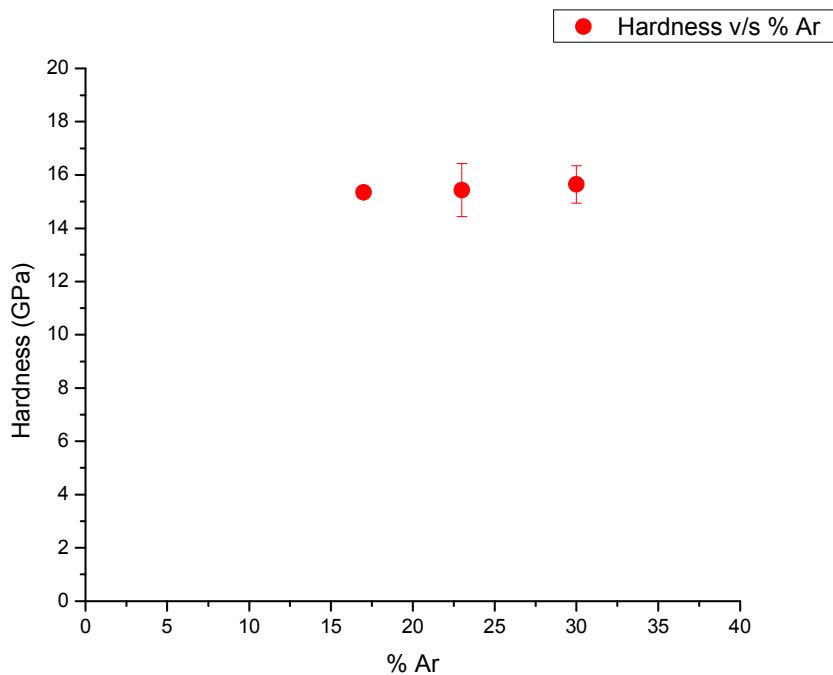
Figure 5.8 Nanoindentation Hardness values as function of CH_4:Ar Ratio

From the above results it can be seen that the increase in RF power has a beneficial effect on the deposition rate as well as hardness. The RF power enhances the plasma density which results in the increase of the deposition rate and hardness. Also, it was observed that above 40 W, residual stresses dominate and leading to film detachment. The experiments with variation in pressure showed that the two counter acting effects; high deposition rate and low

sp^2 content with increase in pressure, find a good compromise around 75 mTorr pressures. At this pressure level, it seems that there is a good compromise between number of collisions and energies of depositing specie in the plasma. The flow rate of the gases does not show any significant change in the deposition rate as well as hardness since power and chamber pressure are the governing factors. But from previous works it was found that at higher power, flow rate has significant effect on the deposition rate. Finally, it was confirmed that also at the present RF power levels, an Ar dilution around 20 % produces a good combination of deposition rate and film hardness.

5.2 Characterization of DLC Films

5.2.1 Scanning Electron Microscopy (SEM)

Fractured cross sections of films 3-b and 3-c were observed by SEM to investigate the film density and adhesion to the surface. Figure 5.9 shows the interface between the Si wafer substrate and the DLC film. The film is featureless without porosity or other visible defects. There was a seamless interface with no visible separation or gaps between the substrate and the film indicative of good adhesion to the substrate.
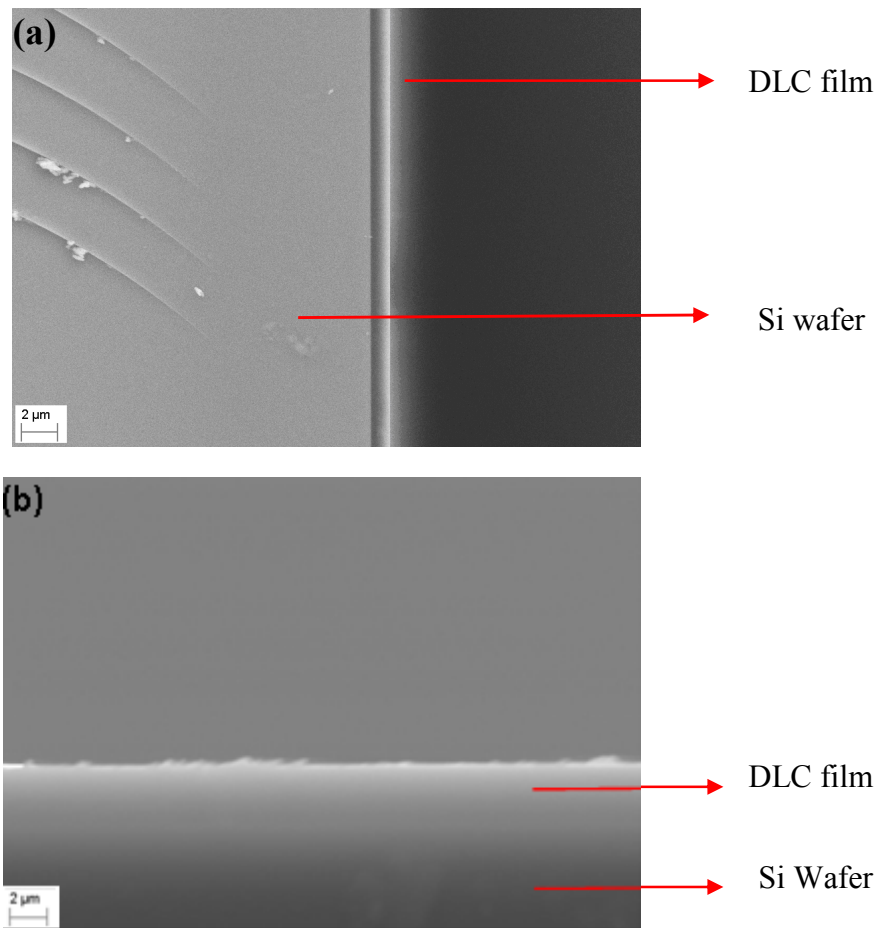
Figure 5.9 SEM micrograph showing cross section of DLC film (a) 3-b and (b) 3-c

5.2.2 Tribological Properties, Wear Rate and Wear Track Morphology of DLC thin films

Pin-on-disc experiments were performed on selected DLC films synthesized at various processing conditions. Their tribological behavior was characterized in terms of coefficient of friction as a function of sliding distance and wear rate. A typical tribological behavior of DLC films exhibits three stages. First, a rapid decrease in the coefficient of friction is observed due to the break-in stage (smoothening of asperity contacts). The second stage involves a much slower rate of reduction in the friction and is due to the initial stages of graphite layer forming in the contact area. In this process, a transfer layer formation may also take place on the pin

counter surface. The third stage is the low friction steady-state due to extensive graphitization taking place in the contact area and the transfer layer. Liu and Meletis[26] provided direct evidence of graphite forming in the transfer layer and proposed the wear-induced graphitization mechanism. In this mechanism, the process of sliding friction provides the energy required for transformation of a thin DLC layer at the contact to graphite leading to low friction.

5.2.2.1 Effect of Power

Figure 5.10 presents the frictional behavior of the three films selected from this series of experiments deposited at different power levels; 25 W (4-a), 35 W (5-a) and 40 W (6-a) powers. All three films show the characteristic three wear stages. The steady state friction coefficient of film 4-a is 0.09, 5-a is 0.07 and that of film 6-a is 0.17. It is interesting to note that a very low friction can be achieved in the 25-35 W power level range. As observed from the hardness response, Figure 5.2, the hardness of the films increases with increase in power. Also, the film deposited at a power of 45 W showed delamination more than likely due to large internal stresses from a higher sp^3 content or lower H content. Thus, the higher friction coefficient for film 6-a can be attributed to higher stresses compared to the films deposited a lower power levels. In such a film, graphitization is expected to take longer and thus, steady state friction is delayed. Ravi *et. al.*[29] observed that the sp^3 content in DLC films remains more or less same by changing power but the H content decreases resulting in higher internal stresses. As a result, the energy required to reach steady state friction is expected to be more in 6-a as compared to films 4-a and 5-a.
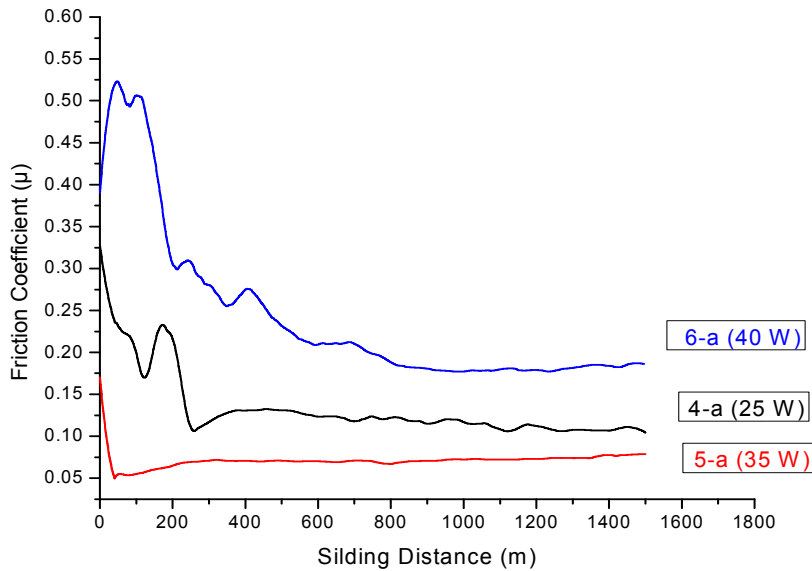
Figure 5.10 Friction Coefficients with variation in Power

The morphology of the wear tracks of all DLC films tested was characterized using optical profilometry. Also, wear rates were calculated by taking two dimensional profiles across the wear tracks. A summary of all friction coefficients and wear rates for the present study is given in Table 5.5.

Figure 5.11 presents typical wear profiles of the above three films tested at various power levels. It can be seen from these profiles that the penetration depth decreases by increasing RF power. For example, film 4-a (25 W) exhibits a penetration of about 0.6 µm whereas film 6-a (40 W) has a penetration of less than 0.3 µm (50% smaller). The results also show that the film with higher penetration is characterized by a narrow contact compared to the rest two films that exhibited a wider contact with the pin. Harder films are characterized by a wider contact which in fact results in a larger contact area and lower contact stresses. The same trend is followed by the wear rate, Table 5.5. These results are consistent with the notion that softer films are characterized with more sp^2 and/or H content and thus, exhibit low friction

but high wear rate; whereas harder films have more sp^3 and/or lower H content and thus, exhibit somewhat higher friction but lower wear rate.
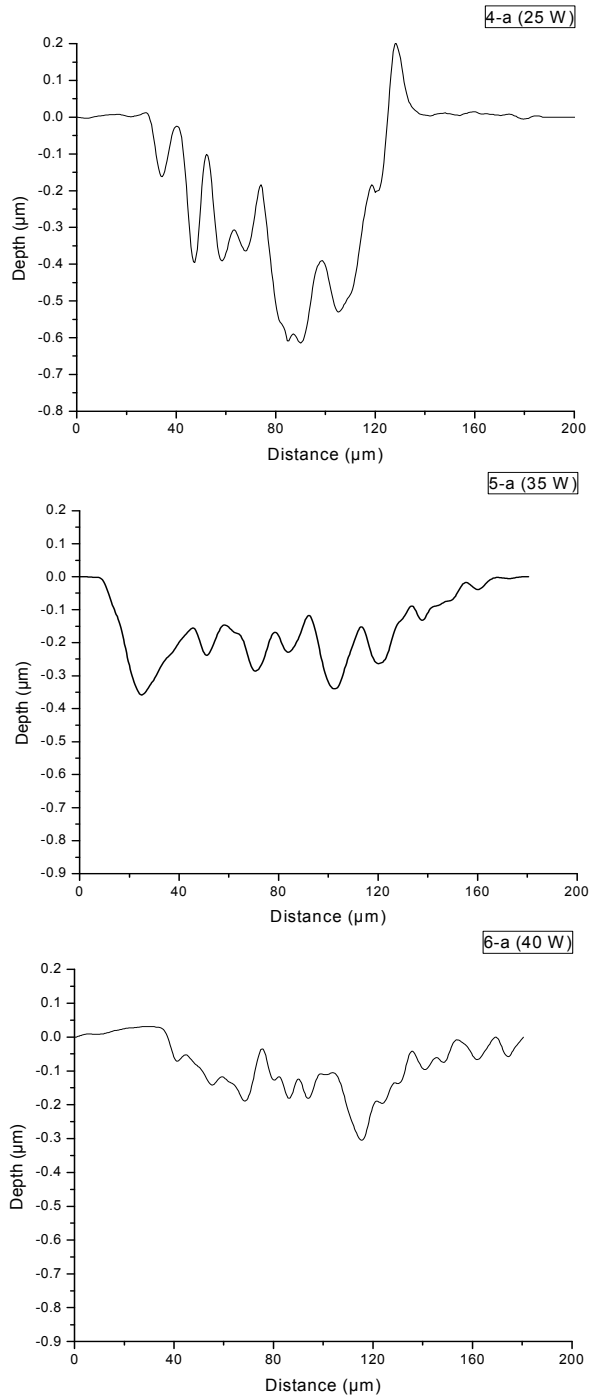

Figure 5.11 Wear Track of DLC films with varying Power

5.2.2.2 Effect of Pressure

Figure 5.12 presents the variation of the friction coefficient with sliding distance for films deposited at different processing pressures; 75 mTorr, 100 mTorr and 150 mTorr pressure. It is interesting to note that all films exhibited low coefficients of friction. The films deposited at lower pressure levels in particular exhibited very low coefficients of friction in the range of 0.06-0.08.
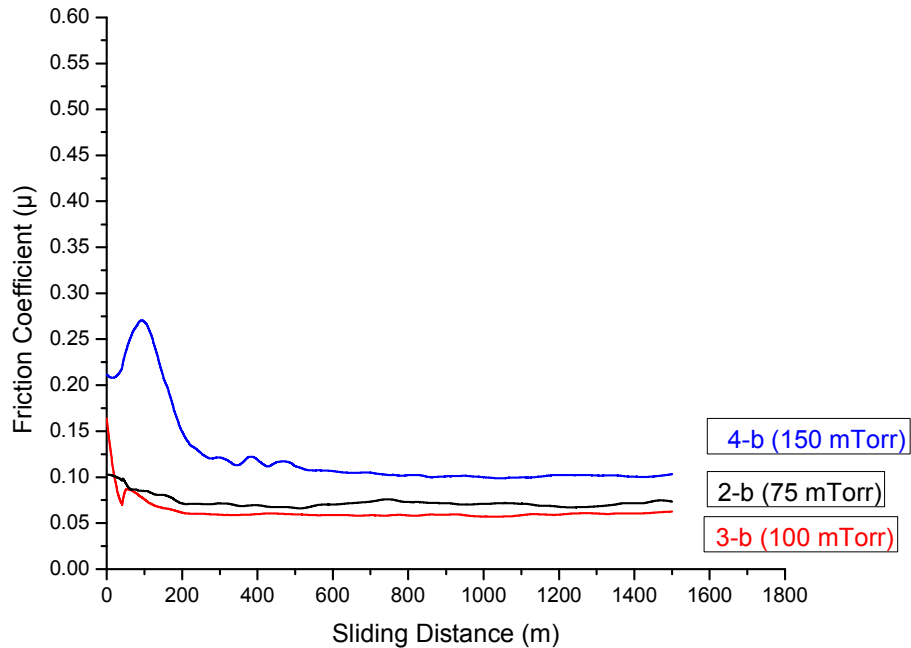

Figure 5.12 Friction Coefficient with variation in Pressure

Film 2-b provides a good combination of low friction and high wear resistance. Film 3-b that was deposited at high pressure is characterized by low friction but high wear rate. This behavior is consistent with the previous results and is attributed to the fact that high pressure enhances the sp^2 content in the film. The width and depth of the wear track of DLC films 2-b (50 mTorr), 3-b (100 mTorr) and 4-b (150 mTorr) are shown in Figure 5.13. It can be observed that the film 2-b exhibits the shallower penetration (~0.45 µm) compared to films 3-b and 4-b (about 0.8 and 0.7 µm, respectively). As a result, film 2-b exhibits lower wear rate, Table 5.5.
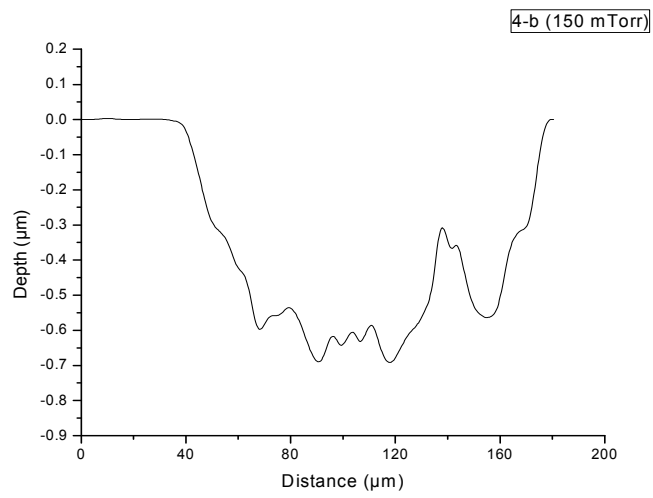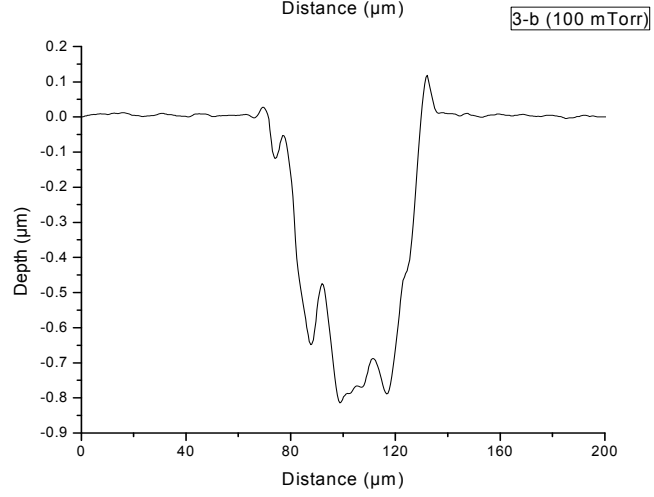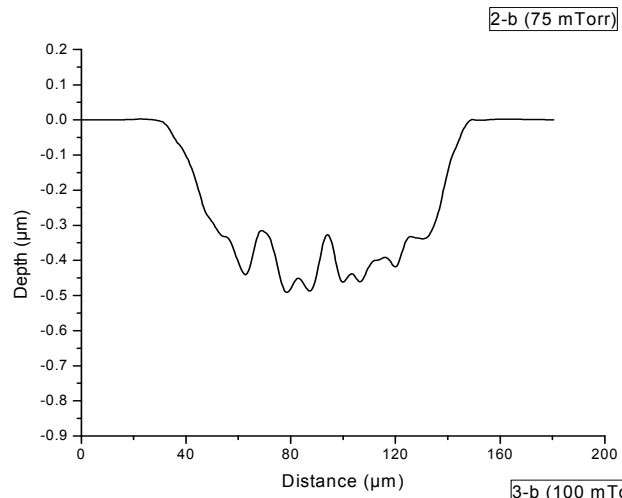
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Figure 5.13 Wear Track of DLC films with varying Pressure

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As discussed earlier, film 2-b was deposited at lower pressure that results in higher sp^3 content and hardness, Figure 5.4. Thus, film 2-b has an excellent combination of ultra low friction (0.08) and wear rate (8x10^{-8} mm^3/Nm). Furthermore, the wear resistance of this film is significantly higher from typical wear resistance of DLC films prepared by DC PACVD (about 10^{-7} mm^3/Nm)[10]. The improved wear resistance of the present films is attributed to film homogeneity resulting from the better plasma uniformity generated by RF compared to DC discharge.

5.2.2.3 Effect of Total Gas Flow Rate

The variation of the friction coefficient of DLC films deposited at different flow rates, varying from 40 to 100 sccm, is shown in Figure 5.14. It can be observed that friction coefficient decreases from 0.22 to 0.07 with increase in flow rate from 50 to 100 sccm. The friction coefficient at 40 sccm is the lowest in this series of experiments exhibiting a value around 0.06. The reasons for the lower friction observed for this film are not clear and may be attributed to the influence of other processing parameters.
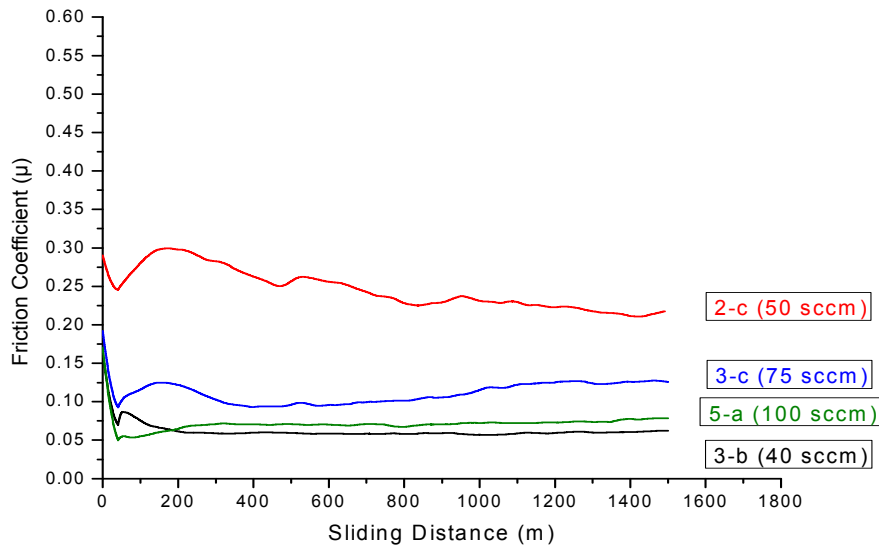

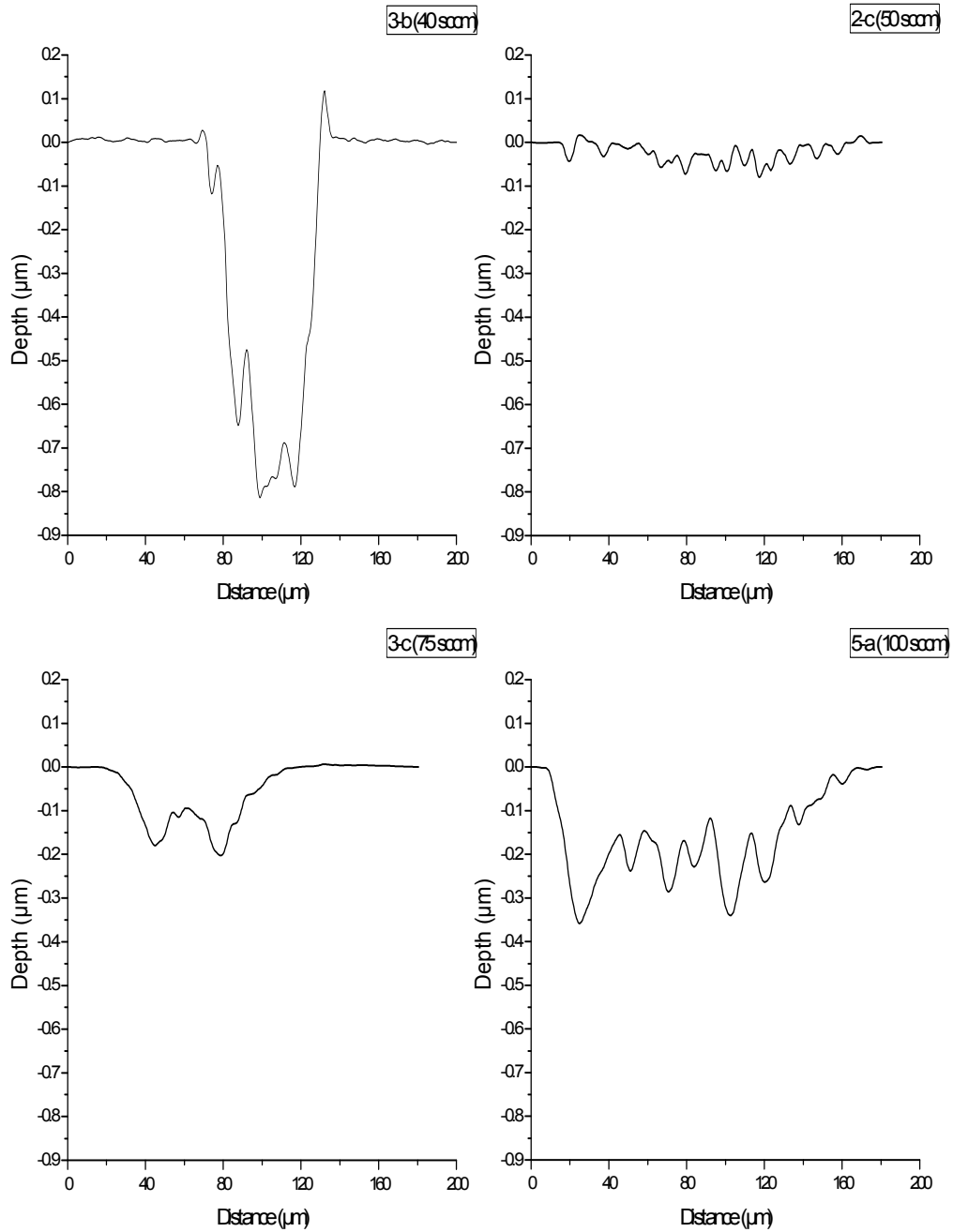Figure 5.14 Friction Coefficients with variation in Total Gas Flow Rate

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Figure 5.15 Wear Tracks of DLC films with varying Total Gas Flow Rate

From Figure 5.15 presents the wear track profiles of DLC films deposited with variation in flow rate. It can be observed that the wear track of 3-b is the deepest which shows large

amount of material removal. The high wear rate in 3-b can be attributed to its low friction resulting from a high graphitic sp^2 content and is consistent with the notion of low friction but high wear rate. By examining the profiles of film 2-c (50 sccm), 3-c (75 sccm) and 5-a (100 sccm) it can be observed that they have extremely low wear whereas film 2-c has negligible wear. The variation of μ (Figure 5.14) shows that friction decreases with increase in flow rate which follows the trend that of high wear rate with lower friction coefficient. Table 5.5 shows that films 2-c and 3-c exhibited an ultra low wear rate in the order of 10^{-9} mm^3/Nm. In fact, film 2-c exhibited the lowest wear rate of all films synthesized in the present work.

5.2.2.4 Effect of CH_4:Ar Ratio

Figure 5.16 presents the effect of the Ar dilution on the coefficient of friction. It is clear that a reduction in the Ar content from 30% to 17% in the discharge causes a reduction in μ. It is significant that an ultra low coefficient of friction of 0.06 was observed at an Ar dilution of 17%. A lower Ar content in the plasma implies lower energetic collisions and a higher H content in the films that may be responsible for the ultra low μ. These films may still have a high sp^3 content and high hardness but are tribologically "soft". Donnet and Grill[31] have shown that the friction behavior can be controlled by the H content of the films. Hydrogen concentrations lower than 34 at% systematically lead to high friction, similar to the friction level of diamond. Ultralow friction is achieved with films that contain at least 40 at% H. Gardos[32] reported that the van der Waals interaction energy between H/H atoms at the contact interface is around 0.08 eV/bond whereas the other interactions have much higher energies (OH/O is 0.2 eV, and C (σ or π)/C is 0.4-0.8 eV) and thus, higher friction.
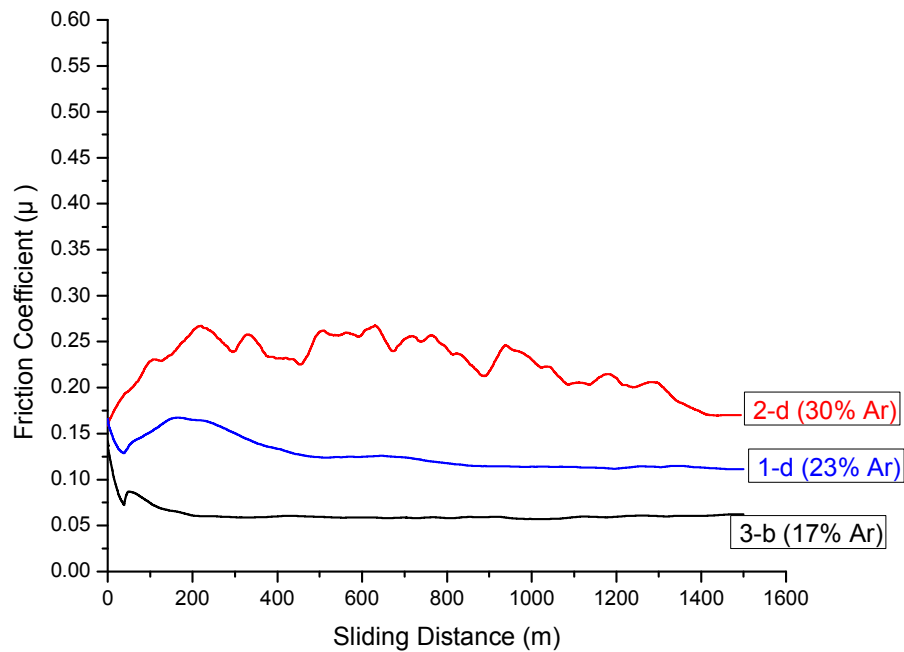
Figure 5.16 Friction Coefficient with variation in CH$_4$:Ar Ratio

Figure 5.17 shows the wear track profile of DLC films in respect to dilution of Ar from 17% to 30%. It is evident that the width and the depth of DLC film obtained at dilution of 17% is way more than that obtained at 23% and 30%. This trend is consistent with the low μ exhibited by this film. Further more, the low wear rate of films 1-d and 2-d are attributed to lower H content as discussed above.

Films 1-d and 2-d have very low penetration of around 0.3 μm compared to 0.8 μm for film 3-b. Further more, the two former films have a wider contact area producing low contact stresses as discussed earlier. Chakrabarti[20] showed that the sp^3 content increases with increase in the Ar content which is consistent with the present data. Higher Ar content is expected to produce more energetic plasma and enhance formation of sp^3 domains.

Figure 5.17 Wear Tracks of DLC films with varying CH$_4$:Ar Ratio

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5.2.3 Transfer layer behavior of DLC films

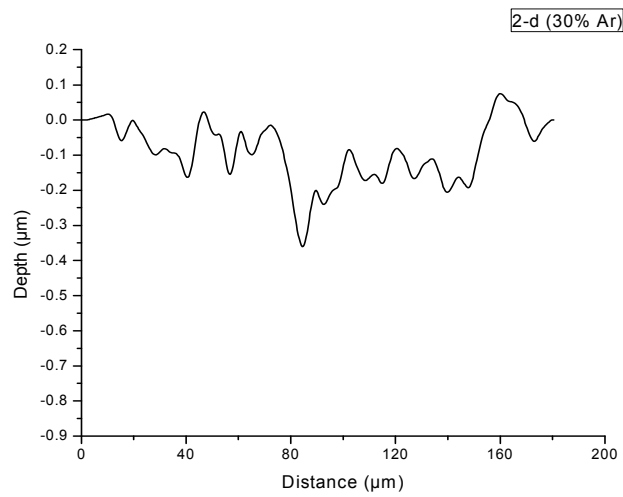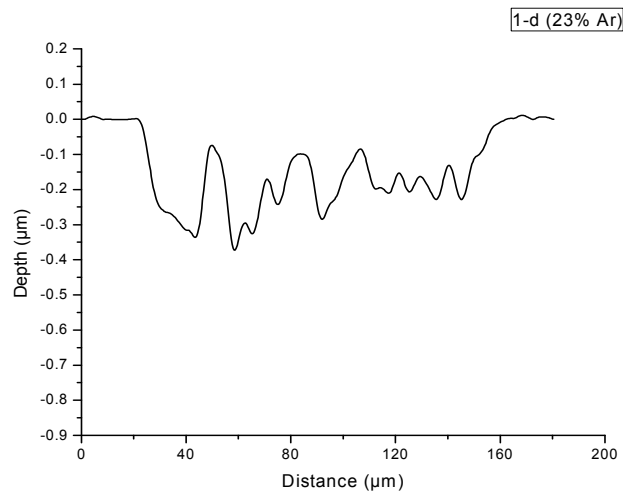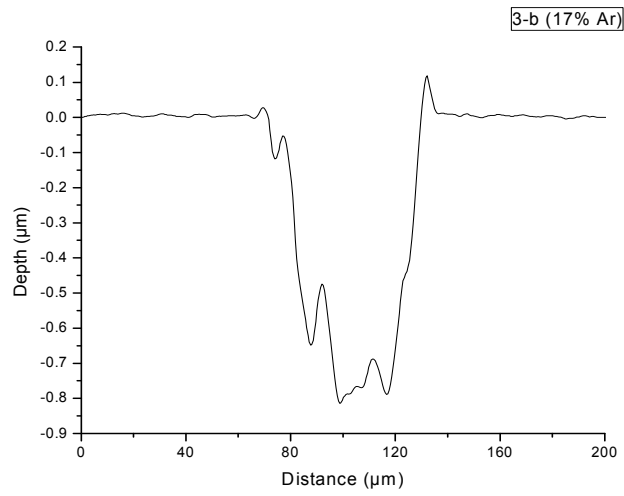SEM examinations were conducted on pin surfaces after wear testing. EDS analysis of DLC revealed only carbon. Figure 5.18 shows SEM images of DLC film 3-b (µ = 0.06). It is clear that a well developed transfer layer exists on the pin counter surface.

Low friction and low wear rate in DLC is consistent with such a transfer layer build up on the pin surface. Significant wear in the initial stages might have created a graphitic transfer layer resulting in decrease in friction coefficient in the long run. Liu and Meletis[26] showed that the reduction in the friction coefficient may be correlated to extensive graphitization and development of graphite layer of critical thickness. They provided direct transmission electron microscopy evidence that the transfer layer is composed of graphite. Sliding-induced heat accumulated on a local contact area probably causes a gradually destabilization of carbon hydrogen bond in sp^3 structure. The ultra low wear rate in film 2-c and 3-c shows that graphitized layer between two surfaces in contact is composed of low-strength atomic hexagonal carbon layers that can undergo repeated shear. Thus, wear rate is determined by the life time of the transfer layer and the transformation kinetics from sp^3 to sp^2. The latter aspect is expected to depend on the characteristics of the underlying film (hardness, sp3 content, uniformity, H content, etc.).
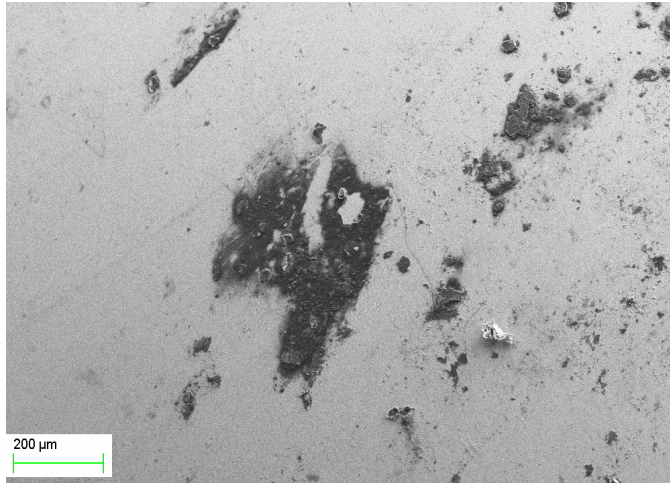
(a)

(b)

Figure 5.18 SEM images of film 3-b after wear testing (a) wear track in DLC film and (b) pin surface

Table 5.5 Friction Coefficient and wear rate of DLC Films

Film Code	Deposition Rate (nm/min)	Hardness (GPa)	Steady State Friction Coefficient	Wear Rate mm^3/Nm
4-a	7.6	14.16	0.09	7.4×10^{-7}
5-a	**9.91**	**14.36**	**0.07**	**5.6×10^{-8}**
6-a	10.59	16.12	0.17	3.2×10^{-8}
2-b	**11.25**	**16.3**	**0.08**	**8.0×10^{-8}**
3-b	**11.4**	**15.3**	**0.06**	**4.7×10^{-7}**
4-b	11.83	11.6	0.12	2.5×10^{-7}
2-c	**10.06**	**14.48**	**0.22**	**5.3×10^{-9}**
3-c	**9.98**	**15.31**	**0.13**	**9.8×10^{-9}**
1-d	13.06	15.43	0.12	3.3×10^{-8}
2-d	11.58	15.64	0.20	2.5×10^{-8}

Table 5.5 summarizes the deposition rate, hardness, steady state friction coefficient and wear rate of all films that were taken into consideration for characterization. A review of the film behavior shows that films 4-a and 3-b have low coefficient of friction (<0.1) but high wear rate (10^{-7} mm^3/Nm). These films were deposited either at low power or high pressure and as discussed earlier, both of these parameters favor formation of sp^2 domains. Films 5-a and 2-b present an excellent combination of low friction (μ ≈0.08) and high wear resistance (<8x10^{-8} mm^3/Nm). Finally, films 2-c and 3-c exhibited the lowest wear rate (<10^{-8} mm^3/Nm) followed by films 1-d, 2-d and 6-a (<3.3x10^{-8} mm^3/Nm). It is interesting to note that the films in that last group with the ultra low wear rate exhibited a moderate friction coefficient between 0.12 and 0.22. Such behavior is characteristic of films with diamond-like character. A careful examination of the frictional behavior of the latter films indicates that steady state friction may have not been reached in these films. Indeed, films with diamond-like character are expected to show slower

graphitization transformation kinetics and thus, somewhat higher friction at least initially. In other words, the steady state stage may take longer time to be reached. In the meantime their wear resistance is high.

CHAPTER 6

CONCLUSION

The following conclusions can be drawn from the present study:

1. A study was conducted to assess the effect of various processing RF PACVD parameters on the characteristics of DLC films. The results showed that an intermediate RF power level around 35 W gives a good compromise between deposition rate and hardness. It was also observed that after 40 W powers the film delaminates due to higher internal stresses. Also, a pressure range between 75 mTorr to 100 mTorr showed to improve film growth and hardness along with low friction. Flow rate showed insignificant impact when considered individually but when combined with other parameters showed a dramatic effect on the film properties. Even though the amount of Ar (17% to 30%) in the discharge has a small impact on the hardness a high deposition rate was obtained at 23% Ar dilution. A combination of above parameters can result in obtaining a desirable film with desirable tribological properties.

2. The films synthesized can be divided into three general categories. In group I, the films with low friction but high wear rate. These are characterized by enhanced graphitic component resulting from either high pressure or low RF power during deposition. Group II involves films with an attractive combination of low friction and low wear rate. Group III has films with a friction coefficient in the 0.12 to 0.22 range and characterized by ultra low wear rate.

3. The present results show that RF PACVD can produce DLC films with ultra low wear

    rate. This is attributed to plasma uniformity generated by RF compared to DC PECVD.

    Such effect is expected to impact DLC film homogeneity.

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