CHAPTER 4
MATERIAL PROCESSING USING THE PLANAR COIL RF
INDUCTIVELY COUPLED PLASMA SYSTEM

4.1 Introduction

The planar coil RF inductively coupled plasma (PC-RFICP) systems developed at the Plasma Research Laboratory as described in Chapters 2 and 3 have been tested for various applications in material processing. These include nitriding of metallic surface; sputter deposition of titanium nitride thin film; plasma enhanced chemical vapor deposition (PECVD) of diamond-like carbon thin film and plasma polymerization.

Work done on nitriding of metallic surface, sputter deposition of titanium thin film, and plasma enhanced chemical vapor deposition of diamond-like carbon thin film have been carried out in previous projects (Kok, 1997; Liew, 2001; Chiew, 2002; Abdul Hakim, 2002) carried out in this lab, and these results will be summarized in this thesis to demonstrate the versatility of the PC-RFICP system developed at the Plasma Research Laboratory, University of Malaya.

4.2 Nitriding of metallic surface – stainless steel

Plasma nitriding is a plasma-activated thermochemical method for increasing the surface hardness, fatigue strength, corrosion and wear resistance of metallic surface. Various metals both ferrous and non-ferrous (Cr, Ni, Al, Ti) can be nitrided. In plasma nitriding, the sample surface is exposed to nitrogen plasma in which the nitrogen ions are accelerated to its surface by the negative potential applied to the substrate. The active species which comprise of nitrogen molecules and ions diffuses into the substrate and the rate of diffusion is temperature dependent (Matsumoto, 1984). Commercial plasma-nitriding reactors
use an abnormal glow discharge, either dc or pulsed. These discharges perform well when nitriding low-alloy and tool steels (Rie et al., 1996), but they are less successful with stainless steel, particularly those grades with an austenitic structure. The high treatment temperature common in commercial nitriding processes causes precipitation of CrN (Zhang and Bell, 1985), resulting in surfaces that are hard and resistant to wear but suffer degraded corrosion resistance. The use of lower treatment temperatures and low-pressure discharges has been found to be effective in addressing this problem (Zhang and Bell, 1985; Menthe, 1995; Collins, 1995). The modified layer so produced contains an as yet unidentified phase, sometimes called S-phase or expanded austenite that is very rich in nitrogen. A similar phase can be produced by ion implantation (Williamson, 1994), and by reactive sputtering (Saker et al., 1991).

The planar coil radio frequency inductively coupled plasma (PC-RFICP) system has been used to demonstrate the nitriding of austenitic stainless steel and titanium substrates. Nitriding of austenitic stainless steel is considered to be more difficult than titanium, because of the high activation energy for nitrogen diffusion and the presence of a surface oxide film which hinders nitrogen diffusion (Ozbaysal and Inal, 1986; Metal Handbook, 1981).

The PC-RFICP system that is used for nitriding of stainless steel sample uses the Π network automatic impedance matching system. The schematic diagram of the PC-RFICP system that used for nitriding of stainless steel has already been presented in Figure 2.2.

The conditions that is required for nitriding of the AISI 316 stainless steel substrates is summarized in Table 4.1.
Table 4.1 Conditions that is used for nitriding of AISI 316 type stainless steel.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Gas</th>
<th>Pressure mbar</th>
<th>RF Power Watts</th>
<th>Substrate Bias</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen</td>
<td>0.055</td>
<td>250</td>
<td>- 400</td>
<td>15 mins</td>
</tr>
<tr>
<td>Cleaning</td>
<td>Argon</td>
<td>1.024</td>
<td>400</td>
<td>- 250</td>
<td>140 mA 15 mins</td>
</tr>
<tr>
<td>Nitriding</td>
<td>N$_2$ + H$_2$</td>
<td>1.055</td>
<td>250</td>
<td>- 600</td>
<td>72 - 57 2 hours</td>
</tr>
<tr>
<td></td>
<td>(9 : 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The admixture of nitrogen and hydrogen gas at a ratio of 9:1 is used as the nitriding gas. The use of hydrogen gas in nitriding gas mixture is necessary under the condition of standard plasma nitriding, as hydrogen is known to increase the nitriding rates (Hudis, 1973; Staines and Bell, 1987; Avni and Spalvins, 1987). After nitriding for 2 hours in the N$_2$/H$_2$ admixture plasma, a quick scratch test on the surface of the stainless steel substrate using milling tool confirms that the substrate has been nitried. The nitried stainless steel surface layer is observed to resist scratch. The surface texture of the substrate has changed from smooth gray color to a dull and relatively rougher gray surface.

4.2.1 EDAX and SEM analysis

The surface morphology of the non-nitried and nitried stainless steel substrate are examined using the scanning electron microscope and are shown in Figures 4.1 and 4.2. The surface morphology of the non-nitried stainless steel substrate shows grain structure. In the nitried stainless steel substrate the grain structure has disappeared and is replaced by a more homogenous and uniform surface morphology.
The different composition of the nitrided layer and the bulk of the substrate will have a different chemical etching rate. The difference in the feature between the nitrided layer and the bulk stainless steel can be observed by viewing the cross section of the nitrided austenitic stainless steel using the SEM after the nitrided sample has undergone chemical etching. Figure 4.3 shows the cross-sectional view of the nitrided substrate with the nitrided layer clearly visible. From the Figure the thickness of the nitrided layer is estimated to be $10 \pm 2 \, \mu m$ and it is uniform across the substrate.

Figure 4.4 shows the energy dispersion X-ray analysis (EDAX) across the cross section of the austenitic stainless steel sample; the percentages of nitrogen, iron and chromium versus the depth of the substrate is shown in this Figure. The result of the analysis displays a significant drop in the percentage of nitrogen, at depth of more than 10 $\mu m$ from the surface.
Figure 4.1  Scanning electron micrograph showing surface texture of the unnitrided austenitic stainless steel.

Figure 4.2  Scanning electron micrograph showing surface texture of the nitrided austenitic stainless steel.
Figure 4.3  Cross-sectional view of the nitrided austenitic stainless steel substrate showing the nitrided layer.
Figure 4.4 The nitrogen (N), iron (Fe), chromium (Cr) contents of the nitrided substrate versus substrate cross section depth.
4.2.2 *Glancing Angle X-Ray Diffraction (GAXRD) analysis*

X-Ray Diffractograms of the substrate before and after nitriding are obtained. The diffractograms for unnitrided and nitrided substrates are shown in Figures 4.5 and 4.6. The typical X-Ray diffractogram for an austenitic stainless steel is presented in Figure 4.5. The X-Ray diffractogram that is shown in Figures 4.6 is similar to the diffractogram of nitried AISI 304 stainless steel reported by Meletis and Yan (Meletis and Yan, 1993). The AISI 316 and 304 stainless steel has almost the same mechanical properties except the composition of chromium is lower, while more nickel and molybdenum added to AISI 316 stainless steel. Hence, the AISI 316 stainless steel is more resistant to corrosion from acids such as phosphoric, acetic and dilute sulfuric acid; as well as sulfurous and halogen salt water. Peaks due to $\varepsilon$-Fe$_3$N and (Fe,Cr)$_2$N are shown in the X-Ray diffractogram of the nitried austenitic stainless steel (Figure 4.6). The feature of the lattice parameters that is obtained in this work is different from those of pure $\varepsilon$-Fe$_3$N. This may be due to the incorporation of other elements such as Cr, into the structure as proposed by Meletis and Yan (Meletis and Yan, 1993). Meletis and Yan suggested that the nitried layer on the stainless steel substrate may have the structure of $\varepsilon$- (Fe, Cr)$_3$N.
Figure 4.5  Typical diffractogram for an austenitic stainless steel.

Figure 4.6  Diffratogram for the nitrided austenitic stainless steel.
4.2.3  Microhardness test

The hardness of the substrate is measured by using a Vickers microhardness tester. The hardness is determined from the equation

\[ H_v = \frac{1.854 \cdot F}{D^2} \]  \hspace{1cm} (4.1)

where \( F \) is the applied load (kg) and \( D \) is the diagonal length of the impression made by the indenter (mm). Using the microhardness tester, the hardness for the nitrided layer is 1365 ± 300 Hv while the hardness of the base metal is 186 ± 8 Hv. The nitrided layer shows an increase in hardness of about 7 times.

Plasma nitriding using the planar coil RF inductively coupled plasma system on the stainless steel substrate with a nitrided layer of 10 \( \mu \)m thick has been demonstrated. The structure of nitrided layer is \( \varepsilon-(\text{Fe,Cr})_3\text{N} \), and hardness of the nitrided surface is 1365 ± 300 Hv.
4.3 Nitriding of metallic surface – Titanium (Ti)

Nitriding of pure Ti sheet has been demonstrated using the PC-RFICP system with LC resonant circuit matching network. The argon-nitrogen admixture gas is used as the discharge gas. The schematic diagram for the configuration of the PC-RFICP system that is used for this study is already depicted in Figure 2.3.

In the nitriding of pure titanium substrate, argon gas is filled to a pressure of 0.015 mbar, and nitrogen is then introduced into the chamber until the desired discharge pressure is reached. The effect of discharge pressure of argon-nitrogen admixture on the nitriding process is carried out at 0.05, 0.1, 0.15, 0.20, and 0.25 mbar respectively. The substrate bias voltage is set at ground potential. The RF power applied is 450W. The duration for all nitriding experiments is 5 hours. Another series of experiments at the same pressures and power are conducted except that now the bias voltage of –500 V is applied to the substrate.

Following the above-mentioned experiments, a third series of experiments are conducted whereby the discharge pressure is set at 0.1 mbar (0.015 mbar argon and 0.85 mbar nitrogen) and the nitriding is carried out at different bias voltages. The bias voltages of 0, -500,-1000 and –1500 V with respect to the ground are used for the nitriding process. In each of these cases, the nitriding is carried out for 10 hours.

The properties of the nitrided titanium substrates are then analyzed using the GAXRD; Carl Zeiss inverted microscope (for metallographic analysis), SEM, AFM and the microhardness tester.

4.3.1 Effect of discharge pressure on the nitriding of Ti

Visual observation in Figure 4.7 shows that among the five samples, only titanium sample nitrided at 0.1 mbar of the argon-nitrogen discharge appears to give the characteristic golden yellow color of the TiN layer. The visual appearance of the
surface of nitrided Ti samples after nitriding at discharge pressure of 0.05, 0.10, 0.15, 0.20, and 0.25 mbar are respectively as shown in Figures 4.7 (a), (b), (c), (d) and (e).

Figure 4.8 shows the substrate current density versus the negative bias voltage for titanium substrate nitrided at different discharge pressure (as mentioned in the previous paragraph). A higher substrate current density indicates higher frequency of ion bombardment on the substrate surface and hence results in higher substrate temperature, which enhance the nitriding process. However, the nitrided layer is not formed because the number of nitrogen species is low, thus resulting in inefficient nitriding process for sample nitrided at discharge pressure of 0.05 mbar. Hence, the nitrided layer is not formed homogenously as visually observed in Figure 4.7 (a) for the nitriding process at 0.05 mbar. In addition to this, the surface sputtering process, which occurs simultaneously, may be more predominant than the nitriding process at 0.05 mbar.

For samples nitrided at higher discharge pressure, i.e. 0.15 mbar and 0.2 mbar, the substrate current density for the both of these discharge pressure is lower and hence the substrate surface temperature is expected to be lower. Renevier and his group (Renevier et al, 1999) suggested that at low temperature, the nitriding performances are limited by a plasma–surface phenomenon that probably involves recombination of nitrogen atoms. They suggested that the heterogeneous N-atom recombination process can lead to the formation of nitrogen molecules. This process actually competes with the diffusion of nitrogen atoms into the material. Hence, the nitrided layer is also not effectively formed on the Ti substrates, nitrided at discharge pressure of 0.15 mbar and 0.2 mbar.

The formation of nitride on sample nitrided indicates that 0.1 mbar appear to be the optimum pressure for nitriding. Renevier and co-workers (Renevier et al,
1999) reported that substrate temperature and nitrogen contents plays an important role in the formation of the nitrided layer.

The nitriding process is repeated under the same parameters and conditions, except substrate bias voltage of –500 V is used. The similar results are obtained. Hence, the discharge pressure of 0.1 mbar of the argon/nitrogen (1: 5.7) admixture appears to be the optimum discharge pressure for nitriding of titanium substrate in this project.
Figure 4.7  Surface appearance of the titanium surface nitrided at different discharge pressure. (a) 0.05 mbar; (b) 0.10 mbar; (c) 0.15 mbar; (d) 0.20 mbar; (e) 0.25 mbar.
4.3.2 Nitriding of titanium substrate at different bias voltage

Titanium substrates are nitrided at 0.1 mbar nitrogen/argon admixture, using substrate bias voltage of 0, -500, –1000, and –1500 V, at RF plasma of 450 W, for a period of 10 hours.

(a) Surface morphology

Surface morphology and topography are investigated by using a Scanning Electron Microscope (SEM). The surface roughness value (denoted by Ra) is measured by AFM.

From the SEM and AFM photographs (see Figures 4.9 (a), (b), (c) and (d)), it can be seen that samples nitrided at higher bias voltage exhibit a more ‘damaged’ surface as compared to samples nitrided at lower bias voltage. The roughness of the surface may be attributed to the relatively intense sputtering when higher bias voltage is applied to the substrate. Ion bombardment at higher negative bias is more intense;
thus, material removal at the substrate surface by sputtering is higher than deposition rate.

The plot of $Ra$ versus bias voltage is shown in Figure 4.10. From the plot, it can be seen that the nitrided surface become rougher as negative bias voltage applied is increased.
Figure 4.9 Scanning electron micrograph (1000X), and AFM 3-D profiling showing the surface morphology of Ti sample nitrided at various bias voltage. (a) 0 V; (b) -500 V; (c) -1000 V; (d) -1500 V (Continued on next page).
Figure 4.9 Scanning electron micrograph (1000X), and AFM 3-D profiling showing the surface morphology of Ti sample nitrided at various bias voltage. (a) 0 V; (b) -500 V; (c) -1000 V; (d) -1500 V
Figure 4.10  Surface roughness versus substrate bias voltage.
(b) **Grazing Angle X-ray Diffraction (GAXRD)**

Plasma nitriding of titanium substrate has been reported to produce a layer of δ-TiN at the outermost layer, followed by ε-Ti$_2$N and nitrogen solid “solution” in α-Ti (α-Ti(N)) (Rollinski, 1989; Rie and Lampe, 1985).

The X-ray diffractogram for titanium samples nitrided at 0 V and -500 V bias voltages are shown in Figures 4.11 and 4.12. It can be seen that for the Ti sample nitrided at 0 V, only peaks due to ε-Ti$_2$N and α-Ti(N) layers are observed. In the case of Ti sample nitrided at –500V, the peaks due to ε-Ti$_2$N and α-Ti(N) are also detected. However, no peak associated with δ-TiN is detected for both samples. The absence of δ-TiN phase may be due to the fact that the Ti substrate temperature is below the δ-TiN phase formation temperature. Renevier and co-workers (Renevier et al, 1999), using an arc discharge method for nitriding of Ti substrates, reported that ε-Ti$_2$N phase was only produced when Ti substrate is nitrided at 850 K for 8 hours. The δ-TiN phase requires a longer duration of about 15 hours. Badini and his group (Badini et al, 1988), using a DC glow discharge technique had shown the formation of δ-TiN phase by nitriding Ti samples at temperatures between 1073 K and 1273 K. Muraleedharan and Meletis (Muraleedharan and Meletis, 1992) by using triode technique, observed δ-TiN phase formation at 500° C (773 K).

Comparing the amplitude of the ε-Ti$_2$N peak between the two samples, it can be seen that sample nitrided at 0 V exhibits higher peak. For peak associated with α-Ti(N), sample nitrided at –500V exhibits a higher peak. This indicates that ε-Ti$_2$N phase layer is thicker for sample nitrided at 0 V when compared to sample nitrided at –500V. This can be attributed to a higher sputtering rate for the Ti substrate bias at –500V. The nitriding rates of both samples are more or less the same.
Figure 4.11  XRD spectra of samples nitrided at 0V and –500 V; Bragg’s angle from 30° to 55°, red line represents sample nitrided at 0 V.

Figure 4.12  XRD spectra of samples nitrided at 0V and –500 V; Bragg’s angle from 55° to 80°, thicker line represents sample nitrided at 0 V.
From the XRD analysis, it can also be observed that the $\alpha$-Ti peak moves towards lower Bragg’s angle for sample nitrided at 0 V and –500V as compared to unnitrided sample. This is as shown in Figures 4.13 and 4.14. Meletis and his co-workers (Meletis et al, 1999) observed the same phenomena on the nitrided Ti using DC glow discharge. They ascribed this observation to an indication of the expansion of lattice parameter due to increased nitrogen content in the titanium metal.

For samples nitrided at –1000 and –1500V, both phases of $\varepsilon$-Ti$_2$N and $\delta$-TiN are present. However, no peak associated with $\alpha$-Ti is detected. This indicates that a sufficiently thick compound layer is formed while nitriding under these bias conditions. The result is shown in Figures 4.15 and 4.16. It can be seen that nitriding at –1000 V produces nitrided Ti sample with higher $\delta$-TiN peak height, compared to Ti sample nitrided at –1500 V. Again, this is attributed to more intense ion bombardment at higher biasing, effectively sputtering away some of the $\delta$-TiN layer which is formed at the outermost layer.
Figure 4.13  XRD spectra showing the shifted peak of $\alpha$-Ti of unnitrided sample and nitrided samples (0 V and −500 V) from $2\theta = 34^\circ$ to $2\theta = 41^\circ$.

Figure 4.14  XRD spectra showing shifted peak of $\alpha$-Ti of unnitrided sample and nitrided samples (0 V and −500 V) from $2\theta = 50^\circ$ to $2\theta = 55^\circ$. 
Figure 4.15  XRD spectra of samples nitrided at –1000 V and –1500 V; Bragg’s angle from $2\theta = 55^\circ$ to $2\theta = 80^\circ$.

Figure 4.16  XRD spectra of samples nitrided at –1000 V and –1500 V; Bragg’s angle from $2\theta = 55^\circ$ to $2\theta = 80^\circ$. 
(c) **Metallographic analysis**

To reveal the microstructure of the titanium specimen, the sample is etched with Kroll’s reagent. The chemical composition of the etchant is shown in Table 4.2.

**Table 4.2  Chemical composition of Kroll’s etchant.**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroflouric acid (HF)</td>
<td>3 ml</td>
</tr>
<tr>
<td>Nitric Acid (HNO₃)</td>
<td>6 ml</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>100 ml</td>
</tr>
</tbody>
</table>

From the microscope digital images presented in Figures 4.17 (a) – (d), it can be seen that the feature of the microstructures of Ti samples nitrided at bias voltage of 0 V, -500 V, and -1000 V are similar. However, Ti sample nitrided at –1500 V exhibits a different microstructural feature. Nitriding at bias voltage of –1500V is accompanied by high substrate temperature which can result in the transformation of the microstructure of titanium. In most cases, this is not desirable, since the change in the microstructure is accompanied also by changes in mechanical and chemical properties of the materials.

From the SEM images, for Ti samples nitrided at lower bias voltage, 0 V and –500 V, as presented in Figure 4.18 (a)-(f), a nitrided layer of thickness of less than 5 µm is observed for both samples. The ε-Ti₂N layer, although detected in XRD analysis, is not distinguishable from the α-Ti (N). This is because the ε-Ti₂N layer appear as a very thin layer on both Ti samples. This explains the high amplitude peak for the α-Ti (N) layer (phase) detected by XRD analysis.
For Ti samples nitried at –1000V and –1500 V, compound layers due to δ-TiN and ε-Ti₂N are clearly visible (see Figure 4.18 (f) to 4.19 (c)). These layers have also been observed by Renevier and his group (Renevier et al., 1999), when nitriding Ti in an arc discharge system for 18 hours. Peaks corresponding to these phases in the XRD spectrum analysis confirm the presence of these two phases. The thickness of the compound layer is less than 2 µm. It is also observed that a mixed ‘phase’ with a different structure is present in the α-Ti(N) region. This may be due to the difference in nitrogen concentration in the α-Ti at different nitriding depth.
Figure 4.17  Digital micrograph showing the microstructure of nitrided Ti substrate at different negative bias voltage (50x). (a) 0 V; (b) -500 V; (c) -1000 V; (d) -1500 V.
Figure 4.18 SEM micrograph of nitrided Ti sample. (a) 0 V (2K X); (b) 0 V (4K X); (c) -500 V (2K X); (d) -500 V (4K X); (e) -1000 V (4K X); (f) -1000 V (8K X)
Figure 4.19 SEM micrograph of sample nitrided at –1500 V.
(d) **Hardness Measurements**

Hardness measurement is conducted by using the Matsuzawa microhardness tester using 100-gram force load. The result is shown in Figure 4.20. The sample nitrided at –1500 V possesses the highest hardness value, averaging at 1105 Hv. This is followed by sample nitrided at –1000 V with average hardness value of 1069 Hv. These hardness values are almost half the value for bulk TiN (hardness value ~2160 Hv). Hardness values of the nitrided titanium measured other researchers is shown in Table 4.3.

**Table 4.3** Hardness value of nitrided titanium obtained by other researchers.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Nitrining Conditions</th>
<th>Hardness (Vickers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meletis et al (1995)</td>
<td>IPAP (8.5 hrs)</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>RF Glow discharge PIII (3hrs)</td>
<td>400</td>
</tr>
<tr>
<td>Tu et al (1999)</td>
<td>DC diode (5 hrs)</td>
<td>1220</td>
</tr>
</tbody>
</table>

Both Ti samples nitrided at 0 V and –500 V only show a minimal improvement in surface hardness as compared to unnitrided sample. The high hardness values that are obtained by sample nitrided at –1000 V and –1500 is attributed to the existence of $\delta$-TiN phase on the sample surface. For sample nitrided at 0 and –500 V, this phase is absent, as seen in the diffractogram that is obtained by the XRD analysis.
Figure 4.20  Vickers microhardness measurement of Ti substrates nitrided using different bias voltage.

The Knoop indentation method is also conducted to obtain the hardness profile corresponding to the depth of nitriding. The hardness measurement is done on the cross section of the sample used for metallographic analysis (see Figure 4.21).
Figure 4.21 A picture showing Knoop indentation along the depth of the nitrided layer.

Figure 4.22 Knoop microhardness profiles of nitrided Ti samples (nitrided at different bias voltage).
From Figure 4.22 (page 275), it can be seen that the hardness near the surface region is the highest, and gradually decreases as the distance from the surface increases. Meletis and his co-workers (Meletis et al, 1999) reported the hardness value to correspond to the nitrogen content diffusing into titanium substrate. Hence, the hardness profiling can be used as an indicator of the depth of the nitrogen diffusion into titanium. For both samples nitrided at –1500 V and –1000 V, the diffusion layer is estimated to be about 70 µm from the surface. For samples nitrided at 0 and –500 V, the hardness values measured remain almost constant throughout the depth investigated. This indicates that the depth of nitrogen diffusion is low compared to Ti samples that are nitrided at higher bias voltage.
4.4 Plasma enhanced physical deposition of titanium nitride.

A study involving the plasma enhanced physical vapor deposition (PEPVD) of titanium nitride film on 304 stainless steels using the same configuration as the system that was used for nitriding titanium substrate is conducted. The schematic diagram of the configuration of this system is shown in Figure 2.3.

The process involves the sputtering of titanium target, which is biased at –800 V. The plasma that is used for this purpose is produced by an admixture gas of 99% argon and 1% nitrogen. The plasma is operated in the H mode. Both the target and the substrate are immersed in the H-mode plasma. The RF power used is 240 W and the operating gas pressure range from 0.5 mbar to 3.5 mbar. The deposition period used is two hours. The effects of deposition parameters such as discharge pressure, substrate bias voltage and the presence of hydrogen gas on the titanium nitride film composition, structure, and quality are investigated.

The deposited titanium nitride films are analyzed by EPMA, XRD, SEM, and AFM to obtain a correlation of the effect of substrate bias voltage, discharge pressure and the presence of hydrogen, on the quality of the film.

4.4.1 Effect of substrate bias voltage

The bias voltage is varied from 0 V to –160 V in steps of 20 V to study the effect of the substrate bias voltage on the composition of the titanium nitride film. The parameters used in this set of study are shown in Table 4.4.

(a) Appearance of TiN film deposited at various substrate bias voltage

The characteristic color of titanium nitride film is golden yellow (Figure 4.23). The quality of the TiN film that is obtained by PEPVD method depends a lot on the parameters during the deposition, which may affect the composition of the titanium nitride film (Igasaki and Mitsuhashi, 1980). The presence of oxygen content in the
film may cause the film to turn brownish in color (Logothetidis et al, 1999). The brownish color may also be due to the difference in film structural arrangement (Nah et al, 1999). The color of the films obtained from this work appears to be golden yellow when deposited in the discharge pressure range of 0.5 mbar to 3.5 mbar. The color of the film starts to turn to brownish black at low substrate bias voltage as shown in Figure 4.24.

Table 4.4 Parameters used in the study of the effect of substrate bias voltage on titanium nitride film deposition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating time</td>
<td>120 minutes</td>
</tr>
<tr>
<td>Target bias voltage</td>
<td>-800 V</td>
</tr>
<tr>
<td>RF power: Forward</td>
<td>350 W</td>
</tr>
<tr>
<td>RF power: Reverse</td>
<td>110 W</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.00 mbar</td>
</tr>
</tbody>
</table>

Figure 4.23 Various articles coated with the golden yellow TiN film.
Figure 4.24  The effect of substrate bias voltage on film appearance.
(b) Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) Results

The crystalline structure of the deposited film surface of the substrate may be altered as the film is growing due to ion bombardment. This alteration may be ascribed to enhanced mobility of deposited ions or atoms on the surface of substrate. The alteration to the crystalline structure of the film may vary according to the substrate bias voltage. The SEM and AFM micrographs showing the structural change at the surface of the films as a result of increasing substrate bias voltage is shown in Figure 4.25. From Figure 4.25 columnar structure can be observed for TiN thin film deposited at the substrate bias voltage of –40 V and below. At substrate bias voltage of –40 V, the surface energy is considered low and hence insufficient to cause surface mobility.

The films prepared at higher substrate bias voltage (–60 V and above) appear to have flat and smooth surfaces. This may be due to the enhancement of surface mobility of deposited atoms as the higher bias voltage mentioned (Sundgren et al, 1981). The enhanced surface mobility destroys the columnar structure, and the valleys between the columns are filled resulting in a film that has fine grain structure with a smooth surface (Sundgren et al, 1983).

Igasaki and Mitsuhashi (Igasaki and Mitsuhashi, 1980) observed that the increase in substrate bias voltage resulted in flat surfaces and the formation of denser film. They explained that the kinetic energy of the argon ions impinging on the film was being absorbed by the deposited atoms or ions and thus enhancing their mobility at the surface of the substrate. This made it possible for the valleys on the surface to be filled by the migrating atoms or ions. Sundgren and his co-workers (Sundgren et al 1981) explained that as the energy of the impinging ions is increased, the
penetration into the lattice of the condensed film and the generation of defect would also propagate. This gives rise to an increase in the number of preferential nucleation sites, which resulted in sites for growth of smaller grains and the destruction of the columnar growth morphology.
(a): Surface morphology of substrate with negative bias voltage of 160 V.

(b): Surface morphology of substrate with negative bias voltage of 120 V.

(c): Surface morphology of substrate with negative bias voltage of 80 V.
(d): Surface morphology of substrate with negative bias voltage of 40 V.

(e): Surface morphology of substrate without negative bias voltage, 0 V.

Figure 4.25 SEM and AFM surface morphology. Surface smoothness decreases as a result of increasing of grain size with decreasing of substrate bias voltage.
The observation seen in Figure 4.25 is supported by variation of the roughness of the film surface (Ra) measured by using the AFM with the increase in substrate bias voltage (Figure 4.26). The roughness of the titanium nitride films are found to be below 10 nm for substrates that are subjected to bias voltage of –60 V and above. For substrate that are bias at a voltage below –60 V the surface roughness increases to 49.605 nm at –40 V, 91.470 nm at –20 V and reduces slightly to 82.214 nm at 0 V.

![Surface roughness vs Bias Voltage](image)

**Figure 4.26** Surface roughness of the films as obtained from AFM scan.

*Electron Probe Micro-Analysis (EPMA) of TiN film deposited at various substrate bias voltage*

The EPMA is used to determine the atomic percentages of elements in the titanium nitride film. Table 4.5 shows the composition for a typical titanium nitride film deposited on stainless steel substrate.

Figure 4.27 shows the effect of substrate bias voltage on the composition of the titanium nitride film (in atomic percentages) as determined by EPMA analysis.
Table 4.5  EPMA analysis results for Titanium nitride.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.2870</td>
<td>2.0560</td>
</tr>
<tr>
<td>C</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Si</td>
<td>0.0020</td>
<td>0.0020</td>
</tr>
<tr>
<td>P</td>
<td>0.0100</td>
<td>0.0080</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ti</td>
<td>71.7730</td>
<td>38.3010</td>
</tr>
<tr>
<td>Fe</td>
<td>0.8630</td>
<td>0.3950</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2380</td>
<td>0.1170</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1330</td>
<td>0.0580</td>
</tr>
<tr>
<td>N</td>
<td>32.3600</td>
<td>59.0560</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0120</td>
<td>0.0060</td>
</tr>
<tr>
<td>Total:</td>
<td>106.6780</td>
<td>99.9990</td>
</tr>
</tbody>
</table>

Figure 4.27  The effect of substrate bias voltage on the atomic percentage of elements in the TiN film.

The atomic percentage of oxygen is seen to drop exponentially from 30.72 % to about 2 % as the substrate bias voltage is increased from 0 to –160V. This suggests
that high substrate bias voltage is required to reduce the oxygen content in the film. The atomic percentage of nitrogen is observed to increase gradually from 34.84 % to 59.91 % as the substrate bias voltage is increased. Added to this, the composition of nitrogen is always higher than that of titanium. The composition of titanium is observed to “oscillate” within the range of 30 % to 40 % with the increase in substrate bias voltage. The film is said to be over-stoichiometric (TiN<sub>x</sub>, X > 1), since the composition of nitrogen is much greater than titanium. This is depicted in Figure 4.28 where the composition ratio for N to Ti for all films deposited at the various applied bias voltage is greater than 1. The analysis obtained from XRD on the bulk titanium nitride however shows that the film composition is stoichiometric, where, TiN<sub>x</sub>, X =1.

![Figure 4.28 Composition ratio of N: Ti and O: Ti versus applied bias voltage](image)

One possible explanation of the observation of higher atomic percentage of nitrogen from the EPMA analysis is that nitriding of stainless steel substrate may have occurred prior to the titanium nitride coating process.
(d) X-Ray Diffraction (XRD) analysis of TiN deposited at various substrate bias voltage

The XRD analysis is used to verify the stoichiometric composition of the films. The crystalline structure of the film can also be determined from its peaks. Generally, the crystalline structure gives sharp peak while amorphous structure is seen as broad peak (Gluster, 1985).

The crystalline structure of the titanium nitride films is affirmed by the sharp peaks obtained by XRD analysis. Figure 4.29 shows a typical XRD diffractogram for a titanium nitride film. The peaks that are seen in the diffractogram resemble the peaks in the diffractogram for bulk titanium nitride (Lifshin, 1999). The XRD analysis of titanium nitride thin films deposited at different substrate bias voltages shows peaks that are due to titanium nitride and stainless steel (see Figure 4.30). However, titanium nitride films that are deposited at substrate bias voltage of –20 V and 0 V, show peaks correspondingly to zeta titanium nitride (Ti₄N₃₋ₓ). This “compound” appears as a black colored film on the stainless steel substrate.

Peaks due to titanium oxy nitride (TiO₀.₃₄N₀.₇₄) or, titanium oxide are not observed. This observation contradicts with the inference derived from EPMA results. The peaks due to titanium oxy nitride (TiO₀.₃₄N₀.₇₄) or, titanium oxide may be too low to be detected by XRD. Nah and co-workers (Nah et al, 1999) reported that the Ti (O, N) compound that is formed, titanium oxide (TiO), has the same crystalline cubic structure, as titanium nitride (TiN) and the lattice of both compounds are almost the same. Hence the TiN peak may also have masked the TiO peak.

Figure 4.31 shows the profile of TiN (111) X-Ray diffraction peak from the XRD that is derived from Figure 4.30. The TiN (111) X-Ray diffraction peak height is observed to decrease, becomes wider, and shift to higher 2θ angle with decreasing
substrate bias voltage. The broadening of the peaks suggests some degeneration of the crystalline structure. The decrease in the peak height may indicate that the number of diffracting crystals in the film decrease with the decreasing substrate bias voltage. The presence of titanium oxides embedded in the film may cause some degree of loss in the crystalline structure of the film structure, and a decrease in film density.

Figure 4.29 Typical XRD diffractogram obtained from the titanium nitride thin film deposited in this study.
Figure 4.30  X-ray diffraction profiles of titanium nitride films for different substrate bias voltage.
Figure 4.31  Titanium nitride (111) diffraction peak. The peak becomes weaker and wider and is shifted to higher angle with decreasing bias voltage, indicating that the film is becoming more amorphous.
4.4.2 Effect of discharge pressure on the quality of the titanium nitride

The study on the effect of discharge pressure on the quality of the titanium nitride is conducted by varying the discharge pressure from 0.5 mbar to 3.5 mbar. Other discharge parameters are fixed during deposition (see Table 4.6).

**Table 4.6** Fixed parameters for the study of the effect of pressure on titanium nitride film deposition.

<table>
<thead>
<tr>
<th>Coating time:</th>
<th>120 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target bias voltage:</td>
<td>-800 V</td>
</tr>
<tr>
<td>RF power: Forward:</td>
<td>350 W</td>
</tr>
<tr>
<td>Reverse:</td>
<td>110 W</td>
</tr>
<tr>
<td>Substrate bias voltage:</td>
<td>-100 V</td>
</tr>
</tbody>
</table>

(a) Electron Probe Microanalysis (EPMA) of TiN films deposited at various discharge pressure

The atomic percentage of nitrogen, oxygen and impurities in the titanium nitride film deposited in the range of discharge pressure from 0.5 to 3.5 mbar do not show any significant change (see 4.32). However, the atomic percentage of titanium drops gradually from 38.19 % for TiN film discharge at 0.50 mbar to 12.52 % for TiN film deposited at 3.50 mbar, indicating a lower deposition rate of TiN at higher discharge pressure (i.e. at 3.5 mbar). At higher pressure, titanium ions in the plasma may find difficulty to travel from the target to the substrate due to a lower mean free path due to high frequency of collision with other ions or molecules. As a result, the probability of reactive bombardment will also be reduced.
Figure 4.32 The effect of discharge pressure on the composition of TiN film as determined from EPMA.

The increase in the atomic percentage of stainless steel elements (Fe, Cr, Ni, and Mn) (see Figure 4.32) is because the titanium nitride film becomes thinner with the increase in discharge pressure. Hence, the EPMA probe is able to “see” more elements in the stainless steel surface. The atomic percentage of nitrogen is observed to remain unchanged (see Figure 4.32) due to the nitriding of stainless steel surface together with the nitriding of titanium.

The atomic percentages for oxygen and other impurities (C, Si, P, and Ca), are found to be very low due to out-gassing from the wall of the chamber.
(b) **XRD analysis of TiN films deposited at various discharge pressure**

The XRD diffractogram is presented in Figure 4.33 for the operating discharge pressure ranging from 0.50 mbar to 3.50 mbar. The titanium nitride peak at the lattice plane of (200) shows the highest intensity, indicating that most of the TiN crystal formed is found in this plane. However, small changes to the intensity of peaks corresponding to (111), (311) and (222) planes are noticed for other discharge pressures operated in this study. As the pressure increases, the peak corresponding to the (222) plane becomes weaker. The peaks corresponding to (111) and (311) planes demonstrate an increase. This points to the change of plane orientation from (222) to (111) and (311) in the crystalline structure of the TiN film as the discharge pressure is increased.
Figure 4.33  The effect of gas pressure on titanium nitride film formation.
4.4.3 Effect of hydrogen on the rate of deposition on titanium nitride film

The effect of hydrogen on the rate of deposition on titanium nitride film is investigated by comparing the deposition process with and without hydrogen gas. Two investigations were conducted experimentally. In the first experiment, the substrate is biased at –100 V and the discharged pressure is set at 0.75 mbar, 1.00 mbar and 1.50 mbar. In the second experiment, no bias voltage is applied to the substrate and the discharge gas pressure is fixed at 1.00 mbar. In all the experiments, only a small amount of hydrogen (i.e., < 1%) is introduced into the discharge system. A high concentration of hydrogen may reduce the sputtering rate of the titanium target and thus decreasing the deposition rate. Table 4.7 shows the fixed parameters that are used in the investigation of the effect of the presence of hydrogen on the deposition process.

**Table 4.7 Fixed parameters for the study on the effect of hydrogen on titanium nitride film deposition.**

<table>
<thead>
<tr>
<th>Coating time:</th>
<th>120 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target bias voltage:</td>
<td>-800 V</td>
</tr>
<tr>
<td>RF power Forward:</td>
<td>350 W</td>
</tr>
<tr>
<td>RF power Reverse:</td>
<td>110 W</td>
</tr>
</tbody>
</table>

Figure 4.34 shows XRD diffractogram for the effect of hydrogen gas on the deposition process under the condition where the substrate is not biased. The diffractogram shows two peaks which correspond to the titanium oxy nitride (TiO\(_{0.34}\)N\(_{0.74}\)) film when the titanium nitride film is deposited in the absence hydrogen gas. These peaks are however not observed in TiN film deposited in the presence of hydrogen gas. The peaks due to zeta-titanium nitride (Ti\(_4\)N\(_{3-x}\)) and titanium nitride (Ti\(_2\)N) are noticed. Both of these titanium compounds are brown in color. This result agree with the explanation given by Heidsieck (Heidsieck, 1999) that hydrogen gas acts as reactive gas which helps to remove oxygen or prevent the formation of oxides during the titanium nitride deposition process.
Figure 4.34  The effect of hydrogen gas for the process without substrate bias voltage.
When the stainless steel substrate is subjected to a bias voltage of -100V, no TiO$_{0.34}$N$_{0.74}$, Ti$_4$N$_{3-x}$ or Ti$_2$N peaks are observed from the XRD diffractogram (see Figure 4.35). The hydrogen gas does not appear to affect the composition of the titanium nitride film. The XRD diffractogram shows no significant difference in the titanium nitride peaks when deposition is conducted with and without hydrogen gas under three different gas pressures. This result suggests that the effect of the substrate bias voltage is more important than the effect due to hydrogen gas in affecting the composition of the TiN film.
Figure 4.35  The effect of hydrogen gas for the process with substrate bias voltage of -100 V.
4.4.4 Cross section metallographic analysis

The thickness of the titanium nitride film can be estimated from cross section metallographic by using the EPMA element mapping and by computer aided microscope. The images obtained from these two techniques are shown in Figures 4.36 and 4.37 respectively. In Figures 4.36 (a) and (b), light blue color indicates the highest concentration of nitrogen and titanium respectively. The thickness of the film that can be estimated from the width of the blue area is found to be around 2 μm.

Using the computer aided microscope, the light area is stainless steel substrate, the dark area is epoxy and sandwiched between them is the titanium nitride film (see Figure 4.37). From the scale, the thickness of the film is estimated to be around 2 μm. The time taken for the PAPVD deposition process is two hours; hence the deposition rate of the film is about 1 μm/h.
(a) EPMA element mapping of nitrogen.

(b) EPMA element mapping of titanium.

Figure 4.36 Cross section metallographic of titanium nitride film by EPMA element mapping shows the film’s thickness is around 2 µm.
Figure 4.37 The cross sectional metallographic of titanium nitride film under computer aided microscope. The thickness of the film is estimated to be around 2 µm.

Scale: 1 division = 1 µm
4.5 **Deposition of diamond-like carbon (DLC) thin film using the PC-RFICP system with LC resonant circuit matching network.**

The configuration of the PC-RFICP that is used for the deposition of the DLC thin film is an inverted system where the planar coil coupled to the matching network is placed at the bottom of the discharge chamber. The LC resonant circuit matching network is also used in the PC-RFICP system that is used for the deposition of DLC films on silicon substrate. The silicon substrate is placed directly on the quartz plate, which serves as a dielectric between the planar coil and the plasma. The silicon is placed directly on the quartz plate so that direct induction of eddy current on the silicon substrate can occur. The induced eddy current is able to heat the silicon substrate to a temperature close to 1000°C. The chamber that is used is a glass chamber. A glass funnel is used to cover the silicon substrate with the purpose of confining the plasma within the glass funnel. The schematic of the configuration for PECVD of DLC film is illustrated in Figure 3.19 (page 209).

Table 4.8 shows the PECVD deposition conditions that are used to deposit diamond-like carbon thin films. PECVD of DLC film requires larger quantity of hydrogen gas mixed with a small portion of methane gas to prevent the formation of excess graphitic forms in the thin film.
Table 4.8 The PECVD conditions used for the deposition of DLC film on silicon substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DLC-1</th>
<th>DLC-2</th>
<th>DLC-3</th>
<th>DLC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF forward power/W</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>RF reflected power/W</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Operation pressure/mbar</td>
<td>0.6-0.7</td>
<td>0.6-0.7</td>
<td>0.6-0.7</td>
<td>0.6-0.7</td>
</tr>
<tr>
<td>Substrate temperature / °C</td>
<td>800-900</td>
<td>800-900</td>
<td>800-900</td>
<td>800-900</td>
</tr>
<tr>
<td>Percentage of Methane gas / %</td>
<td>0.8</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Duration of operation / hours</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

The DLC thin films that have been deposited onto silicon substrate with the PECVD technique using the PC-RFICP system are analyzed with SEM-EDAX and Micro-Raman spectroscopy.

4.5.1 Effect of silicon substrate pretreatment with diamond paste

Nucleation is observed on the substrate surface of sample DLC-2 that has been scratched with diamond pastes (see Figure 4.38). The scratched lines due to surface pretreatment with diamond paste show a higher nucleation growth of the DLC film than the surface of the substrate that is not scratched by the diamond paste. Substrate pretreatment by polishing with diamond paste is therefore an important step to enhance the growth of the diamond-like carbon on the surface of the silicon substrate.

Yugo and his co-worker (Yugo et al, 1990) reported that scratching or roughening of the substrate surface with diamond grit is found to enhance the nucleation density by
up to seven orders of magnitude compared with unscratched Si. Two possible explanations are given for the enhancement of carbon crystallites growth on a scratched surface. Firstly, scratching the substrate creates grooves on the substrate surface with the atom terminating at the surface being removed. This leaves behind dangling bonds, which act as active sites as shown in Figure 4.39. The active species crucial to diamond growth can attach themselves more easily on to the dangling bonds. The other explanation is that the diamond abrasives may leave behind nano-sized diamond fragments, which may act as a seed for diamond-like carbon growth during the deposition process. This may enhance the nucleation of carbon active species from the gas phase in the plasma into the carbon “particles” which give rise to the growth of DLC film at the substrate surface.
Figure 4.38  The effect of the pretreatment on sample DLC-2

Dangling bonds

Si

Si

Si

Si

Figure 4.39  Substrates surface after scratching
4.5.2 Effect of the induction heating on PECVD diamond-like carbon film

The deposition of diamond and diamond-like carbon films by PECVD technique also requires high temperature for the nucleation and formation of the film on the surface of the substrate. The induction heating effect is able to heat up the silicon substrate to 800-900 °C at RF power of 500 W. The effect of induction heating during the PECVD of diamond-like carbon films on silicon substrate has been investigated by placing a silicon substrate labeled as DLC-5 on a ceramic cylinder instead of directly on the quartz plate. Placing the sample DLC-5 on the ceramic cylinder will prevent the sample from being heated up by the induction heating effect since it is positioned away from the planar induction coil. Sample DLC-5 is immersed in the 1% of methane and 99% hydrogen plasma for 15 hours. The DLC film that produced is analyzed by SEM and EDAX.

The SEM micrograph does not show any texture of a thin film coating on sample DLC-5 (see Figure 4.40). The scratched lines caused by polishing the substrate surface with diamond paste also do not show any nucleation of the DLC film. The result of the EDAX analysis as shown in Figure 4.41 indicates only the presence of silicon. This demonstrates that no diamond or DLC film is formed on the surface of sample DLC-5. EDAX analysis on sample DLC-2 however shows the present of carbon peak (see Figure 4.42).

The induction heating process on silicon substrate, which is able to heat the sample to a temperature of 800 to 900°C, is therefore crucial for the nucleation and deposition process of diamond-like carbon film.
Figure 4.40  Surface morphology of DLC-5 without induction heating

Figure 4.41  EDAX spectrum of sample DLC-5
4.5.3  

**DLC film on silicon substrate prepared with 0.8% methane gas**

The SEM micrograph showing the DLC film deposited on the silicon substrate with 0.8% methane gas (DLC-1) is presented in Figure 4.43. The SEM micrograph presents the DLC film with the typical faceted microcrystalline structure. DLC films are similar to those grown by chemical vapor deposition on silicon substrate. The film appears to be homogenous and continuous with sharp pointed pyramidal structures. These pointed structures are useful for electron field emission application of DLC film. The DLC film appears to be polycrystalline, with twinning and many visible crystal defects. The carbon structure appears to be more orderly and hence, may be considered less amorphous than other DLC film samples namely DLC-3 and DLC-4. From SEM measurement, the size of the single crystal formed is estimated to be about 2 to 3 µm.
The micro-Raman spectrum for sample DLC-1 is shown in Figure 4.44. Figure 4.44 (a) shows the presence of the CH stretching band; this band is present in all the DLC samples. This implies that the DLC film deposited are not H free, since methane (CH₄) is used as the C source in this deposition.

The micro-Raman spectrum in Figure 4.44 (b) shows two well-defined peaks at about 1355 and 1580 cm⁻¹. These bands have been assigned as D and G peaks (Kang et al, 1998; Lee et al, 1999). It is well known that the combined feature of D and G peaks represents the typical bonding characteristics of diamond like carbon films (Muranaka et al, 1991). The “G” line can be attributed to the graphitic mode of carbon. Here, the peak shifted by about 76 cm⁻¹ compared to the standard value of 1520 cm⁻¹ of crystalline graphite (Kitabatake and Wasa, 1985). The shift in peak position and broad peak width signify the amorphous nature of graphitic phase. The G line is the “forbidden” Raman peak that is attributed to the presence of microcrystallines of graphite. This line is due to scattering from a zone-bounded phonon activated by the disorder relating to the finite size of the crystalline structure. The relative size of the two peaks gives a measure of the amount of amorphous and microcrystalline non-diamond carbon in the film.
Figure 4.43  Surface morphology of sample DLC-1 (0.8 % of methane gas)
Figure 4.44 Micro-Raman spectrum of sample DLC-1. (a) Raman spectra from 500 cm$^{-1}$ to 4000 cm$^{-1}$; (b) Raman spectra from 1200 cm$^{-1}$ to 1800 cm$^{-1}$.
4.5.4  **DLC film on silicon substrate prepared with 1% methane gas**

The SEM micrograph of the DLC film marked as sample DLC-2 shows a uniform and well-oriented polycrystalline carbon film on the surface of the silicon substrate (Figure 4.45). The structure of the polycrystalline DLC film is similar to sample DLC-1.

The DLC film on the surface of DLC-2 has also been analyzed by Raman spectroscopy and the Raman spectrum shows the two typical D and G bands, which characterize the DLC film (Figure 4.46).
Figure 4.45  Surface morphology of sample DLC-2 (1% of methane gas)

Figure 4.46  Micro-Raman spectrum of sample DLC-2
4.5.5 *DLC film on silicon substrate prepared with 3% methane gas*

In Figure 4.47, a different microcrystalline DLC film is observed to be deposited on sample DLC-3 using 3% of methane. The DLC film appears to have a fine and smooth surface texture. This film is constituted with carbon crystalline structures that appear to be ball-like. The diameter for each of this ball-like structure measures between 4 to 5 µm.

Micro-Raman analysis has also been carried out for sample DLC-3 (as shown in Figure 4.48). The D and G Raman bands similar to that of samples DLC-1 and DLC-2 are also observed that the DLC film on sample DLC-3.
Figure 4.47  Morphology of sample DLC-3 (3 % of methane gas)

Figure 4.48  Micro-Raman spectrum of sample DLC-3
4.5.6  **DLC film on silicon substrate prepared with 5 % methane gas**

DLC film (DLC-4) which is prepared with 5 % methane gas has cauliflower-like cluster morphology at the surface (see Figure 4.49). The cauliflower-like clusters have diameters which measures about 8-10 µm in diameter. The microstructure for this DLC film do not demonstrates any obvious preferential orientation.

The Micro-Raman spectrum obtained from DLC film sample DLC-4 is shown in Figure 4.50. The D and G peaks for DLC films are also observed for this sample.
Figure 4.49  Morphology of sample DLC-4 (5 % of methane gas)

Figure 4.50  Micro-Raman spectrum of sample DLC-4
4.5.7 Discussion

Observation made by using the SEM at the DLC coated on samples DLC-1, DLC-2, DLC-3 and DLC-4 demonstrated a significant change in the morphology of the polycrystalline structure of DLC film when the DLC film is deposited at different percentage of methane gas. At a low percentage of methane gas, the atomic hydrogen etches both diamond and graphite. However, the rate of diamond growth surpasses the atomic hydrogen etching rate, while for other forms of carbon (graphite, for example) the opposite is true. Hence, the surface “rebuilding” of carbon from a saturated sp$^3$-hybridized diamond microstructure to an unsaturated sp$^2$-hybridized graphite structure is minimized and the formation of non-diamond carbon form, which constitutes the impurity in the film, is restrained. From this point of view, it is suggested that the sp$^3$ bonding in the polycrystalline DLC films deposited using 0.8 % and 1 % methane (DLC-1 and DLC-2 respectively) are much higher than the DLC films deposited using 3 % and 5 % methane (DLC-3 and DLC-4 respectively). In addition to this, the morphology of DLC films, i.e. DLC-1 and DLC-2 have a pyramidal faceted feature, which support the fact that carbon with sp$^3$ bonding has a polygon crystalline structure. However, at higher percentage of methane, more sp$^2$ bonding is formed during the growth of the DLC film. This is obviously seen in the surface morphology, which has been described as cauliflower-like in structure on the DLC film deposited on silicon sample DLC-4.
4.6 PECVD of polymeric hydrogenated amorphous carbon (a-C:H) thin film using PC-RFICP system with LC resonant circuit matching network

The PC-RFICP system that is used for PECVD of a-C:H film is using the LC resonant circuit matching network. The LC resonant circuit is installed inside a cage to shield any hazardous stray electromagnetic wave from penetrating into the surrounding. The cage is placed on top of the discharge chamber. The planar coil is positioned above the quartz plate. In this configuration, the substrate is placed on a substrate table below the planar coil and quartz plate. The height of the substrate table is adjustable. The distance between the substrate table and the planar coil is adjusted from 7 to 13 cm (see Table 4.9). The E- mode plasma that is used for the deposition of the a-C:H film is sufficient to give good deposition rate. The gas that is used for the deposition is an admixture of acetylene and argon. The schematic diagram of the PC-RFICP system that is used for PECVD of the a-C:H thin film has already been shown in Figure 2.3.

The deposition parameters used in this study to prepare the a-C:H film is shown in Table 4.9.
Table 4.9 Deposition parameters used in this study to prepare the hydrogenated amorphous carbon thin film.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Acetylene flow rate (sccm)</th>
<th>Argon flow rate (sccm)</th>
<th>Discharge pressure (mbar)</th>
<th>Distance from planar coil (cm)</th>
</tr>
</thead>
<tbody>
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<td>120</td>
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<td>40</td>
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<tr>
<td>100</td>
<td>50</td>
<td>40</td>
<td>3.6</td>
<td>13</td>
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</tbody>
</table>

4.6.1 Hydrogenated amorphous carbon film

The growing interest in hydrogenated amorphous carbon (a-C:H) film stems from the many remarkable similarity that this type of film has with diamond: optical absorption, electrical resistivity, high thermal conductivity, chemical resistance to most acids and solvents, hardness. Moreover, under various deposition conditions,
hydrogenated amorphous carbon film properties are found to change between the properties of diamond, graphite, and hydrocarbon polymer. This flexibility in the properties of a-C:H films, which are due to the presence of two types of bonds, namely $sp^3$ and $sp^2$, makes them particularly suitable for the following applications:

(i) A scratch resistant, non-corrosive, anti-reflection layer for germanium and silicon infrared optical windows and lenses. This application takes advantage of the easy adjustment of the refractive index of hydrogenated amorphous carbon (between 1.6 and 2.2) and the low optical absorption in the infrared spectral region of a-C:H.

(ii) A protective coating for optical elements in high power lasers, taking advantage of the chemical resistance, the hardness, smoothness and low optical absorption of a-C:H.

(iii) A dielectric layer for high temperature devices using the high thermal conductivity and high electrical resistivity of a-CH

(iv) A conductive layer made by doping with elements of group III and V of the periodic table.

A laser fusion target using deuterium-carbon and tritium-carbon bonding in a-C:D:T films.

These applications at the industrial and research level are feasible due to the wide range of properties of hydrogenated amorphous carbon. The properties of a-C:H are directly related to the structure of the films themselves, which depends on the growth conditions. a-C:H films are commonly deposited by a plasma-enhanced chemical vapor deposition (PECVD) method. This method involves the excitation and decomposition of
hydrocarbon gas, such as acetylene, methane, propane through an RF or DC discharge. Two types of plasma species contribute to film growth: (1) chemically active neutral species, called radicals that diffuse from the plasma towards the substrate surface and (2) ions that diffuse and drift towards the electrically biased surface. The PECVD technique is a very popular deposition method for thin films: plasma-assisted gas decomposition allows for low substrate temperatures, in contrast to chemical vapor deposition (CVD), and, under certain conditions, plasma-induced ion bombardment of the film during deposition tends to improve the quality of the film.

(a) **Structure of hydrogenated amorphous carbon (a-C:H) film.**

Hydrogenated amorphous carbon film as the name suggests possesses both carbon-carbon bonds and hydrogen-carbon bonds. Being an amorphous network of carbon and hydrogen, it consists of carbon atoms linked by \( sp^2 \) (trigonal, graphitic-like) and \( sp^3 \) (tetragonal, diamond-like) bonds (Figure 4.51).
Diamond-like carbon can be defined as a metastable phase of amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) containing a significant fraction of sp\(^3\) sites. The remaining sites are sp\(^2\) and occasionally sp\(^1\). A sp\(^3\) site uses its four valence electrons of carbon to form tetrahedral $\sigma$ bonds with four adjacent C atoms, as in the diamond crystal. A sp\(^2\) site forms trigonal $\sigma$ bonds to three neighbors in a plane and a weaker $\pi$ bond normal to this plane, as in graphite (Robertson, 1986). The simplest model of the atomic network of DLC is based on the behavior of a-Si:H, where the bonding tends to follow the principal of local chemical equilibrium (Street, 1990), despite it being a metastable phase. It was assumed that in a network of a-C:H, the sp\(^3\), and sp\(^2\) sites will arrange themselves to minimize the total energy. Analysis of this condition results in the "cluster model" of a-C(:H) (Robertson and O' Reilly, 1987). According to his model, the non-local $\pi$ bonding energy encourages sp\(^2\) sites first to pair up to give
C=C bonds as in ethylene, then combine to form planar 6-fold "benzene" rings, and finally to cluster together to form aromatic, graphitic clusters, within a sp³-bonded matrix. This clustering process maximizes the π bonding energy. The σ, and σ* states then form deep valence and conduction states while the π and π* states form the band edge states, thereby determining the band gap, as shown schematically in Figure 4.52. This model was supported by the realization that the surprisingly low optical gap of DLC could be explained in terms of graphitic clusters, with the gap $E_g$ varying with the number of rings in a cluster as $E_g = 6/M^{1/2}$ eV. However, ion bombardments during deposition play a major role, hence, a-C:H is much more disordered than a-Si:H. The disorder opposes clustering (Robertson, 1995). Thus, the clustering is expected to be limited to single six-fold rings and short chains of sp² sites as shown in Figure 4.53.

The π states still form the band edges. The gap depends primarily on the π bonding, not on other factors such as H content. The band gap of planar, aromatic sp² clusters is given earlier by $E_g = 6/M^{1/2}$ eV, where M is the number of rings in the cluster (Robertson, 1986). Disorder now distorts the sp² structures and mixes σ and π states, reducing $E_g$ to perhaps of order, $E_g = 3/M^{1/2}$ eV (Robertson, 1995).
(b) Plasma Chemistry for the deposition of a-C:H film

In this study, the hydrogenated amorphous carbon films are deposited using the plasma produced from an admixture of argon and acetylene gas.

The interaction of acetylene with argon ions results in the ionization and subsequent dissociation of acetylene. A mixture of hydrocarbon ions and radicals are created in this way.

Ionization of acetylene molecules via interaction with electrons is not possible, because these electrons only have energy of approximately 0.2 eV. The ionization of acetylene occurs through a charge exchange reaction with argon ions via:
Ar$^+$ + C$_2$H$_2$ → Ar + C$_2$H$_2^+$  \hspace{1cm} (4.2)

at a rate $k_{ion} \approx 10^{-16}$ m$^3$ s$^{-1}$, which is the only exothermic ionization reaction possible. The total recombination energy of the argon ion (15.76 eV) is transferred to the acetylene ion formed. Dissociation of acetylene by intermolecular reactions is not probable because the rate is less than $10^{-17}$ m$^3$ s$^{-1}$ and the argon ion density is larger than the acetylene density. Thermal dissociation of acetylene is also considered to be of minor importance because heating of the acetylene molecule occurs via electron collisions, in which only 0.2 eV is transferred; the C-H bond in acetylene is 5.7 eV.

The formed acetylene ion recombines dissociatively with an electron with the following possible reaction products (Gielen, 1996):

\[
\begin{align*}
\text{C}_2\text{H}_2^+ + e^- & \rightarrow \text{C}_2\text{H} + \text{H} & \Delta H = -10.03 \text{ eV} \\
& \rightarrow \text{CH} + \text{CH} & \Delta H = -5.77 \text{ eV} \\
& \rightarrow \text{C}_2 + \text{H}_2 & \Delta H = -9.58 \text{ eV} \\
& \rightarrow \text{C}_2\text{H} + \text{C} & \Delta H = -6.64 \text{ eV}
\end{align*}
\]

(4.3)

at a rate of $3 \times 10^{-13}$ m$^3$ s$^{-1}$. All formed radicals and ion complexes can be electronically and/or rovibrationally excited. Depending on the argon ion and acetylene fluxes, the radicals formed in the set of equations (4.3) shown above, can be ionized and dissociated further.
According to the adsorbed layer model, the film growth includes the incorporation of ions and neutrals in the growing film and the possible re-etching of the a-C:H layer by atomic hydrogen from the plasma. The net deposition rate of a-C:H films depends on two competing processes. One is the adsorption of ethinyl radical fluxed to the substrate surface, which forms an adsorption layer on the surface of a-C:H films and leads to the deposition of a-C:H films. The other process is the etching of C atoms in the adsorption layer by atomic hydrogen, which leads to ion-induced chemical etching.

Gielen et al (1997) studied the deposition mechanism of a-C:H films deposited from C₂H₂ by using a cascaded arc plasma source and proposed that the dissociation of C₂H₂ by means of argon ions and electrons mainly creates C₂H radicals and H atoms:

\[
\begin{align*}
\text{Ar}^* + \text{C}_2\text{H}_2 & \rightarrow \text{Ar} + \text{C}_2\text{H}_2^+ \\
\text{C}_2\text{H}_2^+ + e & \rightarrow \text{C}_2\text{H} + \text{H}
\end{align*}
\]  

(4.4)

The anticipated dominant growth precursor is the ethinyl radical C₂H when using acetylene C₂H₂ as working gas in the deposition of a-C:H films. According to the plasma-surface reaction model proposed by Gielen and his co-workers (Gielen et al, 1997), there exist six plasma-surface reactions for the incorporation of C₂H radicals, hydrogenation, abstraction of hydrogen from the surface, and the hydrogen passivation. However, due to the high cross-section for the hydrogenation of dangling bonds compared with the abstraction cross-section, the density of dangling bonds at the surface produced by this process is very low. Thus, its contribution to film growth is usually negligible. Therefore, only the incorporation of C₂H radicals and hydrogen passivation is taken into
account. When a C$_2$H radical from an incident C$_2$H$_2$ radical flux meets an active site it can chemisorbs. The creation of the new C-C bond on the surface is an exothermic process. The energy is used to break the triple bond into a double bond. At the same time, one of the formed dangling bonds reconstructs with the surface, either by bonding to a neighboring-dangling bond or by replacing a hydrogen atom. The net result of the C$_2$H incorporation in the film is the loss of one active site and the production of one sp$^2$ bond. Figure 4.54 shows the overview of the plasma surface reaction during the deposition of the a-C:H film.
Figure 4.54  Overview of the plasma surface reaction during the deposition of a-C:H film.
Firstly, there is the incorporation of C$_2$H radicals into the film (Figure 4.54 (a)). When a C$_2$H radical from an incident C$_2$H radical flux meets an active site it can chemisorbs. The creation of the new C-C bond on the surface is an exothermic process in which about 4 eV is released. The energy is used to break the triple bond into a double bond. This process needs less than 3 eV. At the same time, one of the formed dangling bonds reconstructs at the surface, either by bonding to a neighboring dangling bond or by replacing a hydrogen atom. The net result of the C$_2$H incorporation in the film is the loss of one active site and the production of one sp$^2$ bond. This process is one of the growth steps as no etching of carbon atoms occurs.

Secondly, a sp$^2$ site can be transformed into a sp$^3$ site (so-called hydrogenation) by the interaction with an H atom (Figure 4.54 (b)) or a C$_2$H radical (Figure 4.54 (c)). In case of hydrogen, the incoming H atom breaks the double bond into two dangling bonds and chemisorbs to one of them. The hydrogen fraction in the film then increases. This process depends on the available H particle flux and the hydrogenation probability. The net result is the creation of one dangling bond and one hydrogenated site and the loss of one sp$^2$ bond. In case of interaction with C$_2$H, the C$_2$H radical breaks the double bond into two single bonds and is bond to one of them. The triple bond of the ethynyl is broken, too, and one of the formed active sites is bond to the surface in a similar way as the direct incorporation of ethynyl. The net result is the creation of one dangling bond, the loss of one sp$^2$ bond, and the insertion of one C$_2$H particle. This process is proportional to the incoming C$_2$H flux and the hydrogenation probability and implies film growth as no etching occurs. Both hydrogenation by H, and C$_2$H lead to the formation of sp$^3$CH$_x$ bonds.

Thirdly, there is the abstraction of hydrogen from the surface. This can either occur by H atoms (Figure 4.54 (d)) or C$_2$H radicals (Figure 4.54 (e)). In both cases, one dangling bond is created. These processes are proportional to the incoming particle fluxes.
Fourthly, hydrogen passivation occurs. This process results in the loss of one dangling bond (Figure 4.54 (f). It is proportional to the passivation probability and the incoming hydrogen flux.

The gain or loss of dangling bonds, sp\(^2\) sites, and hydrogenated sites is a result of each of the process given above.

The etching of a-C:H films has been systematically studied by Vietzke and Haasz (Vietzke and Haasz, 1996). Their research results indicate that the elementary reaction of the chemical erosion of hydrocarbon films through interaction with atomic hydrogen proceeds as follows. Impact of atomic hydrogen on a sp\(^3\) carbon site can lead to production of the radical intermediate and a volatile hydrogen molecule. This radical intermediate can either be hydrogenated by another incoming hydrogen atom, which leads back to the original state, or relaxed by the thermally-activated split off of a CH\(_3\) radical from a neighboring carbon atom. This leads to re-hybridization of the participating carbon atoms and the sp\(^2\) carbon pair. Further impinging hydrogen atoms will hydrogenate the sp\(^2\) groups and transform them in a consecutive number of steps back to the starting sp\(^3\) state, as long as the intermediate radical site is thermally stable. However, this chemical erosion step is thermally activated and needs temperatures well above 400 K to be effective. The activation energy for this process 1.6 eV is significantly reduced compared with a typical C-C bond energy of 3.5 eV because the formation of a C=\(\text{C}\) double bond as a result of this relaxation is accompanied by a notable gain in network binding energy. Jacob (Jacob,1998) suggests that this activation energy can be provided by a low energy ion hitting this radical site or its close proximity. Alternatively, it is also conceivable that an impinging ion can transfer sufficient energy to a surface CH\(_3\).
group in a single collision to break the C-C bond and lead to the release of methyl from the surface. Accordingly, this is a true synergistic effect between the chemical processes active at the surface, which produce the loosely bound precursor groups, and ions with very low energy. This effect was designated ‘ion-assisted chemical erosion’.

Except for the etching of a-C:H atoms by atomic hydrogen, the etching of a-C:H films by the sputtering effect of Ar ion also plays an important role, due to the high flux, energy, and mass of Ar ion in the plasma. Many authors have found that argon bombardment is very important in the film deposition. Chou (Chou, 1992) found that the deposition rates of a-C:H films, which were prepared by plasma-enhanced chemical vapor deposition methods from CH₄, H₂, and Ar mixtures, decrease initially as the Ar flow rate increases and then increase after passing a minimum, which occurs as the Ar flow rate approaches the methane flow rate. Kobayashi and his fellow workers (Kobayashi et al., 1990) observed that both H and C atoms in amorphous carbon films could be etched by using a RF glow discharge Ar plasma bombardment and a higher etching rate was observed at a higher Ar pressure. If we take into account the small binding energy of these physiosorbed radicals in the absorption layer, the sputtering effect of energetic Ar ions will be very important.

Following this model, the net deposition rate of a-C:H films may be expressed in a general manner by,

$$r = r_a - r_e - r_s \tag{4.5}$$

where, $r$ is the net deposition rate of a-C:H films, $r_a$ is the adsorption rate of carbon radicals, $r_e$ is the etching rate of carbon radicals, and $r_s$ is the sputtering rate by Ar ions.
4.6.2 Surface morphology study using scanning electron microscope (SEM)

Figure 4.55 shows the surface morphology of the acetylene based polymeric amorphous hydrogenated carbon thin film deposited on silicon wafer at 50 W, 60 W, 80 W and 100 W respectively. The films appear to be homogeneous over the entire surface with islands embedded on the film. A comparison of the surface morphology for the a-C:H film deposited at RF power of 50 W and 100 W do not show any difference in terms of roughness as reported by Kim and his group (Kim et al., 2004). They reported that plasma polymerized film grown on Si (100) substrates at RF power of 50 W, 70 W and 100 W shows smoother and featureless surface with increase in RF power. They explained that this observation is due to the difference in plasma density. At high power the plasma power can easily break monomer and cluster in the gas phase or on the surface of the substrate. In this study, such observation is not observed. The films all show the same type of surface morphology. This may be due to the monomer used, acetylene, C₂H₂, is smaller. C₂H₂ is also much simpler compared to the larger and more complex thiophene, C₄H₄S molecule used by Kim and his group (Kim et al., 2004). Hence, the radical fragments and clusters are more homogenous in size in the plasma, even though different RF power is applied.
Figure 4.55 Scanning electron micrograph of acetylene based hydrogenated amorphous carbon film deposited using various RF power. (a) 100 W; (b) 80 W; (c) 65 W; (d) 50 W. (Continued on next page)
Figure 4.55 Scanning electron micrograph of acetylene based hydrogenated amorphous carbon film deposited using various RF power. (a) 100 W; (b) 80 W; (c) 65 W; (d) 50 W.
All the polymeric films demonstrated bubbles distributed randomly on the plain surface (Figure 4.56). The plain surface is the polymer that has grown homogeneously. The bubbles can be attributed to "drops" of monomers or oligomers trapped between the layers that attempt to escape, forming small bubbles in the film (Cruz et al, 1997). Small points that appear on the surface of the film deposited at 100 W as seen in the micrograph may be due to the collapsed of small bubbles.

![Figure 4.56 Scanning electron micrograph showing the surface of an acetylene based a-C:H polymeric film.](image)

Figure 4.56 shows the image that is obtained from SEM for a damaged film. This damage is attributed to high residual stress. It was not only correlated to film thickness but also with deposition conditions. The internal stress could not be measured quantitatively from D and G line found in the micro-Raman spectra of hydrogenated amorphous carbon film. This is because of the difficulty to obtain the D and G peaks, due to the high photoluminescence radiation at the background, which superimpose with
the two graphitic peaks of the hydrocarbon film. Besides that, the films deposited are soft and easily scorched by the Ar$^+$ ion laser hitting at the surface of the film during micro-Raman analysis resulting in difficulty to obtain the D and G peaks. From the wrinkles and buckles observed on the damaged film, the residual stress is deduced as compressive stress (Zajickova et al, 2003). In their study, Zajickova and his group (Zajickova et al, 2003) used a pulsed RF discharge to study plasma polymerization to demonstrate that residual stress is influenced significantly by the duration of the discharge pulses. Increasing discharge on-time from 50 ms to 150 ms has been reported by them to reduce the residual stress significantly. Pulsing of the discharge can decrease the substrate temperature and therefore reduce the stress in the films (Kumar et al, 1999).

Figure 4.57  Scanning electron micrograph showing the wrinkles and buckles in a damaged film. Film thickness was estimated to be 2µm.
4.6.3 Surface morphology study using atomic force microscopy (AFM)

The AFM micrographs as shown in Figure 4.58 indicated a-C:H films which exhibit homogenous morphology. The films are all made up of long ridges that are arranged parallel to one another with narrow valleys between them. The ridges are composed of columnar micro-rod like structures. Furthermore, no difference in surface topography is observed for films deposited using RF power from 60 W to 120 W.
(a) 60 W

Digital Instruments NanoScope
Scan size  2.000 μm
Scan rate  1.507 Hz
Number of samples 256

data: Height Data scale 10.00 nm
Engage X Pos -19783.4 nm
Engage Y Pos -42151.3 nm

(b) 80 W

Digital Instruments NanoScope
Scan size  2.000 μm
Scan rate  1.507 Hz
Number of samples 256

data: Height Data scale 10.00 nm
Engage X Pos -19783.4 nm
Engage Y Pos -42151.3 nm

80 Watts 50 sccm acetylene (Scan 01)
ng8086.003
Figure 5.58  AFM micrograph of acetylene based amorphous hydrogenated carbon film deposited at various RF power. (a) 65 W; (b) 80 W; (c) 100 W; (d) 120 W.
4.6.4. The effect of RF power, acetylene flow rate, discharge pressure, and distance of substrate from planar coil, on the deposition rate of a-C:H film

(a) Effect of RF power

Figure 4.59 illustrates the variation of the deposition rate of the hydrogenated amorphous carbon film prepared from acetylene with applied RF power. The deposition rate is generally observed to increase linearly with applied RF power. Yasuda (Yasuda, 1978) explained that the increase in deposition rate with discharge power is not indefinite but will reach a plateau. Further increase in the discharge power will result in the decrease of the deposition rate. Dilsiz and Akovali (Dilsiz and Akovali, 1996), using selected organic compounds for plasma polymerization, demonstrated that the dependence of deposition rates of plasma polymer on applied RF power could be divided into two regions (Figure 4.60). The first region is an increase in the deposition rate with increasing power where polymer formation predominates, and the second region is a decrease or no change in deposition rate with increasing power where ablation or degradation predominates, or at least equal to the polymer formation rates.

The increase in deposition rate with the increase in RF power is explained in terms of the increase in plasma density (and also an increase in free radicals) supplied with energy for the plasma polymerization of the acetylene precursor (Kim et al, 2004). Roualdes et al. (1999) render the increase in the deposition rate with power as due to increasing fragmentation of monomer molecules needed for film growth owing to an enhanced electron density, $n_e$, in the plasma. Raising the incident RF power will monotonically increase the $n_e$. 
Figure 4.59  Variation of deposition rate with RF power for the deposition of hydrogenated amorphous carbon film.

Figure 4.60  Deposition rates of plasma polymers as a function of RF power. (Dilsiz and Akovali, 1996).
(b) Effect of acetylene flow rate

Figure 4.61 shows the variation of the deposition rate of the amorphous hydrogenated carbon film with acetylene (C\(_2\)H\(_2\)) flow rate. A decrease in the deposition rate is observed with the increase in the monomer flow rate when pressure and applied RF power is kept constant. At high flow rate, the deposition rate decreases because the residence time of the feed gases decreases and even activated species may be prevented from reaching the substrate by being drawn away and pumped out. Yasuda (Yasuda, 1978) remarked that polymer deposition rate increases linearly with the flow rate under ideal conditions where the conversion ratio of starting material to polymer is high or remain constant. However, the change in flow rate is often associated with changes in flow pattern that affect the yield of polymer formation or the efficiency of discharge power input. As such, the apparent dependence of the polymer deposition rate on flow rate is often characterized by a decrease of the deposition rate after passing a maximum or a narrow plateau. The effect of the acetylene flow rate that is used to demonstrate the effect of flow rate appears to be in the "downhill" region.

The effect of discharge power, W, monomer flow rate, F, and the molecular weight of the monomer, M, cannot be treated independently with respect to their effect on the deposition rate since plasma (glow) discharge polymerization is dependent on the combined parameter of W/FM. As long as the W/FM values remains above the critical level (W/FM\(_{\text{critical}}\)) where energy input is sufficient for polymerization, the major effect of increasing the flow rate is to increase the feed-in rate, which increases the polymer deposition rate. However, if the W/FM level drops to a certain level as F increases at constant W, where the discharge power is not sufficient to polymerize starting materials
coming into the reaction system (i.e. the plasma), and the polymerization mechanism itself changes. Consequently, the polymer deposition rate decreases despite the fact that more starting materials are supplied to the reaction system. Hence, according to the W/FM parameter, the discharge power must be increased as the flow rate of the starting material increases.

![Graph showing variation of deposition rate with acetylene flow rate](image)

**Figure 4.61** Variation of deposition rate with acetylene flow rate for the deposition of hydrogenated amorphous carbon film.

*(c) Effect of discharge pressure*

The effect of discharge pressure on the deposition rate is shown in Figure 4.62. The requirements for the formation of hydrogenated amorphous carbon film (in fact, any plasma polymeric thin films) are low mean free path, long resident time, and relatively high-energy electron. These conditions are facilitated at high deposition pressure. Plasma polymerization is therefore enhanced at higher pressure. The trend that is illustrated in Figure 4.62 on the effect of pressure on the rate of reaction is in good
agreement with the stated requirements. This study shows the increase in discharge pressure results in the increase in deposition rate.

![Graph showing the variation of deposition rate with discharge pressure for the deposition of hydrogenated amorphous carbon film.](image)

**Figure 4.62** Variation of deposition rate with discharge pressure for the deposition of hydrogenated amorphous carbon film.

*(d) Effect of distance of substrate from planar coil*

The distance of the substrate from the planar coil also affects the deposition rate of hydrogenated amorphous carbon film. As illustrated in Figure 4.63, the deposition rate is observed to decrease as the substrate is placed further away from the planar. Since the discharge chamber and the substrate table are electrically grounded, there is a tendency for the plasma to expand to the wall of the chamber during deposition. Due to this, reactive acetylenic radicals in the plasma are also diffused to the wall of the chamber and deposited at the wall as hydrogenated amorphous carbon film. The further the substrate is from the planar coil, the more will depletion of the plasma density is. As the growth of
the film is dependent on the density of the plasma to supply reactive radicals crucial for film growth, depletion of plasma density will result in slower film growth.

Figure 4.63  Deposition rate versus the distance of substrate from planar coil for the deposition of hydrogenated amorphous carbon film.
4.6.5 Determination of optical properties of the hydrogenated amorphous carbon film by ultraviolet-visible-near infrared spectroscopy

All the polymeric acetylene based amorphous hydrogenated carbon films show transmittance spectrum that rises sharply from 0% to ~ 95% transmittance at the wavelength range of 300-550 nm. The spectrum then level off at the high transmittance value between ~ 80 - 95%, with oscillating pattern (repeating peaks and valleys) in the visible and near infrared regions.

The UV-Visible-Near IR spectra for amorphous hydrogenated carbon films deposited at various RF powers are shown in Figure 4.64 (a). The shift to longer wavelength (corresponding to the "point" where the sudden drop in % transmittance) with the increase in RF power is also observed (Figure 4.64 (b)). The reason for the longer wavelength red shift in the UV-visible spectrum is mainly due to the higher degree of sp³ cross-linking and formation of π electron conjugation bond within the structure of the acetylene based polymeric amorphous hydrogenated carbon film when film deposition is conducted when increasing RF power (Kim et al, 2004).
Figure 4.64  (a) Typical UV-Visible-Near IR spectrum for amorphous hydrogenated carbon film deposited at various RF powers.
(b) The expanded view of the spectrum shown in (a) to present the blue shifts that occur to the films deposited at various RF powers.
4.6.5.1 Effects of deposition parameters on optical properties

The complexity of a-C: H is a result of the allotropic character of carbon. Carbon can adopt different bonding configurations depending on the hybridization of the four valence electron orbitals: four-fold coordination (sp$^3$ hybridization) like in diamond or in methane and aliphatic hydrocarbons; three-fold coordination (sp$^2$ hybridization) like in graphite or in ethylene and olefinic hydrocarbons, as well as in benzene and aromatic hydrocarbons; two-fold coordination (sp hybridization) like in the still controversial carbyne crystalline phase (Kudryavtsev et al, 1996) or in acetylene. It was indeed suggested earlier that, whatever their preparation conditions, a-C:H films contain both sp$^3$ - and sp2 -hybridized carbon atoms, although in very variable proportions (McKenzie, et al, 1983; Koidl et al, 1989). Moreover, even if these two types of carbon atoms are interconnected by strong $\sigma$ bonds, which form the ‘skeleton’ of the disordered C network, they are not randomly distributed in space. It has been shown that, for energetic reasons, the sp$^2$ C atoms tend to pair up and to make double bonds, then to gather into more or less extended $\pi$-bonded clusters based on chain or ring configurations of conjugated double bonds (Robertson & O’Reilly, 1987). This segregation of the sp$^2$ C atoms induces a very unusual intrinsic heterogeneity of the atomic microstructure at a nanoscopic or mesoscopic scale, which is currently described by the so called two-phase or cluster model (Robertson & O’Reilly, 1987). Amorphous hydrocarbon films are assumed to consist of sp$^2$ C clusters embedded in a disordered tetra-coordinated ‘matrix’ formed by the sp$^3$ C atoms. The proportions of sp$^2$ C and sp$^3$ C atoms, as well as their mutual spatial organization, are expected to depend very strongly on the deposition conditions that determine the film growth mechanisms. The incorporation in some cases of large
concentrations of hydrogen atoms (up to 50–60 at. %), which are liable to bond preferentially to either sp² C or sp³ C atoms, can also drastically influence the processes of film formation, and complicates the problem still further.

In a-C:H films the sp² C clusters are connected to each other by a more or less cross-linked three-dimensional sp³ C network, so that the material must rather be considered as a disordered solid exhibiting medium-range bonding fluctuations. Since the π bonds are much weaker than the σ bonds, it can be expected that in a-C:H, the π bonding (in sp² C clusters) and antibonding states will lie within the large energy gap which separates the σ (in sp³ C network) bonding and antibonding states, like in graphite and in all π-bonded systems. The π states are therefore expected to control the a-C:H band edges, and therefore the value of the optical energy gap of this material (Robertson & O’Reilly, 1987). It must be recalled that all a-C:H samples are semi-conducting, and that their gap can vary over quite a large range, typically from 1–1.5 to 3.5–4 eV, according to their preparation conditions. These properties are well explained by the cluster model. Each sp² C cluster is characterized by a local gap determined by the p states, which will depend on the size, and probably also on the nature (ring or chain-like) and on the distortions of this cluster. On the other hand, the sp³ C matrix connecting these clusters is characterized by a larger gap determined by σ states, which should be about the same everywhere. This situation is depicted in Figure 4.65, which shows a random spatial distribution of potential wells with variable widths and depths representing the sp² C clusters, isolated from each other by potential barriers corresponding to the σ band edges of the sp³ C matrix. The presence of a distribution of cluster sizes, which is certainly the case in a-C:H, will therefore induce strong symmetric
fluctuations of the valence and the conduction band edges (a minimum of the conduction band edge corresponding to a maximum of the valence band edge and vice versa) over distances which correspond to several atoms (medium-range fluctuations) (Robertson, 1991).

![Figure 4.65 Fluctuations of the valence and conduction band edges as a function of the distance, as suggested by the ‘cluster model’ (Robertson, 1991).](image)

The changes in the electronic properties of a-C:H films, especially in the values of their optical gap, are often associated with the variations of two sample parameters: the hydrogen content (by analogy with a-Si:H) and the proportion of sp² C atoms (in relation with the cluster model). In the followings, the effects of various experimental discharge parameters on the optical properties of the a-C:H film fabricated in this project is presented.
(a) Optical Energy Gap ($E_g$)

(i) Effect of RF power

Optical energy gaps were observed to decrease with the increase in RF power (Figure 4.66 (a)). This may be due to the increase in applied RF power, which resulted in the increase in $sp^2$ fraction in the film. The volume fraction of $sp^2$ cluster is suggested to increase by increasing the RF power during deposition (Reyes-Mena et al, 1987). In addition to this at lower RF power, the impact energy of plasma species is lower, and hence favors the H incorporation of dangling bonds (also, at lower energy range less C-H bonds are broken). The H atoms originate from the decomposition of $C_2H_2$ monomer. This favors the formation of $sp^3$ hybridization with respect to $sp^2$ ones. As a result, an increase in the optical energy gap may be expected (Marechal et al, 1999).

(ii) Effect of discharge pressure.

The effect of the increase in discharge pressure appears to reduce the optical gaps (Figure 4.67 (a)); suggesting that with the increase in discharge pressure there is an increase in the $sp^2$ fraction in the film. The increase of deposition pressure results in the increase of $C_2H_2$ content in the chamber, and therefore, in the increase of in the flux of reactive ethinyl ($C_2H$) radicals in the plasma. The $C_2H$ radicals will be incorporated onto the growing film to produce $sp^2$ bonds. In addition to this, the energy of the incoming ions decreases with increasing deposition pressure, which results in the decrease of etching rate of ethinyl ($C_2H$) radicals in the absorption layer either by ion-assisted chemical etching by the hydrogen atom or by the sputtering of energetic $Ar^+$ ion. Overall, an increase in $sp^2$ sites in the film is observed with the increase in discharge pressure.
(iii) **Effect of flow rate of acetylene**

The increase in flow rate of acetylene is observed to increase the optical energy gap of the deposited hydrogenated amorphous carbon film (Figure 4.68 (a)). This may be due to the decrease in the sp$^2$ fraction of the film during deposition. As the flow rate of acetylene is increased, more sp$^2$ sites are transformed into sp$^3$ sites through hydrogenation by the interaction with H atom or a C$_2$H radical. In the case of hydrogen, incoming H atom breaks the double bond into two dangling bonds and chemisorbs to one of them. The hydrogen fraction in the film then increases. The net result is the creation of one dangling bond and one hydrogenated site and the loss of one sp$^2$. The C$_2$H radical breaks the double bond of the sp$^2$ sites into two single bonds and is bonded to one of them. At the same time, the triple bond of the C$_2$H is broken to form active sites at the surface of the film. The result is the net creation of one dangling bond, the loss of one sp$^2$ bond and insertion of one C$_2$H particle. The hydrogenation of sp$^2$ sites is shown in the schematic of the film surface reaction (see Figure 4.54). The reason for the decrease in sp$^2$ sites due to their transformation to sp$^3$ with the increase in acetylene flow remains to be investigated in future works.

(iv) **Effect of distance from planar coil**

As the distance of the substrate from the planar coil is increased during deposition, the optical gaps of the film deposited are observed to increase (Figure 4.69 (a)). The increase in the optical gap is a result of the increase in sp3 fraction in the structure of the film. As the distance of the substrate from the planar coil is increased, the density of the plasma is decreased. Hence, the population of energetic species in the plasma, which
affect the surface of the film undergoing deposition, also deteriorates, favoring the passivation of dangling bonds by H atoms resulting in an increase in sp$^3$ fraction relative to sp$^2$ fraction.

(b) Urbach Energy ($E_u$)

Robertson (Robertson, 2002) has proposed two types of disorder that are found in amorphous carbon film, namely homogenous disorder and inhomogeneous disorder. Homogeneous disorder, measured by the Raman G-peak line width is related to the bond angle distortion; while inhomogeneous disorder measured by Urbach energy is related to the statistical distribution of sp$^2$ clusters and chains of different shape and size. The Urbach energy also measures the width of the valence and conduction tail, and the width of the band tail increases with structural disorder in the film.

The Urbach energy is one of the standard measures of electronic disorder in amorphous semiconductors. It is clear that a-C:H has a large disorder, as the Urbach energy of good a-Si:H is about 55 meV, whereas that of a-C:H never falls below 150 meV. The Urbach energy is a measure of the inhomogeneous disorder in the two-phase network, as it measures the range of sp$^2$ cluster sizes present. The inhomogeneous disorder in a-C:H increases continuously with increasing optical gap. This means that the cluster size gets small as the gap gets wider, but the range of cluster sizes remains large in the wide gap a-C:H (Robertson, 2002).

In this study, it has been observed that the Urbach energy does not increase continuously with increasing the optical energy gap. Conversely, the Urbach energy is observed to increase with the decreasing optical gap energy or vice-versa for the various
deposition parameter studies conducted (Figures 4.66 (a), 4.67 (a), 4.68 (a), 4.69 (a)). It has long been known that tail states exist because of the presence of sp$^2$ bonded cluster in a-C:H film. In addition to this, the Urbach energy as mentioned earlier is a measure of the width of the valence and conduction tail, which as a result of the presence of sp$^2$ cluster. The width of this band tail is suggested to increase with structural disorder in the film. Based on these facts regarding the Urbach energy, the conclusion that can be drawn is that as optical energy gap increases, there will be more structural order in the a-C:H film since the number of sp$^2$ bonded C clusters will decrease. Films with lower Urbach energy are relatively more homogenous since the sp$^3$ C matrix is "uniform" with lesser sp$^2$ cluster sites.

According to Fanchini and Tagliaferro (Fanchini and Tagliaferro, 2004) the increase of $E_u$ with increasing optical energy gap in polymer-like a-C:H is not related with an hypothetical increase in inhomogeneous disorder (unsupported by other results) but to the lower density of $\pi$ states and the lowering of the band height $n_\pi$ of the $\pi$ and $\pi^*$ bands involved due to the drop in density, the lower sp$^2$ percentage and the increasing H content.

(c) Refractive Index (n).

The variation of the refractive index values with the applied RF power, discharge pressure demonstrated the same variation pattern. The refractive index (n) values ranges from 1.58 to about 1.68; with exception to the a-C:H film deposited at 30 sccm acetylene where n value of 1.997 is obtained. The refractive index values are observed to increase initially, and then level off to form a "plateau". The refractive index values are observed to decrease with the increase in acetylene flow rate and followed by the leveling off to
give a "plain". The refractive index values for films deposited at various distance from
the planar coil shows a linear increase with the increase in distance.

The n values are also observed to increase with the decrease in optical energy gap
under all the parameters investigated, except for the variation of n with acetylene flow
rate. In the case of the variation of n with the increase in acetylene flow rate, n is
observed to decrease with the increase in optical energy gap. All these are illustrated in
Figure 4.66 (b), 4.67 (b), 4.68 (b), and 4.69 (b).

The increase in $E_g$ with the decrease in refractive index is said to have no relevant
relationship (Fanchini et al, 2001). The increase in carbon network cross-linking can lead to
an increase of the refractive index (Sanchez-Lopez et al, 2000). The increase in carbon
network cross-linking is due to the decrease of hydrogen content in the film. The decrease in
hydrogen content is due to more complete fragmentation of the acetylene in the plasma.
Hence, the hydrogen content indirectly affects the refractive index value of the a-C:H film;
and the relationship between these two parameters is an inverse one. Koidl and co-workers
(Koidl et al, 1991), and also Silva and his group (Silva et al, 1996) observed that when the
density of the film increases, the refractive index of the film increases. The higher
refractive index also suggests a more compact microstructure.
Figure 4.66 Variation of optical properties with applied RF power. (a) Optical Energy Gap, and Urbach Energy vs. RF power; (b) Refractive index vs. RF power. Argon, and acetylene flow rate used are 40 and 50 sccm respectively.
Figure 4.67 Variation of optical properties with discharge pressure. (a) Optical Energy Gap, and Urbach Energy vs. discharge pressure; (b) Refractive index, and optical energy gap vs. discharge pressure. Argon, and acetylene flow rate used are 40 and 50 sccm respectively. RF power used is 100 W.
Figure 4.68 Variation of optical properties with acetylene flow rate. (a) Optical Energy Gap, and Urbach Energy vs. acetylene flow rate. (b) Refractive index vs. acetylene flow rate. Flow rate of argon = 40 sccm. RF power = 80 W.
Figure 4.69  Variation of optical properties with distance from planar coil.  (a) Optical Energy Gap, and Urbach Energy vs. distance from planar coil; (b) Refractive index vs. distance from planar coil.  Flow rate of acetylene = 50 sccm.  RF power = 100 W.
4.6.6  *Investigation of the microstructures of hydrogenated amorphous carbon film using Fourier transform - infrared spectroscopy (FT-IR)*

The typical FT-IR spectrum for the acetylene based hydrogenated amorphous carbon film is shown in Figure 4.70 (a).

The FT-IR spectrum for the acetylene based hydrogenated amorphous carbon film exposed to the air after 10 days is shown in Figure 4.70 (b). Comparing Figure 4.70 (a) and (b), the spectra clearly indicate that after 10 days of exposure to atmospheric conditions, oxidation of the thin film has occurred. This is indicated by the presence of the carbonyl groups (C=O) band at wavenumber 1680 to 1750 cm\(^{-1}\). There is also an increase in the intensity of the band related to hydroxyl stretching (O-H) groups at about 3450 cm\(^{-1}\). This was also observed by Tsai *et al* (1994). Incorporation of oxygen into the plasma polymerized acetylene based hydrogenated amorphous carbon film is clearly observed due to post polymerization reaction of residual free radicals with atmospheric O\(_2\) and H\(_2\)O.
Figure 4.70  (a) Typical FT-IR spectra for acetylene based hydrogenated amorphous carbon film deposited at RF power of 122 W. Flow rate for acetylene and argon gas are 50 sccm and 40 sccm respectively. Discharge pressure is fixed at 2.5 mbar.
(b) FT-IR spectra for the same acetylene based hydrogenated amorphous carbon film after 10 days exposure to atmospheric conditions.
Figure 4.71  (a) IR absorption spectra for a representative polymeric, DLC and ta-C:H sample in the bending (left side) and stretching mode regime (right side) along with fits to vibrational modes. (Ristein et al, 1998).
(b) IR absorption spectra for the hydrogenated amorphous carbon film deposited in this study:
(i) IR absorption spectra bending mode regime.
(ii) IR absorption spectra in the stretching mode regime.
(Continued on the next page).
Figure 4.71  (a) IR absorption spectra for a representative polymeric, DLC and ta-C:H sample in the bending (left side) and stretching mode regime (right side) along with fits to vibrational modes.
(b) IR absorption spectra for the hydrogenated amorphous carbon film deposited in this study:
(i) IR absorption spectra bending mode regime.
(ii) IR absorption spectra in the stretching mode regime.
The IR absorption band profile of the CH bending and stretching modes for the hydrogenated amorphous carbon film is shown in Figure 4.71 (b) (see page 364). When the absorption bands for the bending and stretching modes are compared with that reported by Ristein and his group (Ristein et al, 1998) (see Figure 4.71 (a) in page 363) the film deposited in this study appears to be that of the polymeric amorphous carbon film. For polymeric amorphous carbon film the two bending mode bands due to aromatic $sp^2$ C-H (1456 cm$^{-1}$) and $sp^3$ C-CH$_3$ (1380 cm$^{-1}$) are very distinct compared to diamond-like or tetrahedral amorphous carbon film (ta-C:H film). In addition to this, the C-H stretching mode band for polymeric amorphous carbon is not seen as one band but composed of a few "absorption peaks" that can be seen. These peaks are actually "compounded" of $sp^2$ and $sp^3$ C-H stretching bands. The C-H stretching mode band for diamond-like and tetrahedral amorphous carbon appears as one broad stretching band without any distinct peaks.

4.6.6.1 Hydrogen content, $sp^2$ Fraction and optical energy gap

Hydrogen contributes to the carbon $sp^3$ or $sp^2$ bonding, which in turn affects the hybridization of carbon–carbon atoms during growth leading to graphitic or diamond-like character. Furthermore, the microstructure of a-C:H films is closely related to the total H content (C$_H$) and the nature of C–C and C–H bonds in the film.
One of the direct consequences of hydrogen incorporation in amorphous carbon network is to influence their optical properties. Figure 4.72 shows the values of optical band gaps as a function of total hydrogen content in the a-C:H films. At first instance there appears to be no correlation between $E_g$ and $C_H$. However, a careful look at the figure yields vital information on the role of hydrogen in influencing the film properties.

![Figure 4.72](image)

Figure 4.72  Optical band gaps as a function of total hydrogen content in the a-C:H films. (Som et al., 2005)

Low hydrogen content and high optical gap are representative of highly tetrahedral bonded a-C:H films. On the other hand, high optical gap and high hydrogen content are representing the films that are soft and polymeric in nature. These films show a lower refractive index (1.6–1.8) and most of the hydrogen is found to be bonded in CH$_3$ configuration. Such films are obtained under the growth conditions with high pressures and/or low substrate temperatures. In addition the figure also shows a type of film having a low hydrogen content (9 at. %) and $E_g$ of 1.0 eV. This sample has a high sp$^2$ C–C bonding (>50%) and may be termed as graphitic.
It is now believed that most plasma-deposited amorphous carbon films consist of a mixture of strongly crosslinked tetrahedrally bonded sp³ C and threefold coordinated sp² C. Covalently bonded carbon atoms (sp³ hybrids) constitute a three-dimensional network leading to high hardness of a-C:H films with diamond-like properties. On the other hand, graphitic clusters (sp²) embedded in the network influence the electrical and optical properties.

The properties of a-C:H are usually analyzed in terms of two parameters: the hydrogen concentration, \( C_H \), and the respective fractions of sp² and sp³ C-H sites, which are both dependent on the deposition conditions. It is now widely accepted that the ion energy during film growth is the deciding parameter for the local bonding and hence for the film microstructure and properties.

Casiraghi and his co-workers (Casiraghi, et al 2005) classified hydrogenated amorphous carbons into four classes:

1. a-C:H films with the highest H content (40–50%). These films can have up to ~60% sp³ C content. However, most of the sp³ bonds are hydrogen terminated, and this material is soft and with low density. They call these films polymer-like a-C:H (PLCH). Their band gap is above 2 eV and can reach 4 eV.

2. a-C:H films with intermediate H content (20–40%). Even if these films have a lower overall sp³ C content, they have more C-C sp³ bonds compared to PLCH. Thus, they have better mechanical properties. Their optical gap is between 1 and 2 eV. These films are diamond-like a-C:H (DLCH).

3. Hydrogenated tetrahedral amorphous carbon films (ta-C:H). ta-C:H films are a class of DLCH for which the C-C sp³ content can be increased whilst keeping a fixed H
content. Thus, most films defined in literature as ta-C:H are just DLCHs. However, the ta-C:H films with the highest sp$^3$ content (~70%) and ~25 at.% H content do really fall in a different category as also shown by their Raman spectra, their higher density (up to 2.4 g/cm$^3$) and Young’s Modulus (up to 300 GPa). The optical gap can reach 2.3 eV.

(4) a-C:H with low H content (less than 20%). They have a high sp$^2$ content and sp$^2$ clustering. The gap is under 1 eV. These films are called graphite-like a-C:H (GLCH).

(a) **Effect of RF power**

Hydrogen contents for films deposited at various RF power are observed to decrease with the increase in RF power (Figure 4.73 (a)). Figure 4.73 (b) illustrates that the sp$^2$ fraction of the film increases with the decrease in the hydrogen content when the applied RF power is increased during deposition. The sp$^2$ fraction of the film on the other hand is demonstrated to increase with the decrease in the optical energy gap of the film when the applied RF power is increased during deposition. The optical energy gap is also observed to decrease with the decrease in hydrogen content when applied RF power is increased (as presented in Figure 4.73 (d)).

The following reaction takes place during the deposition of the hydrogenated amorphous carbon film (refer to Figure 4.54):

\[ \text{[Equation]} \]
At the same time the following process where the hydrogen is removed from the film by incoming hydrogen and precursor ions can also take place:

\[ \begin{align*}
&\text{H}_2 + \text{H} \\
&\rightarrow \text{H}_3^+ + \text{H} \\
&\rightarrow \text{H}_4^+ + \text{H} \\
\end{align*} \]

When the RF power is increased, the hydrogen and precursor ions have gained more energy so that processes (d) and (e) can occur more effectively than at lower RF power. Processes (d) and (e) is roughly proportional to the molecular ion energy. Abstraction of hydrogen can take place at H attached dangling bond site and sp\(^3\) sites. Hence a decrease in H content and sp\(^3\)/sp\(^2\) fraction is demonstrated.

(b) **Effect of discharge pressure**

Hydrogen contents for films deposited at different discharge pressure are observed to decrease with the increase in RF power (Figure 4.74 (a)). Figure 4.74 (b) illustrates that the sp\(^2\) fraction of the film increases with the decrease in the hydrogen content when the total discharge pressure is increased during deposition. Likewise in the case of the increase in applied RF power, the sp\(^2\) fraction of the film is demonstrated to increase with the decrease in the optical energy gap of the film when the total discharge pressure is increased during deposition. The optical energy gap is also observed to decrease with the decrease in hydrogen content when total discharge pressure is increased (as presented in Figure 4.74 (d))

The observation of the effect of increasing the discharge pressure on the H content and sp\(^3\)/sp\(^2\) ratio may be due to the increase in the frequency of effective collision
on the surface of the film by molecular ions such as $\text{C}_2\text{H}^+$. The energy supplied by the fixed RF power is sufficient to abstract the hydrogen from either the $\text{sp}^3$ C sites or H attached to the dangling bonds. With the increase in discharge pressure at a fixed flow rate, the frequency of collision to abstract H from the film surface is increased. The consequence of this is the decrease in H content and $\text{sp}^3$ ratio.

(c) Effect of flow rate of acetylene.

Hydrogen contents are noticed to increase in the hydrogenated amorphous carbon films deposited when the acetylene flow rate is increased (Figure 4.75 (a)). On the contrary, the $\text{sp}^2$ fraction of the films decreases with the increase in the hydrogen content Figure 4.75 (b), when the acetylene flow rate is increased during deposition. The optical energy gap is observed to increase with the increase in hydrogen content when acetylene flow rate is increased (as presented in Figure 4.75 (d))

Process (a) results in film deposition, however when flow rate is increased process (c), which results in the increase of $\text{sp}^3$ and process (b) and (f) which results in an increase in H content appear to be more prevailing. Hence, an increase in H content and $\text{sp}^3$/sp$^2$ fraction is observed.
(d) **Effect of distance of substrate from the planar coil.**

Hydrogen contents are noticed to increase in the hydrogenated amorphous carbon films deposited when the distance of the substrate from the planar coil is increased (Figure 4.76 (a)). Like all the parametric studies above, the decrease sp² fraction of the films is usually accompanied by the increase in the hydrogen content as shown in Figure 4.76 (b), when distance of the substrate from the planar coil is increased during deposition. The optical energy gap is observed to increase with the increase in hydrogen content when distance of the substrate from the planar coil is increased (as presented in Figure 4.76 (d)).

As the distance from the planar coil is increased, the ions in the plasma become less energetic. Hence, the abstraction of hydrogen from the dangling bond sites and sp³ C sites by energetic hydrogen and molecular ions become less important. The increase in hydrogen content and the sp³/sp² fraction is therefore due to the relative predominance between process (b) and (f) compared to process (a).
Figure 4.73 (a) Plot of hydrogen content and sp\textsuperscript{3} to sp\textsuperscript{2} ratio as a function of RF power. (b) Plot of hydrogen content and sp\textsuperscript{2} fraction as a function of RF power. (Continued on the next page)
Figure 4.73 (c) Plot of sp² fraction and optical energy gap as a function of RF power.
(d) Plot of hydrogen content and optical energy gap as a function of RF power.
Figure 4.74 (a) Hydrogen content and sp$^3$ to sp$^2$ ratio as a function of discharge pressure. (b) Hydrogen content and sp$^2$ fraction as a function of discharge pressure. (Continued on the next page.)
Figure 4.74 (c) $sp^2$ fraction and optical energy gap as a function discharge pressure.
(d) Hydrogen content and optical energy gap as a function of discharge pressure.
Figure 4.75  (a) Hydrogen content and sp\textsuperscript{3} to sp\textsuperscript{2} ratio as a function of acetylene flow rate.

(b) Hydrogen content and sp\textsuperscript{2} fraction as a function acetylene flow rate.

(Continued on the next page.)
Figure 4.75  (c) $sp^2$ fraction and optical energy gap as a function acetylene flow rate.
(d) Hydrogen content and optical energy gap as a function of acetylene flow rate.
Figure 4.76  
(a) Hydrogen content and sp$^3$ to sp$^2$ ratio as a function of distance from planar coil distance.  
(b) Hydrogen content and sp$^2$ fraction as a function of distance from planar coil distance.  
(Continued on next page,)
Figure 4.76  (c) $sp^2$ fraction and optical energy gap as a function of distance from planar coil distance.  
(d) Hydrogen content and optical energy gap as a function of distance from planar coil distance.
4.6.7 Micro-Raman spectroscopy and the effect of annealing on the hydrogenated amorphous carbon film.

Although it is widely used for characterization of amorphous carbon films, only a few Raman spectroscopic studies have been performed on polymeric a-C:H films due to high level of photoluminescence that make the Raman signal undetectable (Robertson, 2002; Ferrari and Robertson, 2001). The two Raman bands, D (in the range 1325 -1336 cm$^{-1}$) and G (in the range of 1586-1596 cm$^{-1}$) bands, which are characteristics of the amorphous hydrogenated carbon film (a-C:H), are observed to superimpose on a steep photoluminescence (PL) background (Figure 4.77). Kulikovsky and his group (Kulikovsky et al, 2004) reported that films that are aged for a month in the air at room temperature show appreciable increase of the PL background. However, the Raman features of the two bands remain untouched. The use of ultraviolet excitation overcomes this difficulty and makes possible the investigation of the bonding configuration of the a-C:H film. However, the high-energy irradiation may damage the structure of the film (Ferrari and Robertson, 2001). Another way to avoid the photoluminescence is to use low-energy photons for the excitation of the Raman scattering. Veres and his fellow researchers (Veres et al, 2006) has shown that infrared excited Raman spectroscopy is also very effective for a-C:H characterization. Figure 4.78 shows the Raman spectra reported by Kulikovsky and his co-workers (Kulikovsky et al, 2004). The feature of the D and G peaks of the Raman spectra, which is characteristics of the a-C:H film obtained in this work is similar to that obtained by Kulikovsky and his group (Kulikovsky et al, 2004).
Figure 4.77 Raman spectra of amorphous hydrogenated film deposited at various power (60 W to 120 W). Flow rate of argon and acetylene are 40 and 50sccm respectively. Discharge pressure used is 2.6 mbar.
Figure 4.78 Raman spectra of the as deposited, aged, and annealed a-C:H films. Numbers beside the curves indicate the annealing temperatures in vacuum (on the left) and in air (on the right). (Kulikovsky et al, 2004)
4.6.7.1 Microstructure analysis of annealed hydrogenated amorphous carbon film.

The a-C:H film deposited at RF power of 80 W is annealed at 250°C in the air for 45 minutes. The Raman spectra obtained from the annealed film is as shown in Figure 4.79. The Raman spectrum of the hydrogenated amorphous carbon film shows an increase in the intensity of the D and G bands, and the minimum between the D and G band becomes deeper. However, the position shifts to higher frequency of the G band reported by Kulikovsky et al (2004) is not obvious in this work.

Figure 4.79 Raman spectra showing the D and G peaks for the amorphous hydrogenated carbon film which has undergone annealing (at 250°C) and without annealing. The amorphous hydrogenated carbon film is deposited at RF power of 80 W, and the flow rate for the admixture gas argon and acetylene is 40 and 50 sccm respectively. Discharge pressure used is 2.6 mbar.
Zhang and his group (Zhang et al, 2001) reported a broad peak at 1230 cm\(^{-1}\) in the Raman spectra of the a-C:H film before annealing but not the D band. They considered this peak to be a feature of crystalline hydrogenated carbon films. When the film was annealed at 250\(^\circ\)C, the peak at about 1230 cm\(^{-1}\) disappeared and the peak corresponding to the D line, which is generally attributed to disordered or microcrystalline graphite, appeared. The emergence of the D line suggests a transition from metastable crystalline structure to graphite structure has occurred. It has long been known that the G peak shift, the D peak shift, and the D peak intensity in Raman spectra can provide some information about the DLC film structure (Robertson, 2002). In general, for diamond like carbon film, the G peak and D peak of a conventional hydrogenated DLC film will shift towards a higher wavenumber and the D peak intensity will increase when the sp\(^3\) bonding in the films is decreasing. This corresponds to the decrease in diamond-like characteristics and the increase in the graphite-like characteristic of the films.

Table 4.10  Comparison of optical properties of annealed and un-annealed amorphous hydrocarbon films deposited at RF power of 80 W.

<table>
<thead>
<tr>
<th></th>
<th>Film thickness (nm)</th>
<th>Refractive index</th>
<th>Optical Gap (eV)</th>
<th>Urbach Energy (meV)</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 W -without annealing</td>
<td>941.95</td>
<td>1.626</td>
<td>2.693</td>
<td>215.701</td>
<td></td>
</tr>
<tr>
<td>80 W -with annealing</td>
<td>453.66</td>
<td>1.805</td>
<td>1.306</td>
<td>259.558</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.10 shows the comparison of optical properties of annealed and un-annealed amorphous hydrocarbon films deposited at RF power of 80 W. The thickness of the film is reduced after annealing is conducted on the amorphous hydrocarbon film at
250°C. The optical energy gap of the film is reduced, while the Urbach energy increases. The reduction in the optical energy gap is due to the evolution of hydrogen either as hydrogen gas or as hydrocarbons, which leads to an increase in the sp2 fraction in the film, and the formation of larger graphitic clusters (Manage et al., 2000). The increase in the sp² carbon concentration can be deduced from the increase in the absorption of the sp² C=C vibrations at (1580-1600 cm⁻¹) of the hydrogenated FT-IR spectra (Figure 4.80 (a)). The FT-IR spectra for the hydrogenated amorphous carbon film at different regime of the IR spectrum, before annealing and after annealing, is presented in Figure 4.80.

The disappearance of the band characteristic for the C-H and O-H stretching vibrations in the IR transmittance spectra with the annealing temperature indicates the porous structure and large concentration of free radicals in these films (Figure 4.80 (b) and (c)). Disappearance of the C–H band at 2900 cm⁻¹ annealed at 250 °C reflects a deep penetration of oxygen into the film to interact with hydrogen at this temperature to form water. The water formed in this way can easily evaporate at temperatures above 200 °C . This in turn leads to sharp hydrogen loss in the a-C:H film. The water escape from the a-C:H film is also facilitated by low film density (usually 1.2–1.6 g/cm³) (Kulikovsky et al., 2004).

The polymer-like a-C:H sample initially shows two strong peaks at 1700 and 3400 cm⁻¹, caused by C=O and O–H vibrations, respectively. These peaks originate from contamination by ambient atmosphere and indicate a porous film structure, which facilitates effusion of comparably large hydrocarbon molecules. This also supports the reason for the exceptional thickness reduction in this film after annealing (Table 4.10). These peaks decrease strongly after annealing 250 °C, but the C=O peak remains (Figure
Annealing at 250°C also resulted in the C=O band splitting into two bands. The C=O band at 1722 cm\(^{-1}\) and another band around 1629 cm\(^{-1}\) which are characteristics of the C=C vibration band (Figure 4.80 (a)). The presence of the C=O band after annealing is due to the partial oxidation of the film during annealing in the air. Kulikovsky and his fellow worker (Kulikovsky et al, 2004) reported that the C=O disappears after annealing at 770 °C, however, the C=C vibrations remained distinct even after annealing at 770 °C.

The IR spectrum for the C-H stretching mode band at 2800-3300 cm\(^{-1}\) in the annealed film is observed to disappear, as seen in Figure 4.80 (b). The disappearance of the C-H stretching band is due to the drastic release of the bonded hydrogen in the form of H\(_2\) and CH\(_4\) from the film when annealed at 250 °C. This is also indicated by the decrease in the optical energy gap as shown in Table 4.10. The evolution of hydrogen leads to an increase in the sp\(^2\) C site in the film and the formation of large graphitic clusters at the expense of the sp\(^3\) C matrix. The increase in the sp\(^2\) carbon sites after annealing can be deduced from appearance of the sp\(^2\) C=C vibrations (at ~1600 cm\(^{-1}\)) as seen in Figure 4.81 (a). The increase in number of sp\(^2\) carbon sites is due to the loss of hydrogen from sp\(^3\) carbon, which is converted to sp\(^2\) carbon.
Figure 4.80 FT-IR spectra for amorphous hydrogenated carbon film deposited at 80 W, which is annealed at 250° C and without annealing. The discharge pressure is 2.6 mbar. The flow rate for argon and acetylene used for deposition is 40 and 50 sccm respectively. (a) FT-IR spectra for film with annealing and without annealing from 400 – 4000 cm\(^{-1}\). (b) FT-IR spectra for film with annealing and without annealing highlighting the C-H stretching band region from 2800 -3200 cm\(^{-1}\). (c) FT-IR spectra for film with annealing and without annealing highlighting the O-H stretching band region at about 3400 cm\(^{-1}\). (Continued on next page)
Figure 4.80  FT-IR spectra for amorphous hydrogenated carbon film deposited at 80 W, which is annealed at 250° C and without annealing. The discharge pressure is 2.6 mbar. The flow rate for argon and acetylene used for deposition is 40 and 50 scem respectively. (a) FT-IR spectra for film with annealing and without annealing from 400 – 4000 cm⁻¹. (b) FT-IR spectra for film with annealing and without annealing highlighting the C-H stretching band region from 2800 -3200 cm⁻¹. (c) FT-IR spectra for film with annealing and without annealing highlighting the O-H stretching band region at about 3400 cm⁻¹. (Continued on next page)
Figure 4.80 FT-IR spectra for amorphous hydrogenated carbon film deposited at 80 W, which is annealed at 250° C and without annealing. The discharge pressure is 2.6 mbar. The flow rate for argon and acetylene used for deposition is 40 and 50 sccm respectively. (a) FT-IR spectra for film with annealing and without annealing from 400 – 4000 cm\(^{-1}\). (b) FT-IR spectra for film with annealing and without annealing highlighting the C-H stretching band region from 2800 -3200 cm\(^{-1}\). (c) FT-IR spectra for film with annealing and without annealing highlighting the O-H stretching band region at about 3400 cm\(^{-1}\).
The C-H and C-C bonds are broken when they receive enough thermal energy during the annealing. The released hydrogen atoms and some small hydrocarbon units may either recombine to form hydrogen and methane molecules and diffuse out of the films or diffuse in the small units or then form molecular complexes near the surface, leaving hydrogen-less C(sp$^3$)-C(sp$^3$) network behind. The following bond reactions may happen:

Formation of C=C bonds from C-C bonds:

Reaction (a): \[ 6\text{C(sp}^3\text{-C(sp}^3\text{) } \rightarrow \text{C(sp}^2\text{)=C(sp}^2\text{)+4C(sp}^3\text{-C(sp}^2\text{),} \]

Formation of H$_2$ from sp$^3$-H$_n$

Reaction (b): \[ 2\text{C(sp}^3\text{-H } \rightarrow \text{C(sp}^3\text{-C(sp}^3\text{)+H,} \]

Formation of methane

Reaction (c): \[ 4\text{C(sp}^3\text{-H } + 6\text{C(sp}^3\text{-C(sp}^3\text{) } \rightarrow \text{CH}_4 + C\text{(sp}^2\text{)=C(sp}^2\text{)+}\]

\[ 4\text{C(sp}^3\text{-C(sp}^2\text{).} \]

Reactions (a)-(c) are endothermic with energies of approximately 0.11, 0.49 and 0.14 eV, respectively. With hydrogen release and formation of hydrogen-free C(sp$^3$)-C(sp$^2$) bonding clusters, the photoluminescence efficiency is reduced and the Raman scattering band at 1400-1600 cm$^{-1}$ is activated, hence the appearance of the D and G peaks. When the processes proceed, more and more C(sp$^2$)=C(sp$^2$) bonds are simultaneously produced so that they can rearrange into bigger size of C(sp$^2$) atom rings. This is believed to be the reason for the optical band gap shrinking (Zhang et al, 2000).

A problem that is associated with a-C:H film is that they possess high compressive stress, which greatly affects their adhesion to substrate. Consequently, it is difficult to deposit a-C:H film with simultaneous low compressive stress, high hardness,
and high film thickness. This limits their use as protective coatings (Li et al, 2006). Hydrogen incorporation and ion bombardment during the deposition of the a-C:H are associated with the compressive stress and densification of the film.

Recent studies have demonstrated that the post annealing treatment of the hydrogenated amorphous carbon films under certain temperatures can change the structure and decrease the internal stress of the films (Wachter and Cordery, 1999; Mosaner et al, 2003). The reduction of the internal stress can be achieved by sp$^3$ to sp$^2$ transformation, clustering of sp$^2$ carbon, and the diffusion of hydrogen (Li et al, 2006). Benlahsen and his group (Benlahsen et al, 1998) have demonstrated that a decrease in hydrogen concentration in the a-C:H films after annealing reduces the internal stress from compressive to slightly tensile values, overall reducing the magnitude of the stresses. Their results showed that when the annealing temperature was increased, the elimination of porosities in the a-C:H films causes the films thickness (and volume) to decrease. This effect corresponds to atomic rearrangement in the film associated with the densification of films. The porosities motion, as well as diffusional processes, can operate to reduce the stress. The observed stress depends on the rate of stress generation associated with atomic rearrangement relative to the rate of stress relaxation. Their results also show that a decrease in hydrogen concentration modifies the internal stresses from compressive to slightly tensile values suggesting an important structural modification, i.e. the increase in aromatic (or graphite-like region). The release of H makes the films more dense. They mentioned three mechanisms, which were likely to contribute to tensile stress generation during annealing. The first, occurring between 200 to 300 °C, largely involved hydrogen elimination, and volatile species loss.
(carbonization). This effect corresponds to atomic rearrangement in the film associated with the porosities motion and produced a denser material. The thermal stability of a-C:H was limited by the loss of hydrogen and the consequent bonding changes. The second mechanism, occurring between 300 to 400 °C, involves the conversion of olefinic groups into aromatic groups. In this stage, a decrease of hydrogen content caused a rearrangement in the sp² C cluster groups boundary regions and the compressive stress became tensile stress (annealing temperature ~450 °C), a relaxation of volumetric distortions. Finally, for annealing temperatures of 500 °C, an increase of the graphitization of the layers was observed. The tensile stress increased with annealing temperature.

Benlahsen and his group suggested that the increase in stress is most likely due to atomic rearrangement. They found that when the a-C:H film became more compact, as suggested by the decrease in film thickness, the increase in compressive stress could occur. The tensile stress increased with increasing temperature due to the increase in aromatic (or graphite-like) regions in the film.

4.6.8 Electrical properties of amorphous hydrogenated carbon film.

Figure 4.81 shows the I-V plots obtained from two point probe measurements for amorphous hydrogenated carbon films deposited at different RF powers. The plots show a linear relationship between the direct current and applied voltage up to 100 V. The d.c. current measured is in the current range of 0.5-0.25 nA for the series of a-C:H film. The linearity of the I-V relationship demonstrates that amorphous hydrogenated carbon films have ohmic characteristic. The conduction of electricity by amorphous
hydrogenated carbon films is feasible because of the presence of delocalized $\pi$ electrons that come from unsaturated carbon bonds in the structure of these films. Another contribution to electrical conduction is the formation of cross-links in these films that serve as connecting paths that enhance charge carrier mobility across polymeric chains in the film (Rangel et al., 2000).
Figure 4.81 I-V plot obtained from two point probe measurements for amorphous hydrogenated carbon film deposited at different RF power. Discharge pressure is fixed at 2.6 mbar. Argon and acetylene flow rate are set at 40 and 50 sccm respectively.
Figure 4.82 shows the conductivity versus applied RF power plot. The plot shows the decrease in conductivity with an increase in applied RF power. This observation is related to the increase in optical energy gap and decrease in sp² fraction with RF power. The increase in optical energy gap is a consequence of the decrease in unsaturated bonds in the film. This is indicated by the decrease in sp² fraction. This results in the decrease of delocalized π electrons that are crucial for electrical conduction in polymeric film. Hence, the decrease in conductivity with applied RF power (Rangel et al, 2000).

![Figure 4.82 Conductivity of a-C:H film versus applied RF power.](image-url)