CHAPTER 6

Formation of Highly Vertically Aligned Hydrogenated Carbon Nitride Films
6 FORMATION OF HIGHLY VERTICALLY ALIGNED HYDROGENATED CARBON NITRIDE

6.1 Introduction

This chapter presents studies on the fabrication of vertically aligned nanostructured hydrogenated carbon nitride thin films (ns-CN$_x$:H) deposited using the home-built radio frequency plasma enhanced chemical vapour deposition (rf PECVD) at an electrode distance of 1 cm. These studies were carried out to fulfil three different objectives which include:

(i) The determination of optimized parameters in terms of radio frequency (rf) plasma discharging power and nitrogen incorporation.

(ii) The studies of bonding characteristics and the structural evolution as a function of hydrogen and nitrogen bonding.

(iii) The formulation of a growth mechanism of these ns-CN$_x$:H.

The first and second objectives was carried out through the studies of the effects of applied rf power and nitrogen-to-methane flow-rate ratio on the properties of the deposited CN$_x$:H films. Each study is presented separately in two sequential sections beginning with the variation in rf power. From these results, the optimized range of these parameters for the fabrication of vertically aligned ns-CN$_x$:H was determined. The third objective was achieved through the study of deposition duration in which a model of the growth mechanism is proposed.
As compared to Chapter 4, the characterization and analytical methods used are relatively simple. The films were characterized by means of field emission scanning electron microscopy (FESEM), Auger electron spectroscopy (AES), Raman scattering and Fourier transform infrared spectroscopy (FTIR). These measurements were employed since, in these studies, the analysis and characterization relies heavily on the structural and morphological properties of the films. Additionally, high resolution transmission electron microscopy (HRTEM) was used to capture the high resolution image of the vertically aligned ns-CN_{x};H. This was presented for a study of the deposition duration to assist in the modelling of the growth mechanism.

This is the first optimization section which aims to determine the effects of radio frequency power (P_{rf}) on the deposition of the ns-CN\textsubscript{x}:H films and from there to determine the range in which the vertically aligned ns-CN\textsubscript{x}:H films are produced. The progression of this current section from the work carried out so far is as shown in the flow chart depicted in Figure 6.1.

![Flow chart showing the progression of this current section.](image-url)
All characterization was carried out for films deposited on (111) p-type silicon substrates. It should be noted that the diameter of the substrate holder was approximately 10 cm. Thus, although for simplicity and clarity the rf power in this work will be referred to in terms of power (W) rather than power density (W.cm\(^{-2}\)), it should be noted that the power density for the variation is relatively high. \(P_{rf}\) which drives the plasma generation in the chamber was varied between 30 -100 W. 100W was set as the limit due to the constraint and stability of the home-built rf PECVD system. All other parameters, as listed in Table 6.1, were kept constant.

Table 6.1: Deposition parameters for the study of the effects of radio frequency power on the properties of nanostructured CN\(_x\):H thin films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Set values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. rf power *</td>
<td>30 - 100 W</td>
</tr>
<tr>
<td></td>
<td>Power (W) 30 40 50 60 80 100</td>
</tr>
<tr>
<td></td>
<td>Power Density (W/cm(^2)) 0.38 0.51 0.64 0.76 1.02 1.27</td>
</tr>
<tr>
<td>2. Electrode distance</td>
<td>1 cm</td>
</tr>
<tr>
<td>3. Initial substrate temperature</td>
<td>100 °C</td>
</tr>
<tr>
<td>4. Chamber base pressure</td>
<td>(~1\times10^{-5}) mbar</td>
</tr>
<tr>
<td>5. Methane (CH(_3)) mass flow-rate</td>
<td>20 sccm</td>
</tr>
<tr>
<td>6. Nitrogen (N(_2)) mass flow-rate</td>
<td>47 sccm</td>
</tr>
<tr>
<td>7. ([N_2/(N_2+CH_4)]i \times 100%)</td>
<td>70 %</td>
</tr>
<tr>
<td>8. Deposition time</td>
<td>90 minutes</td>
</tr>
<tr>
<td>9. Deposition pressure</td>
<td>0.8 mbar</td>
</tr>
</tbody>
</table>

*indicates the variable parameter for the study
6.2.1 *Surface and cross-sectional images obtained using Field emission scanning electron microscopy (FESEM)*

The FESEM image as a function of $P_{rf}$ is shown in Figure 6.2.

<table>
<thead>
<tr>
<th>RF Power (W)</th>
<th>Surface Image</th>
<th>Cross-sectional Image</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low magnification</td>
<td>High magnification</td>
</tr>
<tr>
<td>30W</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>40W</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>50W</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>60W</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td>80W</td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
</tr>
<tr>
<td>100W</td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 6.2: Variation of FESEM surface and cross-sectional images for films deposited as a function of applied rf power.
For clarification the FESEM surface and cross-sectional images pertaining to the formation of vertical aligned structures are shown in Figure 6.3 below.

<table>
<thead>
<tr>
<th></th>
<th>Surface image</th>
<th>Cross-sectional image</th>
</tr>
</thead>
<tbody>
<tr>
<td>40W</td>
<td><img src="image1" alt="Surface Image" /></td>
<td><img src="image2" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>50W</td>
<td><img src="image3" alt="Surface Image" /></td>
<td><img src="image4" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>60W</td>
<td><img src="image5" alt="Surface Image" /></td>
<td><img src="image6" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>80W</td>
<td><img src="image7" alt="Surface Image" /></td>
<td><img src="image8" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>100W</td>
<td><img src="image9" alt="Surface Image" /></td>
<td><img src="image10" alt="Cross-sectional Image" /></td>
</tr>
</tbody>
</table>

Figure 6.3: Enlarged FESEM surface and cross-sectional images of ns-CNx:H films for films deposited at various applied rf power.
Chapter 6: About Nanostructured CNx Films

The FESEM shows that the nanostructures were produced at $P_{rf}$ powers as low as 40 W. From the surface images, the ns-CN$_x$:H films within a $P_{rf}$ range of 40 - 100 W formed highly dense nanostructured films. However, the cross-sectional images showed that the films produced at $P_{rf}$ of 40 and 50 W were made up of vertically aligned structures which protrude out of what appears to be a compact amorphous film. The ns-CN$_x$:H improved at $P_{rf}$ above 50 W with enhancement in vertical alignment and a structure which appears more uniform all the way through the base of the film. Here it is proposed that with the continuous growth to the film, the vertical growth of the film progresses while the depth of the ion bombardment along the length of the nanostructures is dependent on $P_{rf}$. Thus, at lower $P_{rf}$, the depth of the etching might not be sufficient to suppress the deposition of amorphous components within the base of the film as the nanostructures (and length of the ns-CN$_x$:H) grows. This problem is resolved by the increase in $P_{rf}$ above 50 W where the ion bombardment is higher. The variation in the diameter and length as a function of $P_{rf}$ is shown in Figure 6.4.

![Figure 6.4: Variation in diameter and length of CNx:H nanostructures deposited as a function of applied rf power.](image-url)
The diameter and length increase when $P_{rf}$ is increased up to 80 W. This is considered to be due to the increase in dissociation/decomposition of CH$_4$ and N$_2$ resulting in the increase in reactive species in the plasma which forms the films (Butler and et al. 2009; Hao et al. 2007; Richley et al. 2009). The increase in these values also indicates that the formation of the film from the reaction of these reactive species and the growth surface dominates the plasma etching. In contrast, with the increase in $P_{rf}$ to 100 W, the diameter of the nanostructures formed begin to saturate while their length decreases significantly. This may be due to the increase in the plasma etching which begins to suppress the growth of the film. The combined effects lead to an initial increase in length to diameter aspect ratio up to $P_{rf}$ of 80 W, but subsequently decrease significantly at $P_{rf}$ of 100 W.

6.2.2 Elemental composition determined by Auger electron spectroscopy (AES)

The nitrogen to carbon N/C ratio obtained from AES measurements is shown as a function of $P_{rf}$ in Figure 6.5. N/C increases as $P_{rf}$ increases up to 80 W and decreases significantly when $P_{rf}$ is increased further to 100 W. The increase in this ratio shows an increase in N incorporation. It is believed that N bonding on the film surface may be weaker than that of C-C bonds. Thus, at $P_{rf}$ of 100 W the etching effect may preferentially remove the N bonding on the growth surface resulting in a decrease in the N/C ratio. It is also seen that the variation in N/C is akin to the nanostructure aspect ratio depicted in Figure 6.4 indicating a significant contribution of N incorporation to the growth of the nanostructures.
6.2.3 Structural characteristics determined by Raman scattering spectroscopy

The variation in Raman scattering spectra as a function of $P_{\text{rf}}$ is shown in Figure 6.6. The spectra show prominent D and G bands which were easily deconvoluted using two Gaussian fitting bands at around $(1376 \pm 10)$ and $(1576 \pm 6)$ cm$^{-1}$, respectively. The deconvolution of these spectra with PL background elimination is shown in Figure 6.6 (b) with the corresponding fitting parameters plotted as a function of $P_{\text{rf}}$ shown in Figure 6.7.

Generally, from these graphs, the contribution of each peak varies with change in $P_{\text{rf}}$. With increase in $P_{\text{rf}}$ up to 80 W, the relative strength of the G band becomes more prominent compared to the D band. However as $P_{\text{rf}}$ is further increased to 100W, the relative strength of the G band decreases. This is also clearly seen from the fitting results for the $I_D/I_G$ ratio as shown in Figure 6.7 (e). The $I_D/I_G$ ratio decreases significantly for $P_{\text{rf}}$ between 30 and 60 W, after which it remained quite constant.
Figure 6.6: Variation in Raman scattering spectra for films deposited as a function of applied rf power, whereby (a) shows the raw data obtained and (b) shows the deconvolution of the Raman spectra after photoluminescence background extraction.
Figure 6.7: Gaussian fitting variation for peak position and full width half maximum for
G-band, (a) and (b), respectively, and D band, (c) and (d), respectively, and the corresponding $I_D/I_G$ ratio, (e).

CHAPTER 6: ABOUT NANOSTRUCTURED CN, FILMS

179
between 60 W and 80 W, and then increases as $P_{rf}$ is increased to 100 W. The decrease in this ratio indicates an increase in ordering (Ferrari and Robertson 2000) as $P_{rf}$ is increased up to 60 W and 80 W. In contrast, the increase in $I_D/I_G$ when $P_{rf}$ is further increased to 100 W indicates a sudden decrease in disorder. However, the changes in the ratio do not appear to be dependent on any individual variation in peak position or the width of D and G peaks shown in Figure 6.7 (a) – (d). This suggests that the variation in $I_D/I_G$ may be due to accumulative effect and the predominance of different aspects of the variation in D and G bands. If the assumption that different aspects dominate at different ranges in the $I_D/I_G$ ratio is accurate, then the increase in ordering at the initial increase in $P_{rf}$ up to 80 W may coincide with the decrease in FWHM$_G$ which is due to the removal of bond angle and bond length disorder (Knight and White 1989; Shiao and Hoffman 1996). In the same way, the significant increase in disorder for $P_{rf}$ of 80 to 100 W indicated by the corresponding increase in $I_D/I_G$, coincides with the significant increase in FWHM$_D$ which could be due to changes in the distribution of clusters with different orders and dimensions (Ferrari and Robertson 2000).

The suggested increase in the ordering in the nanostructured film at $P_{rf}$ of 60 W and 80 W is supported by the improvement in the formation of aligned, high aspect ratio ns-CN$_x$:H seen from the FESEM images at these $P_{rf}$. This may also account for the significant decrease in the growth of the film from $P_{rf}$ of 80 W to 100 W as depicted in Figure 6.4. Similarly, a relationship between the ordering and N incorporation could be made from these results. The high N/C ratio (Figure 6.6) particularly at $P_{rf}$ of 80 W, corresponds with the increase in ordering, alignment and aspect ratio of these films. This indicates that the N incorporation and thus, the N bonding in the films may play an important role in the improvement of ns-CN$_x$:H films. This is studied using FTIR and is presented in the next section.
6.2.4 Chemical bonding studies via Fourier transform infrared spectroscopy (FTIR)

The variation in the FTIR spectra as a function of $P_{rf}$ is shown in Figure 6.8. The spectra show the expected functional groups similar to the spectrum of the p-CN$_x$:H described previously in Chapter 4 and 5. This suggests that there are similarities in the bonding configurations of the p-CN$_x$:H and ns-CN$_x$:H films although their structures differ significantly. For clarification and further assessments, the FTIR spectra are redrawn for each region of interest. These are shown in Figure 6.9.

![Figure 6.8: Variation in FTIR absorbance spectra for films deposited as a function of applied rf power in the range of 1000-4000 cm$^{-1}$.](image)

Figure 6.8: Variation in FTIR absorbance spectra for films deposited as a function of applied rf power in the range of 1000-4000 cm$^{-1}$. 
Figure 6.9: Variation in FTIR absorbance spectra for films deposited as a function of applied rf power for (a) sp\textsuperscript{2}, (b) sp\textsuperscript{1} and (c) sp\textsuperscript{3} phases.
Among the variation in each spectral region seen in Figure 6.9, the changes observed for the spectra in the wavelength region of $1800 – 2300 \text{ cm}^{-1}$ are most significant. The changes in this region involve the bonds corresponding to the N sp$^1$-C functional groups of nitrile and isonitrile. Indeed as seen from Chapter 4, the variation in these bonds is considered as being one of the main contributors in the formation of these ns-CN$_x$:H films. These bonds were assessed from the deconvolution of this spectral region as shown in Figure 6.10.

![Figure 6.10: Gaussian fitting profiles for the FTIR spectra in the region of 1900-2300 cm$^{-1}$ for films deposited as a function of applied rf power.](image)

The blue line shows the Gaussian fitting for the spectra (black points) and the red line shows the overall fitting curve.
Note that the magnitude of the peaks for films deposited at $P_{\text{rf}}$ of 60 and 80 W were adjusted to compensate for the lower peak magnitudes of the other films. This was necessary since the assessment of these bonds focused on their peak position rather than the magnitude of the peaks. However, it should be noted that the peaks for $P_{\text{rf}}$ of 60 and 80 W are very strong. Since the strength of the absorbance peak is directly proportional to the content of the bonds, this indicates that the contributions of these bonds are dominant at these $P_{\text{rf}}$ values. In particular for $P_{\text{rf}}$ of 80 W, the content and contributions of these bonds may outweigh the other bonds in the films.

Figure 6.10 also shows the Gaussian fitting and corresponding functional groups which contribute to the wide range of the peaks. Similar to those noted in Chapter 4, these were fitted according to the bonds associated with the isolated and/or fused aromatic rings bonded either to isonitrile ($-\text{N}=\text{C}$) at 2105 cm$^{-1}$ or nitrile ($-\text{C}=\text{N}$) at 2215 cm$^{-1}$ and hydrocarbon molecules which includes $\text{C}_2\text{H}_5$ at 2160 cm$^{-1}$ and $\text{CH}_3$ at 2190 cm$^{-1}$ bonded to isonitrile ($-\text{N}=\text{C}$) and the hydrocarbon groups ($\text{CH}_3$, $\text{C}_2\text{H}_5$, etc.) bonded to nitrile ($-\text{C}=\text{N}$) located as a single peak at 2245 cm$^{-1}$ (Mutsukura and Akita 1999a, 2000). Additionally a peak assigned to HCN at approximately 2060 cm$^{-1}$ (Kundoo et al. 2003) was also added.

In the initial $P_{\text{rf}}$ range of 30 – 50 W, the spectra remain almost the same with the dominant peak being at approximately 2190 cm$^{-1}$ assigned to $\text{CH}_3$ bonded to isonitrile ($-\text{N}=\text{C}$) bonds. With increase in $P_{\text{rf}}$, two significant shifts in the dominant peak position occur at $P_{\text{rf}}$ ranges of 50 – 60 W and 80 – 100 W. In the first range, the strongest peak position shifts from the isonitrile bonded to aliphatic $\text{CH}_3$ at 2190 cm$^{-1}$ (at 50 W) to those bonded to aromatics at 2105 cm$^{-1}$ (at 60 W). From a $P_{\text{rf}}$ of 60 to 80 W the dominance of this peak increases, indicating that this bond is the preferential type of N
bonding in the film. The second major shift in the strongest peak position occurs when $P_{\text{rf}}$ is increased from 80 W to 100 W, where the main peak reverts back to isonitrile bonded to aliphatic CH$_3$ at 2190 cm$^{-1}$. The deconvoluted spectrum for $P_{\text{rf}}$ of 100 W also shows an equally strong peak at 2215 cm$^{-1}$, which can be attributed to the appearance of nitrile bonded to aromatic rings. A certain progression in the role of the aromatic rings is also clearly observed. The contribution of the rings is seen with the increase in the peak attributed to the nitrile and/or isonitrile bonded to aromatic rings at $P_{\text{rf}}$ above 50 W. The increase in the peak corresponds to an increase in the aromatic content in the film. Even with the regression of the strongest peak at $P_{\text{rf}}$ of 100 W, the presence of the aromatic rings remains, though C≡N bonds were connected to these as nitrile rather than isonitrile.

In chapter 4, it was deduced that there is a significant dependence of the isonitrile bonded to aromatics configuration at 2105 cm$^{-1}$ on the formation of highly vertical aligned ns-CNx:H. On the other hand, FTIR and FESEM results in this chapter show that even without the presence of this bond, nanostructured carbon nitride films are still formed. The difference is that these structures are not formed as uniform or as organized as that of the vertically aligned ns-CNx:H presented in Chapter 4. Indeed, it is seen for the films obtained at $P_{\text{rf}}$ of 30 -50 W, the absence of these isonitrile bonding configurations create nanostructures that are flawed by the presence of the amorphous layer and have lower perfection in terms of the shapes and structure of these rods, as shown in Figure 6.3. In contrast, the formation of the improved and higher quality highly vertically aligned ns-CNx:H which were produced at 60 and 80 W, coincides with the appearance of these preferential isonitrile bonds. In this aspect, the increase in the strength in the bonds in this region for $P_{\text{rf}}$ of 60 and 80 W also coincides with a significantly higher N/C ratio (and thus the N incorporation) in the films. This further
emphasizes the preferential type of N bonding in the material and also the contribution of isonitrile bonded to aromatic rings in the formation of these vertical aligned ns-CN\textsubscript{x}:H. The high peak intensity of this bond also suggests a significant increase in aromatic rings in the structures. The increase in the presence of these rings which may incite the formation of ordered graphitic clusters in the films, may explain the decrease in disorder as seen in I\textsubscript{D}/I\textsubscript{G} ratio in Raman results.

When P\textsubscript{rf} is further increased from 80 W to 100 W, the reversion of the highest peak may have caused the changes seen in the structures of the rods formed. To further clarify this, images of the structures for P\textsubscript{rf} of 100 W captured from different angles are presented in Figure 6.11. These cross-sectional images were captured for parts of the films which were scratched to expose these nanostructures.

Figure 6.11: FESEM images for ns-CN\textsubscript{x}:H deposited at applied rf power of 100 W showing (a) the “root”, middle and “tip” sections of the fibers and (b) the enlarged image of the “root” sections.

It is clearly seen that the growth of the structures varied from the “root”, to the “tip” of the fibers. At the root of the film, finer and thinner fibers were formed as seen
in Figure 6.11 (b). As the growth of the film progresses, these fibers amalgamate to form thicker and well spaced nanorods. Combined with the results from Figure 6.4, the evolution and non-uniformity of the growth also leads to a decrease in the length of the rods as compared to that at P_{rf} of 80W. Similarly this also leads to an increase in disorder seen from Raman scattering since the rods formed are not formed as solid columns from the beginning of the growth. This coincides with the decrease in N incorporation at P_{rf} of 100 W (Figure 6.5), together with the significant decrease in C≡N content in the film (Figure 6.8 and 6.9). The reversion of the C≡N peaks to higher wavenumber which gives preference to isonitrile bonded to aliphatic CH₃ and nitrile bonded to aromatic rings, may explain the difference in the growth of these structures compared to those at P_{rf} of 60 and 80 W which shows preferential isonitrile bonded to aromatic rings. Both the CH₃ and nitrile bonds are terminating groups which could lead to shorter-range ordering and decrease in the size of ordered clusters in the film. Similar deduction could explain the lower quality films deposited at P_{rf} of 30-50 W.

It was deduced from the characterization of the films deposited as a function of P_{rf}, that the optimized P_{rf} of 80 W could be employed to form good quality well aligned vertical CNₓ:H nanostructured films. With that, this Prf was used in the following section which presents the effects of nitrogen-to-methane gas ratio in the formation of CNₓ:H films deposited at D_E of 1 cm.

The flow-rate ratio of nitrogen-to-methane gases, $N_2:CH_4$ was varied to study their effects on the growth and formation of these nanostructures. The progression of this current section from the work carried out so far is as shown in the flow chart depicted in Figure 6.12.

![Flow chart showing the progression of this current section](image-url)
As commonly prescribed for similar studies (Valentini et al. 2001b; Valentini et al. 2001a), N$_2$:CH$_4$ was calculated as the ratio of N$_2$ gas flow-rate to the total precursor gas flow-rate, [N$_2$/\(N_2+CH_4\)]. As reference, films deposited from pure methane (N$_2$:CH$_4$ ratio of 0) was also compared. For the depositions with N$_2$ dilution, N$_2$:CH$_4$ was varied between 0.40 - 0.90 with the N$_2$ gas flow-rates varied while fixing the CH$_4$ gas flow-rates at 20 sccm. Using the optimized P$_{rf}$ determined from the previous section, P$_{rf}$ was fixed at 80 W for all films deposited for 90 minutes. Other deposition parameters were also kept constant. The complete deposition parameters used are shown in Table 6.2.

Table 6.2: Deposition parameters for the study of the effects of nitrogen-to-methane gas flow-rate ratio on the properties of CN$_x$:H thin films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Set values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ([N_2/(N_2+CH_4)]^*)</td>
<td>0 – 0.90</td>
</tr>
<tr>
<td>N$_2$:CH$_4$ ratio</td>
<td>0 0.40 0.50 0.60 0.70 0.75 0.80 0.90</td>
</tr>
<tr>
<td>CH$_4$ (fixed) / ±0.1 sccm</td>
<td>20.0 20.0 20.0 20.0 20.0 20.0 20.0</td>
</tr>
<tr>
<td>N$_2$ (Varied) / ±0.1 sccm</td>
<td>0 13.3 20.0 30.0 46.7 60.0 80.0 180.0</td>
</tr>
<tr>
<td>2. rf power</td>
<td>80 W</td>
</tr>
<tr>
<td>3. Electrode distance</td>
<td>1 cm</td>
</tr>
<tr>
<td>4. Initial substrate temperature</td>
<td>100°C</td>
</tr>
<tr>
<td>5. Chamber base pressure</td>
<td>~1x10^-5 mbar</td>
</tr>
<tr>
<td>6. Deposition time</td>
<td>90 minutes</td>
</tr>
<tr>
<td>7. Deposition pressure</td>
<td>0.8 mbar</td>
</tr>
</tbody>
</table>

*indicates the variable parameter for the study
6.3.1 *Surface and cross-sectional images obtained using field emission scanning electron microscopy (FESEM)*

The variation in surface images obtained from FESEM as a function of N$_2$:CH$_4$ ratio is shown in Figure 6.13. The deposition from pure methane (N$_2$:CH$_4$ of 0) produces a uniform film. Nanostructures films began to form in the N$_2$:CH$_4$ range of 0.50-0.75. However for N$_2$:CH$_4$ of 0.50 and 0.60 these structures grew randomly in distribution, length and diameter. They form such clusters scattered over the entire film surface. On the other hand, at N$_2$:CH$_4$ ratios of 0.70 and 0.75, the structures are formed more orderly and well distributed. As the N$_2$:CH$_4$ ratio is further increased to 0.80 and 0.90, the structural characteristics of the films changed again forming amorphous films particularly at the ratio of 0.90. Thus, nanostructured films are formed at a N$_2$:CH$_4$ ratio range of 0.50-0.75 with the optimized range for vertically aligned ns-CN$_x$:H formed at a N$_2$:CH$_4$ ratio of 0.70 and 0.75.

Cross-sectional images of the nanostructured films deposited at N$_2$:CH$_4$ of 0.70 and 0.75 are shown in Figure 6.14. Note that the image magnification was selected for clarification and was taken into account for the structural comparisons. Both films are made up of well-aligned vertical fibers which grew directly on bare Si substrates. The average diameters of the fibers for both depositions are almost similar at $(130 \pm 20)$ nm for N$_2$:CH$_4$ of 0.70 and $(110 \pm 20)$ nm for 0.75. The fibers that grew at N$_2$:CH$_4$ of 0.75 appears to be better organized and formed than those at 0.70 where the structures grew with a slight tilt. However the length of fibers for N$_2$:CH$_4$ of 0.70 at $(5.42 \pm 5)$ $\mu$m is almost double of that of 0.75 at $(2.74 \pm 5)$ $\mu$m, giving a higher aspect ratio. The narrow ratio range in which the vertically aligned nanostructures are obtained is one of the most interesting aspects of this study.
CHAPTER 6: ABOUT NANOSTRUCTURED CN\textsubscript{x} FILMS

Figure 6.13: Variation of FESEM surface and cross-sectional images for films deposited as a function of nitrogen-to-methane gas flow-rate ratio calculated as [N\textsubscript{2}/(N\textsubscript{2}+CH\textsubscript{4})]. Images are taken at two different magnification factors.

Figure 6.14: cross-sectional images taken for the formation of vertically aligned nanostructures at [N\textsubscript{2}/(N\textsubscript{2}+CH\textsubscript{4})] of (a) 0.70 and (b) 0.75. Note that images are shown at different magnification factors chosen for clarification.
6.3.2 *Elemental composition determined by Auger electron spectroscopy (AES)*

The N/C ratio as a function of N$_2$:CH$_4$ ratio is shown in Figure 6.15. N/C ratio increases up to a maximum at N$_2$:CH$_4$ of 0.70. This highest N/C ratio corresponds to the ratio at which the vertically aligned structures are formed. At N$_2$:CH$_4$ of 0.75, the N/C ratio is still significantly high, enough to induce the formation of nanostructures. Subsequently, the N/C ratio decreases significantly with further increase in N$_2$:CH$_4$ and is related to the disappearance of these nanostructures. The results suggest an optimum N/C ratio range, and corresponding N$_2$:CH$_4$ ratio in which these vertically aligned structures are formed. Clearly, N incorporation and its content are crucial aspects which determine the formation of these films. Also here the results show that N/C is not directly proportional to the N$_2$:CH$_4$ ratio but instead shows a specific range in which N incorporation is highest.

![Figure 6.15: Variation of nitrogen to carbon N/C ratio for films deposited as a function of nitrogen-to-methane gas flow-rate ratio calculated as [N$_2$/\(N_2+CH_4\)].](image_url)
6.3.3 Structural characteristics determined by Raman scattering spectroscopy

The Raman spectra of the nanostructures fabricated at different flow-rate ratios with the corresponding deconvoluted spectra with background elimination are shown in Figure 6.16. A photoluminescence background slope corresponding to the presence of hydrogen bonding in the material was observed for the raw Raman data which was eliminated using a non-linear baseline interpolation. The PL background is most significant for the amorphous film deposited from pure methane that is at a N₂:CH₄ ratio of 0.

The spectra consist of broad overlapping peaks of the D and G bands similar to those usually observed for disordered carbon films (Li et al. 2003c). This suggests that sp² clustering within the sp³ matrix makes up the structure of these films. The variation in the calculated band-position \( \omega_D \) for the D bands and \( \omega_G \) for the G bands, and D to G intensity ratios, \( I_D/I_G \) as a function of N₂:CH₄ ratio is shown in Figure 6.17. Generally, the \( I_D/I_G \), \( \omega_D \) and \( \omega_G \) decrease to a minimum at N₂:CH₄ = 0.70 corresponding to the gas flow-rate ratio for the formation of the vertically aligned nanostructures. Additionally, the response in \( \omega_D \) is exceptionally sensitive to the changes in the structure leading to a sharp decrease with the formation of these nanostructures. The decrease in the \( I_D/I_G \) ratio indicates a decrease in the number and/or size of sp² graphitic clusters in the film (Cheng et al. 2001b). This is supported by the red-shift in the \( \omega_D \) which indicates a decrease in the number of ordered aromatic rings (Ferrari and Robertson 2001; Ferrari et al. 2003b, 2003a).
Figure 6.16: Variation in Raman scattering spectra for films deposited as a function of nitrogen-to-methane gas flow-rate ratio calculated as $[\text{N}_2/(\text{N}_2+\text{CH}_4)]$, whereby (a) shows the raw data obtained and (b) shows the deconvolution of the Raman spectra after background extraction.
Figure 6.17: Raman Gaussian fitting for films deposited as a function of nitrogen-to-methane gas flow-rate ratio for peak position and full width half maximum for G-band, (a) and (b), respectively, and D band, (c) and (d), respectively, and the corresponding I$_D$/I$_G$ ratio, (e).
Similarly, the red-shift in the G band indicates an increase in non-six-fold rings in the sp²-clusters (Kovács et al. 2008), which could lead to a decrease in the graphitic cluster size. Thus the Raman results indicate a relatively high degree of disorder for the vertically aligned nanostructured film. This increase in disorder and decrease in graphitic sp² cluster could be due to the sp²-type incorporation of nitrogen that would generate a significant amount of non-six-fold atomic structures (Andújar et al. 2001; Durand-Drouhin et al. 2001; Fanchini et al. 2002b; Fitzgerald et al. 2001; Kovács et al. 2008; Lee et al. 2005; Li et al. 2002; Liu et al. 2001; Neuhaeuser et al. 2000). It should be noted that the G-band position for most of these samples remains higher than that of pure graphite at 1575 cm⁻¹. An exception is the vertically aligned nanostructured film deposited at N₂:CH₄ = 0.70, where the G-band position is closer to that of graphite. This suggests the predominance and influence of sp² bonds in the material.

6.3.4 Chemical bonding studies via Fourier transform infrared spectroscopy (FTIR)

The variation in the FTIR spectra as a function of N₂:CH₄ ratio is shown in Figure 6.18 with the plot of the three regions corresponding to different functional groups shown in Figure 6.19. The spectra are generally similar to those reported for polymeric carbon nitride films seen in chapter 5. The 3 major regions are composed of (a) the sp² phases comprising, among others, the C=C and/or C=N, and N-H bonds within the wavenumber range of 1300–1800 cm⁻¹, (b) the sp¹ phase associated with the C≡N groups within the range of 1800–2200 cm⁻¹, and finally (c) the groups correlated to the presence of hydrogen comprising of sp³ phases of C-H groups within the range of 2800–3000 cm⁻¹ and hydroxyl N-H and/or O-H groups within the range of 3000-3800 cm⁻¹ (Motta and Pereyra 2004; Mutsukura and Akita 2000). The intensities of the
spectra within the region of 1300–1800 cm\(^{-1}\) and 3000–3800 cm\(^{-1}\) seen in Figure 6.19 (a) and (c), respectively, decrease progressively with the increase in N\(_2\):CH\(_4\) ratio. No clear, direct correlation between these trends and the structural and compositional changes were found, which indicates that these functional groups are not the determining bonds which forms these ns- CN\(_x\):H.

![Graph showing FTIR absorbance spectra for films deposited as a function of nitrogen-to-methane gas flow-rate ratio.](image)

Figure 6.18: Variation in FTIR absorbance spectra for films deposited as a function of nitrogen-to-methane gas flow-rate ratio in the range of 1000-4000 cm\(^{-1}\).

In contrast the most significant difference in the spectra is found in the variation in the peak in the wavenumber range of 1800-2300 cm\(^{-1}\) seen in Figure 6.19 (b), which originates from the C≡N functional group. Similar to the studies presented on the effect of applied rf power, this functional group is seen to play an important role in the fabrication of these vertically aligned ns- CN\(_x\):H film.
Figure 6.19: Variation in FTIR absorbance spectra for films deposited as a function of nitrogen-to-methane gas flow-rate ratio in the range of (a) sp², (b) sp¹ and (c) sp³ phases.
The variation in the spectra in this region is re-illustrated in Figure 6.20. For clarification, the intensity of the spectra for the ratio of 0.70 and 0.75 has been reduced to compensate for the significantly lower intensities of the other ratios.

Figure 6.20: Gaussian fitting profiles for the FTIR spectra in the region of 1900-2300 cm\(^{-1}\) as a function of nitrogen-to-methane gas flow-rate ratio.

The blue line show the Gaussian fitting for the spectra (black points) and the red line shows the overall fitting curve.

The broad band in this region is composed of five overlapping bands associated with both nitrile (\(-\mathrm{C} \equiv \mathrm{N}\)) and isonitrile (\(-\mathrm{N} \equiv \mathrm{C}\)) structures (Mutsukura and Akita 1999a,
200). These potential bands include the isolated and/or fused aromatic rings bonded either to isonitrile (−N≡C) at 2105 cm\(^{-1}\) or nitrile (−C≡N) at 2215 cm\(^{-1}\) and hydrocarbon molecules which include C\(_2\)H\(_5\) at 2160 cm\(^{-1}\) and CH\(_3\) at 2190 cm\(^{-1}\) bonded to isonitrile (−N≡C) and the hydrocarbon groups (CH\(_3\), C\(_2\)H\(_5\), etc.) bonded to nitrile (−C≡N) located as a single peak at 2245 cm\(^{-1}\). Using the standard Gaussian fitting methods, the deconvolution of the spectra is obtained in this region and is also shown in Figure 6.20.

Within the wavenumber region of 1900-2300 cm\(^{-1}\), the spectra of the uniform amorphous film deposited from pure CH\(_4\) do not show any peak. This shows that the peaks acquired for the nitrogenated films are due to the incorporation of nitrogen bonding in the carbon network. With the increase in N\(_2\):CH\(_4\) ratio a progressive shifting of the maximum peak to lower wavenumber is seen. The spectra for the nanostructured films with a N\(_2\):CH\(_4\) ratio of 0.40-0.75 shows a significant difference in the peak positions. For a N\(_2\):CH\(_4\) ratio of 0.40-0.60 the spectra were deconvoluted into three peaks corresponding to CH\(_3\) bonded to isonitrile (−N≡C) at (2180 ± 10) cm\(^{-1}\), isolated and/or fused aromatic rings bonded to nitrile (−C≡N) at (2216 ± 5) cm\(^{-1}\) and the hydrocarbon groups (CH\(_3\), C\(_2\)H\(_5\), etc.) bonded to nitrile (−C≡N) at (2245 ± 5) cm\(^{-1}\). The dominant bond for all three films is the isolated and/or fused aromatic rings bonded to nitrile centred at (2216 ± 5) cm\(^{-1}\). The improvement in the structure of the material from a N\(_2\):CH\(_4\) ratio of 0.40 to 0.50 could be related to the increase in the isonitrile bonding at (2180 ± 10) cm\(^{-1}\). The decrease in the C≡N bonds within this region for the ratio of 0.60 coincides with the decrease in the features of the nanostructures and further supports the importance of these bonds in the formation of the nanostructures.
With the formation of the vertically aligned structures at a N₂:CH₄ ratio of 0.70 to 0.75, the maximum peak position shifts significantly to (2115 ± 10) cm⁻¹ which is assigned to isolated and/or fused aromatic rings bonded to isonitrile. This peak is flanked by two key peaks at (2060 ± 7) and (2216 ± 5) cm⁻¹. The latter is similar to the ratios of 0.40-0.50 and is related to nitrile bonded aromatic rings in the material. Its presence indicates that the bond is important in the formation of these structures. On the other hand the peak at (2060 ± 7) cm⁻¹ originates from the absorption of diffused HCN (Kundoo et al. 2003). However, contribution of HCN is presently not fully understood with the relative increase in its peak (2060 cm⁻¹) and reduction in the isonitrile bonds at 2115 cm⁻¹ for the ratio of 0.75 compared to that of 0.70, the length and diameter of the fibers almost doubles. It should be noted that the peaks associated with the ratio of 0.70 and 0.75 in Figure 20 have been reduced for clarity and that these peaks are the dominant peaks in the spectra for the samples as seen in Figure 19(b). Thus the contributions of these bonds in the formation of well-defined vertically aligned nanostructures are crucial. In regard to the vertical alignment and growth rate of the nanostructures, the ratio of 0.70 seems to be the optimum condition. From its FTIR spectra this is associated with the preferential bonds of the isonitrile bonded to aromatic rings in the material. The bonds also suggest a high content of aromatic bonds in the film being part of the architecture that makes up the nanostructures.

In general the importance of N incorporation could be seen from the different structured CNₓ:H films produced with and without N₂ gas dilution. To clearly demonstrate this, the FESEM and FTIR results obtained for various structured films are shown in Figure 6.21. These examples include vertically aligned ns-CNₓ:H deposited at Dₑ of 1 cm for N₂:CH₄ ratio of 0.70 shown in Figure 6.22 (a), and an amorphous CNₓ:H film deposited at the same Dₑ without N₂ dilution, shown in Figure 6.22 (b). Also
included is the p-CN$_x$:H film deposited at $D_E$ of 5 cm for a N$_2$:CH$_4$ ratio of 0.70 shown in Figure 6.22 (c). It is seen that the bonds remain almost the same in terms of sp$^2$-C and sp$^3$-C content within FTIR wavenumber ranges of 1300–1800 cm$^{-1}$ and 2800–3000 cm$^{-1}$, respectively. The main aspect which really sets the ns-CN$_x$:H apart is the strong preferential C≡N bonds in the film at the wavenumber of 1800–2200 cm$^{-1}$. It could be concluded that N incorporation is the determining factor in the formation of these ns-CN$_x$:H and that vertically aligned ns-CN$_x$:H are obtained when isolated and/or fused aromatic rings bonded to isonitrile configuration are the dominant N bonds in the films.

Figure 6.21: Comparison of FESEM surface images and FTIR spectra for (a) ns-CN$_x$:H, (b) non-nitrogenated C:H and (c) p-CN$_x$:H films.
6.4 Effects of Deposition Duration on the Growth of Nanostructured Hydrogenated Carbon Nitride Films

The growth evolution of the vertically aligned ns-CN$_x$:H film was studied by observing the characteristics of the films deposited as a function of deposition duration, $t_D$. The progression of this current section from the work carried out so far is shown in Figure 6.22.

Figure 6.22: Flow chart showing the progression of this current section.
Using the optimized \( P_{rf} \) and \( \text{N}_2:\text{CH}_4 \) ratio where vertically aligned ns-CN\(_x\)::H were obtained, films were produced at \( t_D \) varied between 5 – 90 minutes. The \( P_{rf} \) and \( \text{N}_2:\text{CH}_4 \) ratio were kept constant at 80 W and 0.70, respectively. Similar to the studies on \( P_{rf} \) and \( \text{N}_2:\text{CH}_4 \) ratios, the deposited films were characterized using FESEM, AES, Raman scattering and FTIR. In addition to these, the film deposited at \( t_D \) of 90 minutes was also investigated using high resolution transmission electron microscopy, HRTEM. From the combined results, supported by the information processed from the other previous studies, a growth mechanism of these structures is proposed. The growth mechanism is the main objective for this chapter and as these vertically aligned ns-CN\(_x\)::H are believed to be novel, this proposal is as interesting and as novel as the recently reported leaf-like carbon nitride nanorods (Yang et al. 2006).

Table 6.3: Deposition parameters for the study of the effects of deposition duration on the growth of ns-CN\(_x\)::H thin films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Set values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Deposition duration *</td>
<td>5, 15, 30, 60, 90 minutes</td>
</tr>
<tr>
<td>2. ([\text{N}_2/(\text{N}_2+\text{CH}_4)])</td>
<td>0.70</td>
</tr>
<tr>
<td>3. Methane ((\text{CH}_4)) mass flow-rate</td>
<td>20 sccm</td>
</tr>
<tr>
<td>4. Nitrogen ((\text{N}_2)) mass flow-rate</td>
<td>47 sccm</td>
</tr>
<tr>
<td>5. rf power</td>
<td>80 W</td>
</tr>
<tr>
<td>6. Electrode distance</td>
<td>1 cm</td>
</tr>
<tr>
<td>7. Initial substrate temperature</td>
<td>100°C</td>
</tr>
<tr>
<td>8. Chamber base pressure</td>
<td>(~1\times10^{-5}) mbar</td>
</tr>
<tr>
<td>9. Deposition pressure</td>
<td>0.8 mbar</td>
</tr>
</tbody>
</table>

*indicates the variable parameter for the study
6.4.1 Surface and cross-sectional images obtained using field emission scanning electron microscopy (FESEM)

The variation in growth morphology of ns-CNx:H films deposited as a function of deposition duration, $t_D$, obtained as FESEM images is shown in Figure 6.23.

<table>
<thead>
<tr>
<th>$t_D$</th>
<th>Surface image</th>
<th>Cross-sectional image</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td><img src="image1" alt="Surface and Cross-sectional Image" /></td>
<td><img src="image2" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>15 min</td>
<td><img src="image3" alt="Surface and Cross-sectional Image" /></td>
<td><img src="image4" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>30 min</td>
<td><img src="image5" alt="Surface and Cross-sectional Image" /></td>
<td><img src="image6" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>60 min</td>
<td><img src="image7" alt="Surface and Cross-sectional Image" /></td>
<td><img src="image8" alt="Cross-sectional Image" /></td>
</tr>
<tr>
<td>90 min</td>
<td><img src="image9" alt="Surface and Cross-sectional Image" /></td>
<td><img src="image10" alt="Cross-sectional Image" /></td>
</tr>
</tbody>
</table>

Figure 6.23: Variation of FESEM surface and cross-sectional images of ns-CNx:H films deposited as a function of deposition duration.

Images are taken at two different magnification factors.
The growth of the CN$_x$:H nanostructures begins with the formation of short nanofibers on bare Si substrates. As will be shown later, different from the hollowness seen in CN$_x$ nanotubes (Lu et al. 2009; Singh et al. 2010; Zhong et al. 2001) and nanobells (Bai et al. 2001; Sun et al. 2002; Zhang et al. 2002), these nanofibers have solid interiors and thus are henceforth identified as nanorods. The adhesion between these nanorod arrays and the Si substrates appears to be strong and the base of the nanorods seems well attached on the substrates. This is clearly seen from Figure 6.23 (a), (d) and (e). The conflicting images of Figure 6.23 (b) and (c) are due to the way the substrates were cut to obtain the cross-sectional areas. The force of the cutting causes the dislocation of the arrays from the substrate. In the first $t_D$ of 30 minutes, these nanorods grew irregularly both in distribution and length. The density of the nanostructures and the vertical alignment were enhanced with increase of $t_D$.

Figure 6.24 summarizes the variation in the length and diameter of the nanostructures as a function of $t_D$. As shown, the length and diameter of the CN$_x$:H nanostructures increases progressively with $t_D$. The lengths are measured from the cross-sectional images in Figure 6.23, between the tips of the nanostructures and the substrate surface, while the diameter is estimated at the center of the nanorods. Figure 6.23 (a)-(c) indicate that within the initial 30 minutes, the nanostructures are not well oriented and are slightly bent. As shown in Figure 6.24, the diameter of the structures increases significantly after $t_D \sim 30$ minutes. It is believed that the increase in diameter created constriction between neighbouring nanostructures and force them to grow more vertically aligned thereafter as shown in Figure 6.23 (d) and (e). This reflects the “crowding effect” which has been reported to occur when filamentous carbon grows with high enough density to produce parallel alignment (Melechko et al. 2005).
CHAPTER 6: ABOUT NANOSTRUCTURED CN\textsubscript{x} FILMS

6.4.2 Elemental composition determined by Auger electron spectroscopy (AES)

The spectra of the AES measurement and N/C ratios of the ns-CN\textsubscript{x}:H films deposited as a function of \( t_D \) are shown in Figure 6.25 and Figure 6.26, respectively. The expected peaks corresponding to those of carbon and nitrogen in the energy range of 170-300 eV and 330-410 eV, respectively are apparent for all the thin film samples. However, at longer \( t_D \) the spectra reveal a certain amount of contaminants which originate from the sputtering of the components in the deposition chamber itself. Since the contaminants (mostly metal such as Fe, Al, etc.) were not measurable during 2/3 of the full deposition duration (up to \( t_D \) of 30 minutes), it is believed that these metals did not act as the catalyst for the formation of these CN\textsubscript{x}:H nanostructures. As will be discussed later, this work proves that nitrogen incorporation is the major factor for the formation of the nanostructures.
The N/C ratio increases linearly with $t_D$ and begins to saturate at $t_D > 60$ minutes. The maximum N/C ratio at $t_D = 60$ minutes is high (~0.73) and corresponds to a nitrogen concentration of 42 at. %. Assuming that this film consist of only C and N atoms...
this value implies that two N atoms are bonded to every C atom. This value appears to be exceptionally high and is not reasonable. However, the high N content in the film may be contributed by the presence of various forms of N bonds including those of free molecules such as N₂ or NHₙ related components which are trapped within the films. Moreover, it is likely that the film may contain a certain amount of -N≡N bonds, whose FTIR absorption peaks overlaps those of the strong nitrile and/or isonitrile absorption peaks. These bonds would considerably increase the N/C ratio in the film.

6.4.3 *Structural characteristics determined by Raman scattering spectroscopy*

The variation in Raman scattering spectra as a function of t_D is shown in Figure 6.27 (a). The spectra show prominent D and G bands which were easily deconvoluted using two Gaussian fitting bands within the range of 1333 to 1390 cm⁻¹, and 1558 to 1584 cm⁻¹, respectively. The deconvolution of these spectra with PL background elimination is shown in Figure 6.27 (b) with the corresponding fitting parameters plotted as a function of t_D shown in Figure 6.28.

The G peak shows an initial blue-shift from 1558 cm⁻¹ at t_D of 5 minutes to 1584 cm⁻¹ at t_D of 15 minutes which then saturates up to t_D of 60 minutes. As t_D is further increase to 75 minutes the G band shift back to the lower wavenumber of 1572 cm⁻¹. This final value is close to that of graphite which indicates the presence of graphitic clusters in the film as t_D is further increased to 75 minutes. The variation in the D band is almost the same with a significant blue shift occurring between t_D of 5 to 30 minutes which then saturates at t_D of 30 to 60 minutes. Finally, from t_D of 60 to 75 minute, the D band shifts to a lower wavenumber at 1364 cm⁻¹.
Figure 6.27: Variation in Raman scattering spectra of the ns-CNx:H films deposited as a function of deposition duration, whereby (a) shows the raw spectra, and (b) shows the deconvolution of the Raman spectra after photoluminescence background elimination.
Figure 6.28: Raman Gaussian fitting trends for peak position and full width half maximum for G-band, (a) and (b), respectively, and D band, (c) and (d), respectively, and the corresponding $I_D/I_G$ ratio, (e).
The initial blue shift in both the G and D bands at t_D of 5 to 15 minutes, in contrast to the red shifting seen by Shiao and Hoffman (Shiao and Hoffman 1996), is an indication of an increase in ordering in the films. Indeed the increase in I_D/I_G within the same t_D range indicates an increase in six-fold graphene-like sp^2 bonded clusters (Ferrari and Robertson 2000; Kovács et al. 2008). This coincides with the evolution of the structural growth from cone-like nanostructures to a more condensed formation of nanofibers, seen from Figure 6.23.

Within the t_D range of 15 to 60 minutes where the D and G values are almost constant, the growth of the films is not dependent on sp^2 clustering. Similarly this also indicates that the structure of the film (in terms of clustering) remains almost constant with the growth of the films, even with increase in N incorporation. In contrast, when t_D is increased to 75 minutes, the peak position of the D and G bands, and I_D/I_G decreased. The decrease in I_D/I_G indicates a decrease in size and/or number of clusters in the film (Cheng et al. 2001a; Cheng et al. 2001b). This may be due to the change from a graphene-like clustering to a more graphitic-like sp^2 clustering in the films. This is indicated by the red shift in G band to 1572 cm\(^{-1}\), which coincidently is close to that of graphite at 1575 cm\(^{-1}\) (Chu and Li 2006; Lin et al. 2007).

6.4.4 Chemical bonding studies via Fourier transform infrared spectroscopy (FTIR)

FTIR absorption spectra for our CN_x:H nanostructures are shown in Figure 6.29. The spectra are shown without film thickness correction. In this way the assessment of the bonding properties could be carried out in direct relation to the film growth. These spectra show the presence of the N–H, C=C, and/or C=N stretching (1300–1800 cm\(^{-1}\)),

---

212

---
C-H\textsubscript{n} groups (2800-3000 cm\textsuperscript{-1}), C≡N groups (2000-2200 cm\textsuperscript{-1}) and N-H and/or O-H bonds (3000-3700 cm\textsuperscript{-1}) (Motta and Pereyra 2004; Mutsukura and Akita 2000). The O-H bonds in a-C:H may be due to post-contamination of hydroxyl absorbed in the pores of the material (Fanchini et al. 2005). For clarification, plots of the spectra within the three regions corresponding to different functional groups are shown in Figure 6.30.

Though weak, the presence of sp\textsuperscript{3} bonds in the films contributed by the C-H\textsubscript{n} groups could not be ignored. However, the preference of sp\textsuperscript{2} bonds in the samples is supported by the stronger and more prominent band in the region of 1000-1800 cm\textsuperscript{-1} due to the N-H, C=C, and/or C≡N stretching bands. In addition, there is an obvious increase in C≡N bonds after 30 minute deposition duration.

![Variation in FTIR absorbance spectra of the ns-CN\textsubscript{x}:H films deposited as a function of deposition duration in the range of 1000-4000 cm\textsuperscript{-1}.](image)

Figure 6.29: Variation in FTIR absorbance spectra of the ns-CN\textsubscript{x}:H films deposited as a function of deposition duration in the range of 1000-4000 cm\textsuperscript{-1}.
Figure 6.30 Variation in FTIR absorbance spectra of the ns-CN_x:H films deposited as a function of deposition duration in the range of (a) sp^2, (b) sp^1 and (c) sp^3 phases.
In line with the studies on $P_{rf}$ and the $N_2:CH_4$ ratio, a significant change in the C≡N groups (2000-2200 cm$^{-1}$) is observed with variation in $t_D$. Further analysis is focused on this region and deconvolution using Gaussian fittings are utilized as shown in Figure 6.31. Note that the intensities of the spectra for films deposited at $t_D$ of 60 and 90 minutes was reduced (by a factor of 10) to compensate for the lower intensities of the other films. This allows the shift in the preferential peak with the variation in $t_D$ to observed. It should be remembered though, that the prominent intensities of the C≡N bonds for $t_D$ of 60 and 90 minutes are important aspects to be noted.

Figure 6.31: Gaussian fitting profiles for the FTIR spectra in the region of 1900-2300 cm$^{-1}$ of the ns-CN$_x$:H films deposited as a function of deposition duration. The blue line show the Gaussian fitting for the spectra (black points) and the red line shows the overall fitting curve.
The variation in the peak position and spectral deconvolution shown in Figure 6.31 shows some interesting aspects for the growth of these ns-CN$_x$:H films. One of these aspects is the absence of the prominence of the peak at 2105 cm$^{-1}$ for $t_D$ below 30 minutes. As discussed in the studies of $P_{rf}$ and the N$_2$:CH$_4$ ratio in section 6.2.4 and section 6.3.4, respectively, this peak is ascribed to that of the isolated and/or fused aromatic rings bonded to isonitrile (≡N=C) (Mutsukura and Akita 1999b; Mutsukura 2001). This bond was seen to induce the vertical alignment of ns-CN$_x$:H films. The absence of this peak in the initial growth of the ns-CN$_x$:H film for $t_D$ of 5 and 15 minutes, indicates that these bonds are not the reason for the formation of nanostructured CN$_x$ films. In particular, the maximum peak for $t_D$ of 15 minutes is ascribed to CH$_3$ bonded to isonitrile at wavenumber of 2190 cm$^{-1}$, and isolated and/or fused aromatic rings bonded to nitrile at 2215 cm$^{-1}$. Note that the preference of these bonds in this film is similar to that of the films deposited at $P_{rf}$ of 50 W and a N$_2$:CH$_4$ ratio of 0.50, both of which also form nanostructured films. This supports the proposition that the formation of ns-CN$_x$:H films does not necessarily need this bond to be present.

With further increase in $t_D$ above 15 minutes, a change in the preferential C≡N bonding configuration is seen. A slow shift in the maximum peak to the isolated and/or fused aromatic rings bonded to isonitrile at 2105 cm$^{-1}$, occurs at $t_D$ of 30 minutes. At $t_D$ of 60 minutes and particularly at 75 minutes, the amount of this preferential bond increases exponentially (Figure 6.30 (b)), so much so that at $t_D$ of 75 minutes this peak dominates the other bonding peaks over the entire measured FTIR spectra range (Figure 6.29). The shift and dominance of this particular isonitrile bonding configuration particularly at $t_D$ of 60 and 75 minutes, coincides with the improvement in vertical alignment of these structures. Thus, even though this bond may not be necessary for the
formation of CNₙ nanostructured films, its contribution to the vertical alignment of the structures is crucial. The persistence in this similar observation in the studies of the effects of P, and N₂:CH₄ ratio further emphasize these relationships.

It should be noted also that the peaks at the higher wavenumber associated with the isonitrile bonded to CH₃ and nitrile bonded do not disappear even as the maximum peak corresponding to the change in bonding configuration changes with increase in t₀ to above 15 minutes. The significant increase in the strength of the isonitrile peak at 2105 cm⁻¹ may be related to the significant increase in the N/C ratio shown in Figure 6.26. The increased N incorporated at higher t₀ seems to induce the formation of these preferential isonitrile bonds in the film. An explanation of the increase in N incorporation with t₀ will be discussed later.

6.4.5 Atomic scale imaging using high resolution transmission electron microscopy (HRTEM)

Figure 6.33 shows the HRTEM images of the CNₓ:H nanostructures deposited for 90 minutes. The large image of the vertically aligned ns-CNₓ:H is depicted in Figure 6.32 (a), while higher magnification images are shown in Figure 6.32 (b) and (d) for the tip of the nanorod and Figure 6.32 (c) and (e) for the mid section of the nanorods. From these images it is seen that the nanorods are made up of randomly distributed nanocrystallites surrounded by an amorphous matrix. The sizes of the crystallites range from approximately 2 to 20 nm in diameter. From both the selected area electron diffraction (SAED) pattern and atomic resolution image shown in Figure 6.32 (f) and (g), respectively, it is seen that these nanocrystallites have a 6-fold hexagonal symmetry structure. The ratio of the inter-plane distance between d₁₀₀ and d₁₁₀ was calculated as approximately 1.7, identical to that of graphite (d₁₀₀/d₁₁₀=1.732).
Figure 6.32: High resolution TEM at varied magnification for the upper tip of the nanostructures formed for the deposition duration of 75 minutes (a)-(e). (f) and (i) are the SAED pattern obtained for the nanocrystallite cluster and amorphous components. (g) and (h) shows the atomic resolution images and EDX spectrum of the crystallites.
Additionally, high-resolution EDX analysis on these nanocrystals was carried out and the spectrum is shown in Figure 6.32 (h). The result shows that these crystallites consist of carbon, with no detectable nitrogen content. The presence of Au in the spectrum is expected since the sample was previously coated with Au prior to the FESEM imaging. Other trace signals are either from the TEM grid or contaminants originating from the deposition chamber. The latter coincides with the contaminants observed in AES. Thus, from these results it is postulated that these clusters are made up of graphitic C nanocrystals, and that nitrogen (and hydrogen) is integrated in the surrounding amorphous matrix. The amorphous matrix acts to keep these crystallites together in the columnar structure which makes up the nanorods.

### 6.5 Growth Mechanism Proposed

Based on what have been discussed so far, a proposed growth mechanism for these vertically aligned CN\textsubscript{x}:H nanorods is put forward. A schematic illustration of the proposed mechanism is shown in Figure 6.33.

**Figure 6.33: Schematic illustration of the proposed growth mechanism for the vertically aligned CN\textsubscript{x}:H nanorods.**
It is proposed that the directional electric field generated by the rf plasma is important for the formation of these CN_x:H nanostructures. This electric field initiated a directional flux of ionic growth species of carbon and nitrogen. Apparently, the carbon-nitrogen phase is energetically less stable than the graphite phases. Thus, a crystalline phase of the nano-graphite is formed while the carbon-nitrogen phase remained as amorphous, as shown in Figure 34(a).

As discussed in Chapter 4, due to the close proximity of the electrodes, intensive ion bombardment on the growing surface is expected. Apparently, the crystalline graphite phase has higher resistance to plasma etching than the amorphous carbon-nitrogen phase. This has lead to a higher etching rate for the amorphous component and left behind the more stable islands that have more graphite inclusion. This is why lower nitrogen contents were detected for short deposition duration. The amorphous phase functions as the matrix that holds the graphite nanoclusters together and form scattered islands as shown in Figure 34(b). As the growth process continues, these islands will grow in size [Figure 34(c) and (d)], and stabilize more amorphous carbon-nitrogen phase and thus increase the overall nitrogen content of our samples with increase in the deposition duration. Owing to the directional flux of the grow species, a sub-implantation process in the direction normal to the substrate surface will lead to a columnar growth mode instead of lateral diffusion. Thus, vertically – aligned nanostructures are formed on the initial islands. In addition, the isonitrile bond in the amorphous matrix creates a charge polarity that promotes the columnar growth mode as they tend to align along the direction of the electric field.
6.5 Summary

ns-CNx:H films were deposited using the home-built rf PECVD system at a DE of 1 cm. These films were studied in term of P_{rf} and N_{2}:CH_{4} ratio to determine the optimum deposition parameters for the fabrication of vertically aligned CNx:H nanorods. Using these optimized parameters, the growth of the nanorods was studied as a function of deposition duration t_{D}. The study began with the variation in P_{rf}. ns-CNx:H films were produced at P_{rf} as low as 40 W. The diameter and length of the structures increases with the increase in P_{rf}, and was attributed to the increase in dissociation/decomposition of the CH_{4} and N_{2} precursors. The highest aspect ratio was obtained at P_{rf} of 80 W which coincides with the maximum N content and increase in ordering in the film. N incorporation plays an important part in the improvement in the structure and order in these ns-CNx:H films. The bonding characteristics of these ns-CNx:H is similar to their p-CNx:H counterparts. However the N bonding in these films greatly influences the formation of these ns-CNx:H. The most significant N bonding in these films is seen in the preference of isonitrile bonded to fused or isolated aromatic rings in the films. Although these bonds are not necessary to form CNx:H nanostructure, they are important in the improvement in the alignment and aspect ratio. Thus, the optimized P_{rf} in the fabrication of these vertically aligned CNx:H nanorods is at 80 W.

Subsequently, the effects of N_{2}:CH_{4} ratio on the formation of these ns-CNx:H was studied. The films were deposited at a P_{rf} of 80 W and D_{E} of 1 cm. This study shows that that N incorporation is crucial in the fabrication of these ns-CNx:H. The vertically aligned CNx:H nanorods were obtained over a narrow N_{2}:CH_{4} range of 0.70 to 0.75. This corresponds to the increase in N content in the films. However it is the significantly higher N incorporation at N_{2}:CH_{4} ratio of 0.70 that produces the highest
CHAPTER 6: ABOUT NANOSTRUCTURED CNₓ FILMS

aspect ratio. At this N₂:CH₄ ratio, N incorporation induces a decrease in the graphitic cluster size. Furthermore, in the formation of these vertically aligned nanorods, there is a preference in the bonding of isonitrile bonded to fused or isolated aromatic rings in the films, similar to what was seen for the study on P rf. The optimum parameter in the formation of these vertically aligned CNₓ:H nanorods was determined as a N₂:CH₄ ratio of 0.70.

The effects of deposition duration, t₀, on the ns-CNₓ:H films deposited at P rf of 80 W, N₂:CH₄ ratio of 0.70 and Dₑ of 1 cm was determined. The study monitors the growth progression which starts from the initial formation of short nanofibers on the bare Si substrate and later the formation of vertically aligned nanorods. The alignment, uniformity and density improve with increase in t₀ particularly after 60 minutes. This is attributed to the increase in N incorporation in the films and a significant increase in graphitic clustering. At higher t₀, N is preferentially bonded as isonitrile bonded to fused or isolated aromatic rings which correspond to the increase in the vertical alignment. It was also seen that these nanorods are made up of C nanographitic sp² clusters (2-20 nm in diameter) embedded in an amorphous matrix. N is presented in the amorphous plane which surrounds, encapsulates and holds the nanographitic crystallite together. The proposed growth mechanism involves the combined contribution of ion bombardment, directional flux of growth species and subplantation. Columnar growth dominates over lateral diffusion. The directional electric field from the plasma and the presence of partial charge from the isonitrile bonds [−N⁺≡C⁻] induce vertical growth in the direction of the field.