Chapter 3

CARBON NITRIDE

3.1 Background

![Diagram of carbon nitride structures]

Figure 3.1: (a) Tetrahedrally-bonded hexagonal $\beta$-C$_3$N$_4$, in the $a$-$b$ plane. Each $sp^3$-hybridized carbon atom is bonded to four nitrogen atoms in a tetrahedral geometry and each $sp^2$-hybridized nitrogen atom is bonded to three carbon atoms in a triagonal planar geometry. (b) Zinc-blende-like cubic C$_3$N$_4$. (c) Single layer of graphitelike rhombohedral C$_3$N$_4$. Reproduced from Liu and Wentzcovitch [64].

The hardest material known at present is diamond, with a hardness of about 100GPa, while the second hardest material c-BN has a hardness of only 50GPa. Liu and Cohen calculated, in their
Table 3.1: Some properties for the various phases of C$_3$N$_4$. Reproduced from Liu and Wentzcovitch [64].

<table>
<thead>
<tr>
<th></th>
<th>Ref [64]</th>
<th>Ref [65]</th>
<th>Cubic</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>6.41</td>
<td>6.44</td>
<td>3.43</td>
<td>4.11</td>
</tr>
<tr>
<td>$c/a$</td>
<td>0.375</td>
<td>0.383</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$ (degrees)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>70.5</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>437</td>
<td>427</td>
<td>425</td>
<td>51</td>
</tr>
<tr>
<td>E (eV/formula unit)</td>
<td>47.71</td>
<td>40.75</td>
<td>46.56</td>
<td>47.85</td>
</tr>
<tr>
<td>Average bond length (Å)</td>
<td>1.45</td>
<td>1.47</td>
<td>1.48</td>
<td>1.36</td>
</tr>
<tr>
<td>C-N-C bond angle (°)</td>
<td>~108-120</td>
<td>~108-110</td>
<td>~116</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{3}$</td>
<td>$P\bar{4}3m$</td>
<td>$R3m$</td>
<td></td>
</tr>
<tr>
<td>Atoms radii (Å)</td>
<td>$r_C=0.77, r_N=0.70$</td>
<td>$r_C=0.70, r_N=0.65$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

papers [65, 66], the properties of the hypothetical compound $\beta$-C$_3$N$_4$ (space group $P\bar{3}$), which has a structure similar to tetrahedral $\beta$-Si$_3$N$_4$ (space group $P6_3/m$). Because the sp$^2$-sp$^3$ hybridized bonds between the tetrahedrally bonded C-N is shorter than the bond length of C-C in diamond, it is predicted that the bulk modulus will be larger than diamond. The three-dimensionally tetrahedrally-bonded structure would thus have a high isotropic hardness. They indicated that the material would have mechanical and thermal properties similar to diamond. On top of that, the strength, hardness and high corrosion and wear resistance of Si$_3$N$_4$ (which the $\beta$-C$_3$N$_4$ structure has been based on), suggest that the hypothetical C$_3$N$_4$ compound could have improved structural properties.

Further calculations have also predicted that C$_3$N$_4$ can exist in two other types of structures, a zinc-blend-like cubic structure (space group $P\bar{4}3m$) and a graphite-like phase with rhombohedral stacking (space group $R3m$) [64] (see Figure 3.1 and Table 3.1). Both the zinc-blend-like and $\beta$-C$_3$N$_4$ phases have similar structures, with each C atom having four N neighbours and each N atom bonded to three C atoms. The angles between the C-N-C bonds, however, are different for both the structures. The bond angle for the zinc-blend structure is close to 109.47° and for $\beta$-C$_3$N$_4$, 120°. The local coordination for this structure is similar to that in the hexagonal phase, except that the N atoms form sp$^3$ bonds rather than sp$^2$ bonds. The graphite-like phase consists of “holey” graphite-like sheets with rhombohedral stacking order (ABCABC...). Each of the C atoms have three N atoms as neighbours (three-fold coordinated), as is one of the four N atoms in each unit cell. The other three N atoms are only two-fold coordinated, having only two C neighbours with one C atom missing. The interlayer bonding for the sheet structures is expected then to be weak.

Since the first theoretical prediction of the empirical model of a covalent solid formed by car-
bon and nitrogen [65, 66], many investigators have tried to synthesize such a compound. Various techniques have been attempted, plasma depositions of various hydrocarbons [67], ion implantation [68], reactive rf sputtering of carbon targets in a nitrogen atmosphere [69, 70], dc magnetron sputtering of a carbon target in nitrogen atmosphere [71], plasma enhanced chemical deposition [72, 73] and shock wave compression of carbon nitride precursors [74]. Many have claimed to have synthesized the crystalline phase of \( \beta \)-C\(_3\)N\(_4\), while others report the formation of an amorphous CN\(_x\) phase of varying C-N ratio. Some particles in the crystalline phases have been reported to be 0.1-0.5 \( \mu \)m in size [75, 76], although a majority of the reported sp\(^3\) \( \beta \)-C\(_3\)N\(_4\) are very tiny, \( \leq 10\)nm, and are only found in very small volume fractions of the mainly sp\(^2\)-type bonded films. It is most probable that \( \beta \)-C\(_3\)N\(_4\) is unstable, and would tend to revert to a more stable form of sp\(^2\)-type structure. However, the calculations performed [65, 66] showed that the cohesive energy of this structure should be large enough to yield a metastable solid. Most of these nanocrystals were claimed to have the predicted hexagonal \( \beta \)-C\(_3\)N\(_4\) structure following TEM diffraction analysis.

Some have also claimed to observe new structures not predicted previously. Bursill et al. have reported a face-centered cubic structure having a cell parameter of \( a=6.30\)\( \AA \) and a 10:1 C:N (Ca and O were also present) ratio based on EELS [77]. A tetragonal C-N structure with lattice constants \( a=5.65\)\( \AA \) and \( c=2.75\)\( \AA \) has also been reported [78]. The C:N ratio was 1:0.8. Teter and Hemley [79] had also done some theoretical calculations based on a hexagonal \( \alpha \) phase for the C\(_3\)N\(_4\) with \( a=6.4665\)\( \AA \) and \( c=4.7097\)\( \AA \) (space group \( P31c \)). Other forms of C-N type nucleation observed are CSi\(_x\)N\(_y\) and CN\(_x\)H\(_y\), depending on the method of synthesis, i.e. the substrate used and the precursors present.

It is important to ensure that the N precursors have enough energy during the growth to bond tetrahedrally with the C atoms. Other carbonaceous and H precursors will vie to form bonds with the C. Therefore the N active species must also have enough energy to break any formed C-C or C-H bonds. In most of the deposition methods Si substrates were used while graphite samples were used for the sputtering methods. Most films produced so far have low concentrations of N. Higher concentrations seem more difficult to obtain. However, concentrations of 57 at.% [80] and 80 at.% [81] have been reported. It has been suggested that the presence of atomic N during growth can be crucial for obtaining films with high concentrations of N [82]. The presence of N has also been found to reduce the friction coefficient [83]. It has also been suggested that the presence of N could increase the hardness of the CN\(_x\) films [84, 85].

The aim of this study is to synthesize and characterize the CN films produced in the quest of \( \beta \)-C\(_3\)N\(_4\). Some investigations have reported the formation of amorphous nitrogen-rich carbon films, incorporating a nanocrystalline form of \( \beta \)-C\(_3\)N\(_4\) structure. However, many of the CN films have low concentrations of N. In this study, the CN films are obtained by high-energy plasma deposition of carbon and nitrogen species onto quartz substrates. To characterize the deposited films, the elemental (C/N ratio and any other elements present) and structural composition (nature of
bonding) need to be established. Due to the inhomogeneity of the films, the local bonding in the films is spatially very inhomogeneous too, posing great difficulties in analysis. This inhomogeneity means that different analytical tools are required for the study. Microanalysis techniques that are often used (and which will also be used here) for local elemental distribution are Rutherford Backscattering spectroscopy (RBS) together with particle-induced x ray emission spectroscopy (PIXE), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), while Raman spectroscopy, EELS and TEM studies will be used to investigate the structural composition and local bonding in the films. Scanning electron microscopy (SEM) is used to study the morphology of the film’s surface. TEM and EELS were used to identify the carbon and nitrogen phases (sp\(^2\) or sp\(^3\)) and also to identify the structure/phase through diffraction methods and study of the high resolution images. The techniques used will be discussed briefly in the next few paragraphs.

### 3.2 Analysis Methods

**Auger Electron Spectroscopy (AES)**

RBS, AES and PIXE are used to identify the composition of the films and also the C:N ratio. Because the films grown are thin (<300nm), AES and XPS spectroscopy studies are applicable as they are good surface analysis techniques due to their high surface sensitivity. The spatial resolution of AES is of the order of 2\(\mu\)m. A low electron energy beam (\(\leq 10\)keV) is used on the sample. AES can detect any element that is above He in the periodic table, thus making it suitable in our study of C-N-Si-O systems. AES is also capable of depth profiling, which is ideal for the composition study of the CN\(_x\) films as a function of depth. Due to the nature of the film/substrate that is being studied, the Auger transitions that will occur will be based on the K-shell ionization (\(KL_{2,3}L_{2,3}\) transitions). The kinetic energy of the escaped electron is given by:

\[
E_{KL_{2,3}} = E_K - E_{L_{1,2}} - E^*_{L_{2,3}}
\]  

(3.1)

where \(E_i\) are the binding energies of the \(i\)th atomic energy levels. \(E^*_{L_{2,3}}\) is the binding energy of the \(L_{2,3}\) level in the presence of a hole in the \(L_1\) level. As any sets of atomic binding energies are not the same for any two elements, the analysis of the Auger energies leads to elemental identification. Similar to EELS, the different phases of an element due to the chemical shift in the binding energy of the ionized core level will produce varying line shapes. The fine structures or line shape of the peaks will provide information about the valence band density of states (hence, the electronic structure) and the chemical environment of the sample (see Figure 3.2). The diamond spectrum contains more fine structures on the lower energy side of the main Auger peak than either graphite or amorphous carbon. The more damage there is to the lattice structure, the more “smeared out” the fine structures will be. Insulators, however, tend to cause some problems in proper calibration of the spectra. Because the emitted electrons constituting the secondary electron emission have
low energies, they are easily attracted back to the sample even if the sample has been charged minimally positive due to the loss of electrons. This would cause the elemental peaks to shift down in energy. The situation is reversed if the sample is charged negatively.

**Xray Photoelectron Spectroscopy (XPS)**

XPS may not have as high spatial resolution as AES, but does not damage the sample as much as AES. XPS is also not as affected, to the same extent, by the fact that the samples may be insulating as in AES, since the electron current densities are much lower. The incident x-rays give rise to photo-electron emission according to the equation:

\[
E_k = h\nu - E_B - \phi
\]  

(3.2)

where \(E_k\) is the measured electron kinetic energy, \(h\nu\) is the energy of the excitation radiation, \(E_B\) is the binding energy of the electron in the sample and \(\phi\) is the work function. This kinetic energy is unlike the kinetic energy of an Auger electron, whose value is independent of the excitation radiation (see Equation 3.1). Again, similar to EELS and AES, XPS is able to identify the atoms of the same element under different environments by the line shape. However, many of the binding energy shifts are small (≈ 0.2eV) and the line width of the peaks are 1-2eV which makes the shift difficult to detect. A disadvantage in using XPS and AES is that reference materials are needed for proper calibration of the data. On top of that, XPS has a further disadvantage. The binding energies of some common elements have been reported in the literature to vary, even when referenced to the gold Au 4f\(_{7/2}\) line of 84eV. The graphite C 1s line has been reported to occur at energies from
284.5 to as much as 285.2 eV. This makes an exact identification of the type of bonding present difficult. Most often carbon (or graphite) formed as contaminant on the surface is used as reference despite the associated uncertainties. The binding energies of the peaks must also be regarded with caution due to the fact that the energies are also dependent on the thickness of the layer, the method used for referencing and the accuracy of the energy calibration of the spectrometer on which it is determined. Furthermore, comparison between results from different laboratories may not be meaningful unless the spectrometers are properly calibrated.

In many cases, the XPS spectrum consists of a number of overlapping chemically shifted peaks, of different shapes and intensities. One method of analyzing the spectrum is to fit it with functions. The most common functions are Gaussian and Lorentzian. The basic basic shape of an XPS peak is Lorentzian, but may be modified by factors like instrumental and phonon broadening to give a Gaussian contribution. The final peak shape is usually asymmetrical due to various loss processes. In this current study, the XPS line shapes are represented by mixed Gaussian-Lorentzian functions in the forms of pseudo-Voigt functions. The function used has the form similar to the one used by Brigg et al. [86]:

\[
f(E) = A \left[ M \omega / [(E - E_0)^2 + \omega^2] + (1 - M)(\sqrt{\ln 2/\omega}) \exp[-(\ln 2 (E - E_0)^2/\omega^2)] \right]
\]

where \( A \) is the peak height, \( M \) is the profile shape factor, \( E_0 \) is the energy at peak center and \( \omega \) is the FWHM. \( M \) is 0 for pure Gaussian and 1 for pure Lorentzian. Fitting of the spectrum is performed iteratively using the Marquant-Levenberg \( \chi^2 \)-fitting method, until the goodness-of-fit \( \chi^2 \) is reduced to the required level. Before any fitting of the peaks could be done, the background must be removed from the spectra. Accurate removal of the background is essential as it may involve distortion of the data, and incorrect quantification of the elements. Various methods have been used by different authors. In this study, a simple linear background is assumed and is removed after drawing a straight line joining the first and last set of points of the peak. This is a crude method, but the main merit of this approach is that the original data is not altered.

Auger emission can also occur in XPS, since a core hole is created in the absorption of an x-ray photon in XPS just as it is by the interaction with an incident electron in AES. Auger features can be observed when a wide or survey scan is performed. Thus, XAES is one way to study AES transitions whilst minimizing damage to the samples, together with increased energy resolution which would help in identifying fine structures. The analysis of XAES results is similar to that of XPS. While XPS and XAES have the advantage of better energy resolution than AES, AES has the advantage of better spatial resolution.

**Rutherford Backscattering Spectroscopy (RBS)**

RBS is commonly used to identify elements in thin films or surface layers, to measure the concen-
trations of the constituents and also to estimate the density distribution in depth. This technique involves the sample or target being bombarded with very energetic (in the MeV range) particles and detecting the scattered particles. Due to the high energy of the incident particles, the scattering would involve both the nuclei of the incident ion and target atom. The energy of the scattered ions or particles carries the compositional, scattering depth and structural information of the target material, thus identifying the elements present. Some of the high energy incident ions are capable of traveling a certain depth into the target material undergoing inelastic collisions before being scattered. These ions would carry the depth information required for a depth profile determination of any given constituent of the sample. Chu et al. [87] present a more detailed description of the theory behind this spectroscopy. The quantitation of the RBS spectra requires a standard for energy calibration. Using the fitting program RUMP, the calibrated parameters of the standard sample can then be used to quantify the unknown (CN)$_x$ films. Although RBS is capable of 1μm in lateral resolution, it has poorer depth resolution compared with AES.

**Photon Induced Xray Emission (PIXE)**

PIXE is mainly caused by primary induced x-rays and x-rays due to atomic shell vacancies caused by bremsstrahlung, and secondary electrons together with Auger electrons. This spectroscopy has high mass sensitivity. The spatial resolution is high (in the order of microns) because of the ability to focus the beam to a fine spot and PIXE also has a high spatial energy resolution, ~150eV. PIXE uses MeV particles (α-particles or protons) to irradiate the sample and, by analyzing the emitted x-rays the percentage of the elements present for Z > 12. One of the advantages of using proton particles as incident photons instead of electrons is that the bremsstrahlung production (background) is far less. The cross-section for x-ray production is about the same for MeV protons as for 10keV electrons. Due to the higher energy protons, this technique of study is then suitable for bulk analysis, and not limited to the surface only, as compared to AES or XPS. On top of that, the amount or density required for detection using x-rays is much less than if electrons are used as the detector. However, full analysis (for quantification of composition) of the PIXE spectrum, like RBS, requires comparison with a known standard for calibration. Because 3MeV proton or α-particles can penetrate to a depth of the order of 50μm, this would enhance the uncertainty and reduce the depth resolution. Rough surfaces would cause substantial loss of emission intensity, especially if the random roughness of the surface is significant relative to the x-ray attenuation length in the specimen. This technique also assumes a homogeneous depth elemental distribution within the specimen. Therefore, concerns for thick-target PIXE micro-analysis must take into account are:

- depth of the film and target
- surface and sub-surface shape of the film
- contribution from background matrix, around and below the film, of the elements of interest
lack of knowledge of homogeneity the sample area

This technique is employed together with RBS due to its capability to study bulk contents and trace elements. By contrast to AES and XPS techniques, RBS and also PIXE techniques used in this study produce information that is independent of the chemical bonding in the samples, i.e. whether the C-C bonds are sp² or sp³ types will not be known from the data. However, this allows quantitative elemental analysis, i.e. atomic concentration can be obtained. This assists in quantifying the C:N ratio of the deposited films. Moreover, the detection sensitivity of RBS and PIXE are much better than AES or XPS, 0.1ppm (parts per million), 1ppm, 1000ppm and 1000ppm for PIXE, RBS, AES and XPS respectively. However, reliable compositional prediction/simulation requires accurate parameters, hence simulation of a known standard must be performed initially for calibration. Among all these techniques, EELS still offers the higher spatial resolution and also a higher measured signal. Furthermore, quantitation of EELS data is much easier as it does not require a standard to be used unlike AES and RBS. The only drawback is that EELS requires very thin samples. The other analysis methods used here, for example Raman and EELS, have been discussed in the previous chapter.

3.3 Experiment

3.3.1 Sample Preparation

The experimental set-up is shown in Figure 3.3. The chamber, made to hold high plasma pressure, is filled with nitrogen at 300kPa. The capacitor is discharged through the gap between the two graphite electrodes (~2mm). The third electrode is placed very close to the discharging gap and is connected to the Ruhmkorf coil. The third electrode is needed to act as a trigger for the discharge of the capacitor. The capacitance was 12.5 µF. The coil provides a high discharge voltage, of about 4kV, across the electrodes. The relative position of the third electrode also controls the discharge voltage. There is a diode in the Ruhmkorf coil to prevent the capacitor from discharging through the coil. The substrate used was quartz glass. This substrate, unlike silicon or pure quartz, is mechanically stable enough to withstand the plasma shock pressure which could go up to 400MPa when placed close to the electrodes.

The further away the substrates are from the electrodes, the lower the deposition rate. However, ablation of the substrates will occur if the distance is too close. Hence, a compromise between deposition and decomposition of the substrate must be observed. The number of discharges/pulses governs the thickness of the films. This too may influence the redeposition of the ablated material. Another factor of influence on the quality of the film is the time between discharges. If the time between two discharges is too long, the heat would have dissipated from the substrate surface while too short a time will help build up the surface temperature. Long discharging time (number
of pulses per time) will also influence the amount of heat accumulated on the surface and hence, the quality of the film.

Different sets of films were obtained by varying parameters such as the number of pulses, distance (d) between substrate and electrodes, plasma pressure, time between discharges and discharging time. For one set of samples, the varying parameter was the distance between the substrate and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate/electrode distance, d(mm)</th>
<th>Number of discharges</th>
<th>Discharge rate (min⁻¹)</th>
<th>Voltage (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#F0</td>
<td>1</td>
<td>3000</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
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<td>#F4</td>
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</tr>
<tr>
<td>#F5</td>
<td>3</td>
<td>3000</td>
<td>16</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.2: Deposition conditions for the (CN)ₓ films studied.
the electrodes. The three samples in this set were obtained with the substrate distance, \(d\) being 1, 2 and 5mm. The number of discharges were kept to 3000 for all these films. The voltage supplied was 4kV and the plasma pressure was 300kPa. In another set, the distance \(d\) was kept constant at 3mm and the total number of discharges was also kept constant. However, the discharge rate was varied. Discharge rates of 12, 14 and 16 per min were used. A voltage of 3kV was used and the plasma pressure was kept to 200kPa. Table 3.2 lists the samples studied and their deposition conditions.

### 3.3.2 Analysis

The morphology of the film surfaces were obtained with a Hitachi S-530 SEM. AES and XPS techniques were then performed on the samples using the FISONS VG 310-F instrument at the Physics Department, RMIT. The AES spot size of the beam was 50nm and the energy of the incident electrons was kept low, 10keV, to avoid charging and destruction of the samples. The samples were found to charge under the beam even when the energy of the beam was at 3keV. To avoid more charging, silver conducting paint was used around the film perimeter and the samples were stuck onto the stubs with conducting carbon tapes. Auger sputtering with argon ions were performed on some of the samples. The angle of the sputtering gun was 30° and spectra were collected at every 100Å. The XPS data were collected at a 60° tilt from the incident beam of 4keV. Both AES and XPS spectra were collected with the help of Dr Steve Johnson.

![Schematic diagram of the MARC microprobe target chamber](image)
RBS data on the samples were collected on the microprobe with the help of Roland Syzmanski and Dr Andrew Saint. The microprobe is part of the Pelletron facility at University of Melbourne. It consists of a vertical single-ended 5MeV NEC Pelletron accelerator, which utilizes a RF ion source and 90° analyzing magnet to produce an ion beam of 0.2-5MeV. For the present studies, a beam of 3-10μA has been used. The system was operated under high vacuum conditions, ~10^-7 Torr. 1 and 2MeV α-particles and 3MeV protons were used for analysis. The ion beam can be operated in both the spot (for analysis of small areas of interest) and scanning (for distribution analysis) modes. In the scanning mode, triangular wave forms are used for both x and y scans. The scanning coils are powered by two wave form generators. The frequencies are selected so as not to produce a Lissajous figure, but to cause as uniform a scan as possible. The x-ray spectrum was collected with an energy dispersive x-ray detector Si(Li), positioned at 135° from the incident beam (to minimize background collection), above the beam axis and has a Be window in front of the detector. A second detector (a passivated implanted silicon PIPS surface barrier detector) is placed at an angle of 145° (scattering angle of 175°) with a solid angle of 23.5msr for the detection of the back-scattered incident beam. The beam current was fed to a current digitizer in order for the charge to be calculated. A schematic of the target chamber is presented in Figure 3.4.

A standard consisting of quartz, ZnBO and Au was normally used for system calibration. The spectra from the standard and the samples of interest were fitted, using RUMP, in the same manner to produce more reliable results. Initially, the spectra from the standard were simulated in order to obtain precise analytical parameters such as beam energy and beam incident angle. Using these simulated parameters, and specifying the concentration of the second layer (ie. that of SiO₂), the top layer of the CNₓ films were then simulated to obtain the atomic concentration of the elements of that layer. The areas studied were similar to the areas from which AES and XPS results were obtained for better co-relation between different techniques. Elemental mapping of the surface areas were also performed using the RBS and PIXE techniques. The areas mapped are ~1000x1000μm² for all the samples. 3MeV proton particles were used for this analysis.

For the preparation of the samples for TEM and EELS analysis, some of the films were scrapped off the substrate with a sharp scalpel knife. The powder obtained was ground with a pestle to produce a finer powder. This was then sprinkled onto holey-carbon films and also onto copper 1000-mesh grids before analysis with the electron beam. Again, the 4000 JEOL JEM electron microscope coupled with a Gatan PEEL Spectrometer was used. Similar conditions as reported earlier (see Section 2.3.1 on page 18). Finally, the samples were studied using the Raman spectrometry method, with the 514.5nm argon excitation line and a Dilor spectrometer. Silicon, SiC, various forms of carbon and Si₃N₄ data were also collected using Raman spectroscopy, diffraction and EELS as references. Dr Kerry Nugent again helped with the Raman spectroscopy.
3.4 Results and Analysis

3.4.1 Morphology Analysis

3.4.1.1 SEM

Figure 3.5: SEM analysis of the various (CN)$_x$ film surfaces. Typical surface morphology for regions (a) around the periphery of deposition, (b)-(c) around the center of deposition and (d) in the ablated area of the samples. All deposited films showed similar features regardless of electrode-substrate separation, discharge rate or applied voltage. Note the “cauliflower”-like growth in (a) and the “columnar-type” growth of the film in (c).

The films obtained from the method used appeared to be dark and powdery. The center of the substrate in cases where the distance between the substrate and electrodes are close, were ablated leaving a small region with little or no deposited film. Similarly, when the distance between the substrate and electrodes is large, little film was found to have been deposited. Distances of 1-3mm appear to produce films with “smoother” surface texture and larger deposited areas. When
viewed with the SEM, the thickness of the film was found to vary from 3-15\(\mu\)m depending on the deposition condition and the distance from the center (see Figure 3.5). The morphology of the surface ranges from “cauliflower-like” to a smoother, columnar-type of film. The “cauliflower-type” structures were observed in regions away from the centers of the deposition. The columnar-type part of the films are not continuous, but have “cracks” of 0.5-1.0\(\mu\)m running through the surfaces. The sizes of each separated “grain” was observed to vary in size. Each “grain” appears to consist of many smaller grains or particles growing in a columnar-type structure. It is not truly a columnar structure, but most likely a built-up of overlapping grains or particles and new grains growing on top of the overlapping grains (see Figure 3.5(d)). The average grain/particle size, in and near the center of deposition is \(\sim 0.8-1.0\mu\)m. This is large, compared to most other reported grain sizes of 0.1-0.5\(\mu\)m. There are no apparent facets on the grains, or they are too small to be resolved properly by the 25kV SEM. All deposited films showed similar morphologies, except for sample F0 whose surface had been ablated due to the closeness of the substrate and the electrodes.

### 3.4.2 Compositional Analysis

#### 3.4.2.1 Auger Spectroscopy

AES showed that the main elements found in the films are carbon with some nitrogen together with silicon and oxygen (see Figure 3.6). The binding energy for carbon, nitrogen, oxygen and silicon were observed at approximately 265eV, 380eV, 510eV and 1610eV respectively. The surface structure of the films were observed to be similar to the those observed using SEM. Figure 3.6 shows the morphology of the film surfaces as a function of distance from the centers of deposition. As with the previous observation, there did not appear to be any dependence of the morphology of the films on the deposition parameter (ie. electrode-substrate distance, discharge rate and applied voltage). Using the Fisons software, the atomic contents of the elements were calculated and some of the atomic concentrations were plotted as a function of distance from the center of deposition (ie. the position at which the tip of the carbon electrodes were placed) (see Figure 3.7). It was assumed that the deposition was radially uniform.

It was found that the carbon concentration initially decreases and then increases with increasing distance from the center of deposition, while the nitrogen concentration was found to increase and then decrease with increasing depth. This effect is due to the non-uniformity of the distribution of nitrogen in the plasma. The nitrogen would have most likely been “pushed” to be concentrated away from the center of deposition at each discharge, thus making the nitrogen concentration higher there than at the center. This concentration effect could also be observed in other films of various deposition parameters. The overall concentration of C was found to be higher than of N, independent of distance from center. There was, however, no observable co-relation between the
concentration and morphology of the surface. Figure 3.7(e) showed a very large concentration of N at a depth of 300-400Å. This large concentration could be due to a N bubble being trapped at that level.

The concentration of the elements were also found to vary with depth and also on the location of the area of interest. Since the films are composed predominantly of carbon, the depth scale was calibrated by using the literature value of the graphite sputtering rate under argon ion bombardment. Although this does not necessarily provide an accurate calibration of the depth scale, it was appropriate in this case since the atomic concentration as a function of depth plots was only used as a comparison of the general trend. The C contents was observed generally to be higher
than N content on the top few angstrom. The atomic concentration for C and N contents then remained approximately constant with depth for all regions close to the center of deposition, as shown in Figure 3.7(c) and (d). At the same time the Si concentration in the same regions was also observed to be very low. For areas away from the center of deposition, there was no observable trend in the C and N concentration ratio. In one case, there was an decrease in the concentration of C with depth (Figure 3.7(e)) while there was an increase in the C concentration (Figure 3.7(f)) in another case. Similar results were observed by Gurarie et al.\textsuperscript{[89]} The concentration of Si appear to increase with depth for regions away from the center of deposition. Figure 3.7 suggests that
the degree of spatial inhomogeneity is not correlated with the change of deposition parameters (ie. substrate-electrode distance and discharge rate) at least for the parameter range studied here.

By differentiating the Auger spectra (refer to Figure 3.8). It is not possible to conclude whether the differentiated spectra showed graphite signature or amorphous carbon signature due to the subtle differences between them, but it is definitely not a sp³ carbon signature. It is likely that there is a mixture of graphite and amorphous carbon present. The fine structures in the diamond signature are much more prominent than observed here (see for comparison Figure 3.2). It was observed that there did not appear to be a change in the fine structure as a function of depth. Varying electrodes and substrate distances also did not appear to cause any observable differences except for the film which was deposited using the closest electrode/substrate distance. The carbon signature was found to indicate a more amorphous type of carbon in this case. Overall, the carbon compounds that had formed are of the sp²-type of structure.

**3.4.2.2 RBS and PIXE**

All of the acquired RBS spectra were fitted using the RUMP program, and some are presented in Figures 3.9 and 3.10. The fitted atomic concentration are listed in Table 3.3. All simulated model has the SiO₂ substrate layer taken into account. There does not seem to be much change in the concentration with varying deposition conditions and location or position of the regions of interest. All the samples indicate a presence of 30-40% N and of 20-30% C when the spectra were
Figure 3.9: RBS spectra obtained, using 3.05MeV He\(^{++}\), from the sample which was placed at a distance of 3mm (F5) from the discharging electrodes. Some of the spectra were fitted using RUMP, and their results are tabulated in Table 3.3 together with the distance of the corresponding areas from the center of deposition.

![RBS spectra](image1)

Figure 3.10: RBS spectra obtained, using 3.05MeV He\(^{++}\), from the sample which was placed at a distance of 2mm (F1) from the discharging electrodes. Some of the spectra were fitted using RUMP, and their results are tabulated in Table 3.3.

![RBS spectra](image2)

collected in “spot” mode. This would produce a C:N ratio of 1:1 or at most 1:2. There appears to be a large concentration of Si (20-50\%) in the films. This is most likely due to deposition of Si from the ablation of SiO\(_2\). RBS had detected some O, and other impurities like Fe and Ca.
Table 3.3: Atomic concentration for the main elements found in the top layer of some of the CN$_x$ films, obtained from fitting of the RBS spectra with RUMP. The concentration of the elements were obtained by initially specifying the concentration of the second layer (the SiO$_2$ substrate with Fe and Ca impurities), and then varying the concentration of the first layer till the simulated data fitted the experimental data. See Section 3.3.2 for more detail.

The Fe and Ca impurities are most likely contributed by the substrates, indicating the impurity of the SiO$_2$ substrates. Spectra collected in the “scan” mode, on the other hand, showed more variation in the elemental contents. However, the variation in the concentrations do not follow any observable trend. Analysis via elemental mapping of the spectra, as shown in Figure 3.11, indicate that the films were deposited almost homogeneously, for the scanned areas studied. Scan sizes of 1000x1000$\mu$m were performed. The elemental maps also showed that Si and O appeared to be deposited homogeneously together with the (CN)$_x$ films (although in smaller amounts than C or N). Si and O could have formed a complex phase with C and N. They could also be due to the detection of the quartz substrate where the observed top (CN)$_x$ film is thin or when more energetic particles like protons are used as the incident ion. In some regions, Si was detected in restricted areas whereas C, N and O were still found to be distributed homogeneously. The observed O is then due to some form of contaminant originating from the nitrogen source or upon exposure to the atmosphere.

The PIXE data observed in the study showed that trace elements like Ca, Fe, Co, Ar and Cu are present in the samples (see Figure 3.12). Ag peaks were also observed in one sample, due to the Ag paste being used to increase the conductivity of the highly resistive substrates. The quartz substrate would be the most likely source of for the other impurities. Elemental mapping of PIXE (see Figure 3.13(b)) spectra shows that most of the impurities and Si were found to be distributed within the deposited film (see spectrum “B”) while Ag was found to be accumulated outside the deposited film regions (see spectrum “C”). Figure 3.13(a) showed that the RBS spectrum extracted
Figure 3.11: RBS elemental mapping for the sample F1, with d=2mm and 7 discharges/min. Each of the elemental maps shows the density distribution of the different elements as stated in the figures (C, N, O, Si and Fe). The spectrum was obtained using (a) 1 MeV He$^{++}$ particles and (b) 3.08 MeV H$^+$ particles. The percentage scale of the concentration elements are also presented. Scale used is 1.5cm:1000μm.

from the region of interest also indicated the presence of C, N and O, as shown in spectrum “B” in Figure 3.13(a). However, impurities like Si and Fe were not observed at all in the deposited films. The RBS spectra extracted from outside the deposited films area of interest only showed Si edge, with no detectable O edge (see spectrum “C” in Figure 3.13(a)). This indicates that Si may have been redeposited on to the sample. The quartz substrate would have been ablated and decomposed during deposition due to the high pressure and discharges from the electrodes,
Figure 3.12: PIXE spectra obtained from various areas of the (CN)$_x$ films in samples (a) F1 and (b) F4 using 3MeV protons. The spectra appear to be independent of the sampling area.

Figure 3.13: (a) RBS and (b) PIXE region mapping using 3MeV protons. The spectra shown are obtained from selected regions in the scanned maps. Spectra B were extracted from the “purple” regions and spectra C were from the “green”regions, with the overall spectra presented as A.
allowing redeposition of Si back on to the sample. The original scan from the area (ie. when no extraction has been performed) is shown as spectrum “A”.

From the gathered AES, RBS and PIXE data discussed above, it can be seen that while AES is very surface sensitive, both RBS and PIXE are not as sensitive. AES results showed a larger variance in C and N content as a function of position while RBS and PIXE appear to show a smaller one. It is very difficult to elucidate the structure of the films because of this spatial and depth inhomogeneity, the data obtained being dependent on the analysis method being utilized.

### 3.4.3 Structural Analysis

#### 3.4.3.1 XPS

Figure 3.14: XPS survey spectra, with the deposited films parameters and location of the survey as listed. The distance between substrate and electrodes and the total number of discharges were kept constant for all spectra, while varying the number of discharges/min.

XPS survey scans presented in Figure 3.14 corresponding to various (CN)$_x$ films grown under conditions where the deposition rates were varied (varying total deposition time) with the total discharge and the distance between the electrodes and substrates kept constant. The main struc-
Figure 3.15: Examples of fitted XPS peaks with Voigt-type functions for (a) carbon, (b) nitrogen, (c) oxygen and (d) silicon.

...
Table 3.4: Fitted XPS parameters for the N and C peaks, together with some possible bonding states for the various samples. The references are taken from: (1) Woo et al. [91], (2) Ricci et al. [72], (3) Diani et al. [92], (4) Holloway et al. [93] and (5) Little et al. [94] and (6) Rossi et al. [83]. The C=N bonding states may include the C≡N states too. The SiNₓ bonding state has been assigned to a silicon nitride phase, while the the C-N peak has been attributed to the C₃N₄ phase by their respective authors.

Both the XPS C and N peaks could be fitted with 3 peaks while the Si and O peaks with only 2. The fitted parameters are listed in Table 3.4, with their possible bonding structures or states. The FWHM values appear to be very large, more than 3eV in some cases. This could be attributed to local disorder in the bonding states or there may be a convolution of several more peaks. The assigned C-N bond (attributed to C₃N₄ structure) could, however, also match well with the peaks fitted from nitrogen plasma enhanced polyimide [90]. The main phases which would most likely contribute to the XPS spectra are silicon nitride, SiC, graphite, oxygen contaminants and different phases of CN. Several of the peaks could not be assigned as yet.

The peaks assigned to SiC, SiNₓ and graphite can be observed in all the spectra collected, regard-
less of the deposition conditions. However, the peak assigned to SiC by Woo et al. (283.37eV) was assigned to C≡N by Ricci et al. (283.6eV). Due to the slight charging of the films and uncertainty in fitting of the peaks, it is difficult to be accurate in our values. The contributions from the CN bonding states however, were found to vary from sample to sample with no observable correlation between their presence, positions and the deposition conditions. It must be noted that charging of the samples may have caused some shifting of the peaks. Many authors have attributed the 398-399eV peak to the C≡N bonding state\[^{82, 93, 95}\]. However, not all the 398-399eV peaks have been assigned as such in this study due to the fact that the corresponding 286-288eV peak of the C 1s peak which is related to the covalent C-N structure of C≡N\[^{91, 93, 96}\] was not observed at the same time. Similar criteria has also been taken when assigning the other peaks. A crucial point to note is that while the Auger spectra are spatially selective, the XPS data are not and have been collected over a very wide range of compositions and morphologies. Hence, it would not be surprising that the measured FWHM values were found to be large and that there is a mixture of bondings present.

### 3.4.3.2 Raman Spectroscopy

Raman spectra were obtained from the samples which were grown with differing electrodes-substrate distances, \(d\). The sample which had the smallest distance between electrodes and substrate (1mm) appear to produce only a:C type of spectra ie. very clear D and G peaks at 1360cm\(^{-1}\) and 1590cm\(^{-1}\) (see Figure 3.16(a)), together with a slight broad peak at \(\sim\)620cm\(^{-1}\). The Raman spectra obtained from the samples which were grown further from the electrodes were observed to be slightly different. The D and G peaks were observed, as expected, with additional peaks at 183, 206, 226, 303, \(~\)520, 615, 798, \(~\)930 and 962 cm\(^{-1}\). Both the 930cm\(^{-1}\) and 960cm\(^{-1}\) peaks are broad and they overlap to form a twin band.

The triplet 183, 206 and 226cm\(^{-1}\) together with the 930cm\(^{-1}\) peaks have been observed in the Si\(_3\)N\(_4\) sample, as presented in Figure 3.16(d). The sharpness of the triplet peaks indicates that these lines arise from well-defined crystalline material. However, there was no evidence of these Si\(_3\)N\(_4\) peaks in the sample with \(d=5\)mm. The 520cm\(^{-1}\) peak has been attributed to the presence of crystalline Si, while the \(\sim\)800cm\(^{-1}\) peak has been attributed to cubic SiC\[^{97}\]. The observation of crystalline Si peak in some of the Raman spectra supports the PIXE data discussed previously, ie. regarding the deposition of Si onto the films. Since the 962cm\(^{-1}\) was observed only in the presence of the 930cm\(^{-1}\) peak, the former peak is then also attributed to Si\(_3\)N\(_4\). Only two peaks, 302cm\(^{-1}\) and 615-620cm\(^{-1}\), have yet to be assigned. Ricci et al.\[^{72}\] had suggested that C≡N has stretching modes around 1600cm\(^{-1}\) while C-N modes around 1440cm\(^{-1}\). The spectra showed that the presence of the triplet peaks were not observed in all areas, suggesting that the films are not homogeneous. On the other hand, elemental mapping with RBS had suggested homogeneity in
Figure 3.16: Raman spectra taken from various areas for the (CN)$_x$ films obtained using (a) d=1mm and (b) d=2mm (c) d=5mm as the separation between the electrodes and substrate, taken at various distances from the center of deposition. (d) is a Si$_3$N$_4$ spectrum.

However, RBS results are most likely highly averaged out due to the size of the probing beam (5-10 times larger), resulting in a more homogeneous distribution.

Raman spectra were collected as a function of distance from center of deposition for two of the samples (presented in Figure 3.17). It can be observed that the normalized intensities of the D and G peaks (normalizing to the Si peak) decrease with increasing distance from the center of deposition. The intensity of the D peak appeared to be larger than the G peak in all cases. The FWHM of both peaks did not appear to change with distance. Also present in the spectra is a slight shoulder in the G peak at $\sim$1610cm$^{-1}$ (D’ peak). This peak, like the D peak, corresponds to local maxima in the phonon density of states of graphite. Breakdown in the ordering and lost in the long-range translational symmetry leads to the relaxation of the k=0 selection rule for Raman spectroscopy and phonons with non-zero k vectors contributing to the spectrum, leading to the observation of the D and D’ peaks. The presence of D and G peaks indicates that there is disordered graphitic material in the film. However, since the D’ peak could be resolved from the G peak, the disorder is not extensive, ie. there still exists some long-range symmetry. The D peaks were fitted with a Lorentzian curve while the G peaks were fitted with the asymmetric BWF line.
shape as stated in Equation 2.10. The fitted parameters are listed in Table 3.5.

From Table 3.5, the FWHM values of both peaks did not appear to vary much with distance from center of deposition. However, there is a slight difference between the two sets of results. The sample which was deposited with d=5mm have narrower FWHM for both D and G peaks when compared with the set with electrode-substrate distance d=2mm. The D’ peak also appear to be more resolved from the G peak in this set of data. This indicate that the disorder in the film is less when the substrate was placed further away from the electrodes when depositing. The $I_D/I_G$ ratios was also observed to decrease with distance from center of deposition. It has been shown

![Graph](image_url)

Figure 3.17: Raman spectra as a function of distance from center of deposition, for (a) d=2mm (F1) and (b) d=5mm (F2). The distance increases from the center of deposition in the direction of the arrows. Some of the spectra shows the triplet Si$_3$N$_4$ peaks at 183, 206 and 226cm$^{-1}$. 

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Table 3.5: Lorentzian and BWF fits for the D and G peaks of the (CN)\textsubscript{x} films. The first set of results was obtained from the sample deposited at 2mm (F1) from electrodes while the second set at 5mm (F2) from the electrodes. FWHM/q is the coupling parameter which measures in-plane graphitic order. The D’ peak was observed in almost all of the spectra.

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that the ID/IG ratio is inversely proportional to the in-plane crystalline size (L\textsubscript{a}) for disordered graphite \cite{98} over the L\textsubscript{a} range of 2.5-300nm for laser wavelengths of 514.5nm\cite{99}. However, Mc-Culloch et al.\cite{100} has suggested that for highly disordered graphitic materials with L\textsubscript{a} < 2.5nm, a decrease in the ID/IG ratio represent a further increase in disorder in the system. This is a more acceptable explanation for this case. Towards the periphery of the deposition, the conditions for deposition is less optimum than in the center leading to a more amorphous/disordered type of film being formed. The FWHM/q values are smaller for the sample with d=5mm, but still do not approach zero. From all the observations made, it can be concluded that the (CN)\textsubscript{x} films studied do not possess or possess very little ordering in their structures. If the crystalline form of CsN\textsubscript{v} exists in these films, it will exist in very small amounts, and very randomly scattered among the more amorphous carbon nitride, silicon nitride and a:C environment.

3.4.3.3 EELS

The energy resolution (ie. FWHM of the zero-loss peak) for these spectra was 3-4eV. EELS spectra obtained from the samples showed that the (CN)\textsubscript{x} films are mainly spatially inhomogeneous on the micron scale. Some selected spectra which were commonly observed are presented in Figure 3.18. Carbon, most likely in the form of graphite, was detected in most regions observed while nitrogen and silicon were detected in some. The regions show varying ratios of these elements, with no trends observable at all. Carbon was detected in its sp\textsuperscript{2} form, with a slight π-peak (287-288eV) in
Figure 3.18: EELS spectra for the (CN)$_x$ films taken from various regions. C and N were observed in some regions, while other regions appear to show the presence of impurities including (SiN)$_x$. The corresponding core-loss spectra are shown inset. The arrow in (a) indicates the presence of the $M_{2,3}$ Fe edge.
most areas, and the low-loss peak at 23-25eV. Surface plasmon peak was not observed in the low loss energy spectra. The density of the films (using Eq 2.9) ranges from 1.71-2.02g/cm³.

The N core-loss peak also appeared to indicate a slight π* structure at ~400eV in the N edge. According to Bursill et al [77], this implies a trigonally-bonded structure which is consistent with the tetrahedrally-bonded hexagonal β-C₃N₄ (see Figure 3.1). However, although this structure has planar trigonally-bonded N this does not necessarily mean that there is π-bonding. It has been stated that three of N’s five electrons form sigma bonds with three carbon neighbours and the two remaining electrons are thought to form a lone pair [65], with no π-bonding. Moreover, tetrahedrally bonded β-Si₃N₄, whose structure C₃N₄ is based on, does not show any π-peak in its N K-edge.

There were also other elements detected in the presence of C and N, Si and O being the most frequently observed elements, with the Si L₃-edge at 100eV and the O K-edge at 532eV. There may be some complex forms of C, N and Si in the films. In some regions, (SiN)₅ compound was detected, and the SAD from such regions confirmed that there is Si₃N₄ present (see next section). Assuming a (CN)₅ compound, the ratios of C:N were found to vary from as little as 1:1 to as much as 6:1. There were a few EELS spectra which indicated the presence of an edge at ~58eV attributed to Fe M{₅ and also the presence of CaCO₃ low-loss peak and L- and M-edges (350eV and 35eV respectively). Both Fe and Ca were also detected in RBS and PIXE.

3.4.3.4 TEM and Diffraction

The films were found to be mainly in amorphous form, with few crystalline regions. Diffraction patterns show that the main contribution to the presence of polycrystalline structures are SiC and Si₃N₄. Amorphous carbon/graphitic diffraction rings were the most common diffraction observed while polycrystalline type patterns were also observed. Some of the diffraction patterns are presented in Figure 3.19 and the results tabulated in Table 3.6 and 3.7. See Appendix B.3.2 for more diffraction patterns. It appears that the deposited films may likely comprise mixtures of cubic SiC, graphite, C₃N₄ and Si₃N₄ components. However, i-C also seemed to fit in well with the measured data. Moreover, different phases of C₃N₄ may also be present together. Both the hexagonal β-C₃N₄ (a=6.43Å and c=2.46Å, space group P3) and the zinc-blend-like cubic (a=3.43Å, space group P43m) structures could be present in the deposited films. There are one or two diffraction rings which could not be indexed to any of the expected phases. All possible phases, such as CaC₂, SiO₂ and hexagonal SiC were considered when identifying the rings.

Tiny single-crystal regions were also observed. Their results are presented in Table 3.8. Studies of different regions and different samples produced some SAD patterns which were not found to be consistent with any obvious structures. This indicates that there may exist some complex single-crystal structural phase/phases which has yet to be identified. In all regions studied, there
Figure 3.19: Some of the diffraction patterns obtained from the (CN)$_x$ films. The single-crystal diffraction patterns (with their respective zones as shown) were indexed to $\alpha$-C$_3$N$_4$ phase. More diffraction patterns are presented in Figure B.10.

only seemed to be a few regions which appear to indicate the presence of crystalline C$_3$N$_4$. As like the polycrystalline regions, there appears to be more than one phase of C$_3$N$_4$ present. Besides the $\beta$-phase, a phase corresponding to the predicted $\alpha$-C$_3$N$_4$ ($a=6.4665\text{Å}$ and $c=4.7097\text{Å}$) may also have been observed in some regions. Crystalline phases such as SiC ($a=4.36\text{Å}$) and NaCl ($a=5.64\text{Å}$) were also commonly observed. The interplanar angles for all the planes for each of the identified phase match well with the measured/experimental angles. Most regions which exhibited polycrystalline or single-crystal patterns were very sensitive to electron beam damage, making it not possible to obtain any HRTEM images of the areas. The observation of C$_3$N$_4$ phases and of other impurities like SiC and Si$_3$N$_4$, and also the crystallinity of the C$_3$N$_4$ phases appear to be present for all the samples regardless of the deposition conditions. Therefore, varying the deposition conditions appear only to have influence on the morphology of the films, but no overall
Table 3.6: d-spacings of diffraction patterns from samples F1 and F0, and some reference data. The d-spacings of $i$-carbon were calculated with $a=4.25\ \text{Å}$ [52]. $d_{\text{graphite}}$, $d_{\text{Si}}$, and $d_{\text{SiC}}$ are obtained from the listed ASTM tables. The $\beta$-$C_3N_4$ is of hexagonal structure with $a=6.43\ \text{Å}$, $c=2.46\ \text{Å}$, while the $C_3N_4$ d-spacings were based on the theoretical zinc-blend-like type cubic structure with $a=3.43\ \text{Å}$.

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<td>1.16</td>
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<td>1.05</td>
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<tr>
<td>0.94</td>
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<td>0.962</td>
<td>0.99</td>
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</table>

Almost all the regions observed indicates that amorphous nature is predominant in the films. It was not possible to obtain HRTEM images from any the regions due to the instability of the films. Amorphization of the crystalline regions was found to occur very quickly. The degradation of the films is most likely a contribution to the absence of sp$^3$ carbon edge in the EELS spectra.
Table 3.7: Examples of d-spacings of the diffraction patterns from samples F0 and F4, with some reference data. The d-spacings of i-carbon were calculated with $a=4.25\,\text{Å}$. $d_{\text{Si}t}$, $d_{\text{SiC}}$, and $d_{\text{graphite}}$ are obtained from the listed ASTM tables. The Si$_3$N$_4$ d-spacings were calculated from the $\beta$ phase, with $a=7.607\,\text{Å}$, $c=2.911\,\text{Å}$, while the C$_3$N$_4$ d-spacings were based on the theoretical zinc-blend-like type cubic structure with $a=3.43\,\text{Å}$.

### 3.5 Discussion

From the various methods used to deposit the (CN)$_x$ films, it was found that, for the same total number of discharges, the distance between the electrodes and substrate of $d=2$ to $3\,\text{mm}$ would produce the least ablation of the substrate and a thicker ($10-15\,\mu\text{m}$) film. The deposited films also has a larger area of film with a “smoother” surface morphology. With $d=5\,\text{mm}$, the thickness of the
Table 3.8: Possible identification for some single-crystal diffraction patterns and their corresponding EELS results. Some of the diffraction patterns could not be indexed properly.
film was found to be \( \sim 5 \mu m \) only. Assuming an uniform film deposition, AES results showed that the atomic concentration of C on the surface was found to increase with increasing distance from the center of deposition, while the concentration of N decreased simultaneously. Near the center of deposition the concentration of C and N were found to remain almost constant with depth while at the peripheral of the films, the concentration of C and N did not appear to have a general trend as a function of depth. It must be remembered that depth-profiling introduces distortions in the collected spectra mainly due to sputtering-induced topographical and compositional changes of the sample surface. This will broaden the measured profile. Preferential sputtering of one element over another may also occur, consequently misleading results will occur.

The electron beam in AES has been found to induce desorption of oxygen \[^{101, 102}\]. This can lead to enhanced sputtering on the area. Desorption of O will then also result in a lower detected concentration of O in further analysis with other methods. XPS results support the fact that surface concentration of N is higher around the center of deposition than at the periphery. Fitting of the XPS peaks with Voigt-type functions appears to indicate the presence of some \((CN)_x\) phases together with \((SiN)_x\), C=O, N=O, C-C and Si-C bonding states. AES results indicate a C concentration of 60-90\% and 5-40\% for N. However, RBS appears to indicate a 20-40\% C content and 30-40\% N content. This discrepancy could be due to systematic error while analyzing the data. The concentration of O in general appeared to be lower than expected for SiO\(_2\). This could be due to desorption of O during AES depth-profiling.

Furthermore, RBS has detected a higher concentration of Si and O, while very little of Si and O were observed in the AES spectra due to the fact that most of the RBS spectra were collected from both the film and substrate layers. Using TRIM simulation (and referring to Figures 3.9 and 3.10), 2MeV particles will have penetrated into 5.4±0.1\(\mu m\) of \((CN)_x\) film, assuming the density of the film is close to that of graphite since graphite appears to be the dominant phase present. The deposited films would be \(\sim 15\mu m\) thick (see SEM results) away from any ablated or peripheral regions. Therefore, the substrate material should not be detected when the spectra are taken from the “thick” film region. Hence, the detection of large concentrations of Si is most probably not due to the substrate. While depth profiling was performed for the AES, the maximum depth studied was only 2000\(\AA\), considerably shallower than the thickness of the films, and so would not have detected the substrate. 1MeV alpha particles would have only penetrated to a depth of 2.6±0.1\(\mu m\).

However, 3MeV protons would have gone through at least 74.4±1.4\(\mu m\) of the film, ie would have penetrated through the film and into the substrate. In this case, a lot more O would be observed together with Si, and very little N or C, and this was indeed found to be the case. Only one region which was analyzed using 3MeV proton particles showed a large concentration N and Si, with little or no C and O (see Figure 3.11). Due to the fact that little O was observed here the most likely phase present is some form of \((SiN)_x\) compound, probably \(Si_3N_4\). It can be concluded that the RBS spectra obtained using 1 and 2MeV alpha particles is most likely due to the deposited
(CN)$_x$ films only while 3MeV protons would yield results from the film together with that from the substrate. It must be noted that the presence of voids, holes and cracks in the films will complicate the analysis of the RBS data.

The spatial/lateral resolution using AES technique is $\leq 1\mu$m and a depth resolution of $\approx 1$nm (or more, due to sputtering) while RBS has lateral and depth resolutions of 1-10$\mu$m and 20-40nm respectively. This suggests that while RBS produces a more “averaged” elemental concentration, it is less sensitive to surface roughness. Since the roughness or features are in the order of the resolution or smaller ($\sim 1-15\mu$m), the features would appear more “smeared (averaged) out”, hence a lower concentration of the elements. Elemental mapping under such conditions would not produce high lateral resolution maps and the distribution of the elements will not be correctly mapped. Due to the low depth resolution of the RBS system and the thickness of the CN$_x$ films being in the same order or smaller, the spectra would contain information from both the film and substrate layer making the analysis of the spectra more difficult. The big discrepancy is the fact that elemental mapping with RBS showed that both C and N were homogeneously distributed, while the atomic concentration found in the AES and also RBS spectra indicated otherwise. There was a 10-30% difference in the atomic concentration, depending on the location of the area of interest and the analytical tool used.

Deconvolution of the measured RBS spectra will be required with respect to the sampling or information depth and involves a prior knowledge or estimate of the composition of the layers below. It was assumed in this analysis that the second layer consist mainly of the quartz substrate and some impurities like Fe and Ca. However, there is certain to have some form of SiC and Si$_x$N$_{1-x}$ compound in that layer too. Due to the uncertainty in attributing the relative quantity of these compounds in the films, quantitative content of C and N is difficult to be determined exactly. Having a lower depth resolution would also “average” the elemental concentration more since the volume studied would be larger. AES, whose lateral resolution being smaller than the size of the features, is more dependent on the contours and locations. However, this technique would then produce results from very localized areas and would not give a “true” picture of the films. On the other hand, such high lateral resolution means that the AES analysis would produce a high spatial resolution maps. Depth profiling will also provide a depth-resolved map of the elements for comparison. From the spatial resolution factor, it would not be surprising that RBS produce a much lower atomic concentration of the C and N elements than AES since the RBS spatial resolution is much lower. However, the detection of large concentrations of Si (compared with AES results) cannot be explained.

Raman spectra indicate that the intensities of the D and G peaks decrease towards the periphery of the films. The Raman spectra shown in Figure 3.16 have been normalized with the aid of the Si peak for more accurate comparison of the intensity or yield of the carbon peaks. It must be pointed out that the size of the laser spot is only $1\mu$m in diameter, smaller than the lateral resolution of
RBS. This would mean that the Raman spectra, similar to AES, reflect very local results. However, the general trend of the C concentration with distance seemed to hold for both the samples studied. Both the D and G peaks were observed in all the regions, and they closely resemble those observed in diamond-like carbon (DLC). Both the D and G peaks appear to be rather sharp and narrow, indicating some sort of ordering in the structures. Due to the polycrystalline nature of most of the diffraction patterns, the ordering would be short range. The presence of Si$_3$N$_4$ was confirmed with the observation of the triplet peaks at 182.7, 206.4 and 225.9 cm$^{-1}$ in several regions.

Because of the intensity of the D and G peaks, it would not be surprising that the main features shown in the diffraction patterns would be of graphitic nature. Most regions were observed to show an amorphous nature, with diffuse diffraction rings. However, polycrystalline-type of rings and single-crystal Bragg’s spots were also observed. The main contributions to the polycrystalline rings appear to be C$_3$N$_4$, β-Si$_3$N$_4$, SiC, graphite and even the i-C phase which had been mentioned earlier in Chapter 2. The C$_3$N$_4$ appear to consist of different phases, both β and zinc-blend-like cubic phases were observed. The β phase is consistent with the one predicted by Liu and Cohen [65] and has been observed by many authors. The cubic phase which had been predicted by Liu and Wentzcovitch [64], however was not (as far as this author can tell) found to be reported previously. It must be noted that this phase, observed in polycrystalline form, was found mainly to co-exist with the β-C$_3$N$_4$ phase. This makes its proper identification difficult to confirm. The diffraction patterns obtained all show a mixture of different phases. This created extra difficulties in identifying the actual phases present.

Once again, most of the crystalline regions appear to consist of several different phases intergrown together, making proper identification difficult. The main contribution to the single-crystal patterns is SiC, with a few regions exhibiting β-Si$_3$N$_4$ phase and fewer more still may be with C$_3$N$_4$ phase. Again, different phases of C$_3$N$_4$ (β and α) appear to be present. The α phase, with $a=6.4665\,$Å and $c=4.7097\,$Å[79] and of space group P31c, had been also observed by Wang et al. [78]. On top of that there were a few SAD patterns which were not consistent with any of the previously observed structures, implying that there could still exists more complex structures of (CN)$_x$ or even CN$_x$Si$_y$. There was also one diffraction pattern which had spot spacings, interplanar angles and axial ratio which corresponds to a FCC structure with lattice parameter $a=6.5\,$Å, similar to the FCC phase observed by Bursill et al. [77] ($a=6.3\,$Å). However, no further evidence of such phase was made in any other areas.

It is interesting to note that most of the areas with EELS spectra which indicate the presence of N and C produced diffraction patterns which were consistent with a graphitic or amorphous carbon phase. Furthermore, EELS results show a much lower nitrogen concentration than expected for C$_3$N$_4$ phases. However, this could be due to the fact that the EELS probe size may be large enough to sample simultaneously regions of nanocrystallite C$_3$N$_4$ and amorphous carbon, and hence reducing the overall percentage of N detected. However, care had been taken to ensure
regions of interest were at the center of the field of view for all spectra and diffraction patterns taken. There were a few of these areas which produced polycrystalline/single-crystal diffraction, some of which could still not be identified properly. As presented in Table 3.7, the EELS results do not appear to match well with the diffraction results. This could be due to the different probe sizes of the different techniques. A selected area size of 40-55µm (at 100K magnification) was normally used to obtain the SAD patterns while no selected area aperture was used at all when collecting the EELS spectra with an objective aperture of 30µm (at 100K magnification) and a 2-3mm aperture at the EELS spectrometer in place.

Both the C and N edges in the EELS spectra exhibit a slight π* edge. A π*—π* plasmon peak was observed at ~5-8eV in some regions, indicating little sp³-type C bonding present. On the other hand, the π* for C is less pronounced in most cases, than for pure sp² bonding (glassy-carbon or graphite (see Figure 2.2)). This indicate that there may be a very low concentration of sp³ sites present. However, the fine structures in the differentated AES spectra for the carbon peak is still very similar to that of graphite. The C plasmon peak was found to vary between 23-25eV. Using the Eq 2.9, the local mass density of the films were found to be 1.71-2.02g/cm³. Graphite has a density of 2.26g/cm³ while diamond is 3.52g/cm³ and diamondlike carbon is 1.5-2g/cm³.

### 3.6 Conclusion

There does not seem to be any observable co-relation between the yield or concentration of the elements and the deposition conditions for the films studied using all those techniques used. However, there seemed to be a co-relation between elemental concentration of the film and the position from the center of deposition, regardless of initial deposition conditions. The film morphology appears to be smoother and less ablation occurs when the substrate was placed further away from the electrodes, at least from a distance of 2mm to 5mm. However, the thickness of the deposited film were still observed to vary slightly, even for this small change in electrode-substrate distance.

The deposited films were shown to be quite inhomogeneous as the diffraction patterns, EELS spectra, AES spectra and XPS spectra results depend on the region of interest. On the other hand, elemental mapping with RBS appear to indicate otherwise. It may be argued that the RBS spectra are dominated by the substrate contribution, and hence not accurate. However, homogeneity of the films were observed even for spectra which were collected using alpha particles which would not have penetrated into the substrate regions. The concentration of the elements was also found to vary with the techniques used. Different size probes (beam spot size) and sensitivity (lateral resolution) are the only plausible explanations so far for the differences.

Although the main composition of the deposited films were found to be SiC and amorphous carbon, there were regions which showed evidence of C₃N₄ being present. It appears that the films
are most likely composed of a mixture of SiC, amorphous carbon, $\beta$-Si$_3$N$_4$ and different phases of C$_3$N$_4$, together with some CaCO$_3$ and some form of Fe and also O contaminant. The presence of these additional phases/elements (Ca, Fe and O) were confirmed in all the techniques used. Hence, the contaminants are from the films and not introduced during the analysis. They would most likely be introduced from the carbon rods during the deposition or from the impure quartz substrates. Similar contaminations were also observed by Bursill et al. [77] in their films, which had been prepared in the same apparatus. There is some evidence that the C$_3$N$_4$ phases observed here are the predicted $\beta$, $\alpha$ and even the zinc-blend-type cubic phase. There were also some diffraction patterns which could not be identified to any known or expected phase, indicating the existence of some complex structure. It must be remembered that a considerable amount of amorphous (CN)$_x$ would most likely exist in the deposited films.

Although the diffraction data from this study and from many others appear to be consistent with the theoretical prediction of the hexagonal ($\beta$ and $\alpha$) and cubic C$_3$N$_4$ structure, it is important to point out that the overall N stoichiometry has been found to be much less than expected for C$_3$N$_4$ in most cases. Moreover, the percentage of crystalline phase within the films is very low. Especially worrying is the fact that the EELS results taken from similar regions as the diffraction patterns showed a much lower N concentration of 20-50% only. However, as discussed in the previous section, the EELS probe size and hence the sampling area may be the cause in the discrepancy. Because all forms of C$_3$N$_4$ have been calculated to be metastable, it is not surprising then to find many other forms of (CN)$_x$ in the films independent of the method of deposition or growth. Given the inhomogeneous nature of the (CN)$_x$ films studied here, and the fact that the samples were scraped off the substrate it is not surprising that the diffraction data showed such a range possible structures. The C-N multiple bonds could arise from C=\ce{N} and C≡\ce{N}. Depending on the substrate and precursors used, other impurities could be Si$_3$N$_4$, SiN$_x$, CN$_x$, CN$_x$H$_y$ and CN$_x$Si$_y$.

Although the different techniques seemed to be somewhat inconsistent with each other, the general trend showed that the main carbon phase present is of the sp$^2$-type. If sp$^3$-type of carbon exists, it will be in very isolated and tiny regions. In conclusion, it was found that varying the deposition conditions appear to have only influenced the morphology of the films, with no overall apparent change in the chemical effects of the films. Since the structure of $\beta$-C$_3$N$_4$ compound has been based on the $\beta$-Si$_3$N$_4$, a thorough study on Si$_3$N$_4$ could assist in understanding the possible properties of the hypothetical C$_3$N$_4$. However, it must be noted that Si$_3$N$_4$ is difficult to study due to its complex crystal structure and its sensitivity to impurities and other effects related to sample processing.
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