Chapter 5

CONCLUSION

5.1 Summary

To summarize the results drawn from the studies of carbon materials:

- Raman spectroscopy indicates the presence of point defects in irradiated diamond. This defect appears as a peak at 1630 cm\(^{-1}\) when single crystal diamond has been irradiated with low doses of low to medium energy ions. The peak begins to disappear when the dose is above \(1 \times 10^{14}\) for 300 keV Xe ions.

- There appears to be a linear relationship between the FWHM of the ESR signal and \(T^{-1/4}\). This implies a variable-range hopping type of conductivity is dominant, where conducting pathways are formed between small graphitic islands. The conducting pathways are thought to be formed from clusters of defects around each ion track.

- HRTEM results do however, support such a theory, as no ion tracks nor graphitic clusters were observed at all. If the clusters do exist, they would be much smaller than the predicted size of 20 Å by Prawer et al. \(^4\) and therefore could not be resolved properly. However, irregularly shaped and distributed amorphous regions (of \(sp^3\) and \(sp^2\) nature), were observed from the dose of \(3 \times 10^{13}\) and above.

- Both EELS spectroscopy and diffraction patterns also support the fact that the diamond remained partially intact, even at quite high doses. The EELS results did not show any particular trend in its fine features in relation to the dose. Both \(sp^3\) and \(sp^2\) features were observed in all the irradiated samples, with no observable evidence of graphite.

- The \((CN)_x\) films were found to be unstable and were mainly amorphous. The small crystalline regions that exist in the films were mainly polycrystalline in nature with very few single-crystalline areas. The main contribution to the crystalline phases was SiC while the amorphous phase was due to graphite or amorphous carbon. \(Si_3N_4\) and, most probably, \(C_3N_4\) were found only in few areas. \(Si_3N_4\) was found in the \(\beta\)-phase while \(C_3N_4\) appeared to have formed in the \(\beta, \alpha\) and even cubic phases.
- Elemental composition or the concentration of the elements obtained from different techniques were also found not to agree with one another. AES spectra appear to indicate a higher percentage of carbon and nitrogen to be present, compared to other techniques used in our study. On the other hand, RBS spectra showed a much higher percentage of Si and O present due to the substrate, with little carbon and nitrogen. EELS also indicated only few areas which showed the presence of N and C together, with C the main element detected. Diffraction patterns obtained, however, do indicate the presence of C$_3$N$_4$ in some regions.

- Even with implantation energy in the MeV range, co-relationship between various methods of analysis was not possible. While Raman was consistently showing the presence of the sp$^3$-type point defects, both EELS and diffraction showed the presence of only diamond and/or $i$-C. The discrepancy highlights the different detection sensitivities and probe sizes.

- Clusters of sp$^3$ type of carbon have been found in quartz which have been irradiated with high doses of carbon and subsequently annealed. The presence sp$^3$ carbon has also been confirmed by EELS and SAD. SAD analysis appear also to indicate the presence of $i$-C within the quartz structure.

### 5.2 Conclusion

ESR results had strongly shown that variable range hopping type of electrical conductivity is dominant in irradiated diamond. A percolation or a gradual amorphization model had been previously used to explain such conductivity (see Chapter 2). In the percolation model, electrical conduction occurs via hopping between amorphous carbon or graphitic clusters. However, from the above TEM and diffraction summary, graphitized clusters were not observed at all. On the other hand, it has been shown that whilst irradiated diamond has remained partially intact even at high doses, damage to the tetrahedral structure produces irregularly shaped and inhomogeneously distributed amorphous sp$^2$ regions of short range order. But, unlike Si, no critical amorphization dose was observed for diamond. All these observations suggest that electrical conductivity will occur via hopping between the localized states from the defects which overlap to form an impurity band structure. It must be stressed that the conducting centers are found to be sp$^3$ and sp$^2$ in nature, and not graphitic. No graphite was detected at all with the analytical techniques used in this study. This is still consistent with the gradual amorphization model for conduction.

The most important fact that can be drawn from the studies of high energy implantation is that of the creation of $i$-C phase in the damaged diamond samples. This structure was observed also in the carbon nitride films and the carbon-irradiated quartz. However, regions which show such structure is most likely in the nm scale, and is therefore impossible to isolate them for further analysis. $i$-C is a cubic polycrystalline phase found embedded in amorphous diamondlike carbon films, together
with other phases such as chaoite and turbostratic carbon.

The study performed on the carbon nitride films is not conclusive. Different methods of study appear to yield different results. However, it can be broadly concluded that there appear to be evidence of small regions of polycrystalline $\beta$, $\alpha$ and cubic $C_3N_4$ inhomogeneously scattered in the amorphous carbon nitride films and among SiC, $Si_3N_4$, $SiN_x$, $CN_xH_y$ and $CN_xSi_y$. It is not surprising to have detected such a wide range of possible structures due to the inhomogeneity of the films. However, the definite presence of the various phases of $C_3N_4$ is still doubtful as the C:N concentration ratio found from the different analytical techniques is still far from the expected 3:4 ratio. Carbon was found to be mostly in $sp^2$ form, as indicated by the $1s - \pi^*$ peak at the leading edge of the EELS core-loss spectra. The nitrogen was also detected, with the $1s - \pi^*$ peak at the k-edge. Differentiated AES spectra of the carbon peak indicates a graphitic type of phase, ie. with a longer range order.

The carbon nitride films were found to produce inconsistent results. While RBS elemental mapping indicates homogeneous distribution of the elements independent of deposition conditions, AES and XPS spectra showed that the concentration of the elements are dependent on the position from the center of deposition. Electron diffraction patterns also seemed to indicate an inhomogeneous distribution of elements. All these inconsistency is most likely due to the spatial resolution, limit of detection sensitivity and the probe size factors. While RBS and PIXE have much better detection sensitivity, their lateral resolution is poor compared to that for AES or EELS techniques. And while the EELS technique has high detection sensitivity and lateral resolution, the probe size is at least 100nm. Electron diffraction technique has lateral resolution of around 10nm, but it is sensitive to long range ordering. Hence, it is not surprising then that the results obtained can not be co-related properly. To compound the problem further, the carbon nitride films, as mentioned earlier, were found to be very inhomogeneous (at least to nm scale). These two factors strongly influences the reason as to why there were not any observable change in any trend under various deposition conditions.

The fact that the EELS spectra were obtained using a probe of large size (even when the smallest probe spot is used) would then explain the big discrepancy between HRTEM images and diffraction patterns with EELS results. This fact is demonstrated again and again in this thesis. Both TEM and diffraction results were obtained with a smaller probe size than that used for EELS. Hence, co-relating between results is made difficult, if not impossible.

Many techniques have been used in this study to characterize in detail structures of implanted diamond, CN films and carbon-implanted quartz. However, the results from the methods employed did not appear to co-relate well with each other in most cases studied here, as explained in the previous paragraph. On the other hand, the presence of $i$-C phase appear to be consistently detected in the irradiated carbon forms, ie. in the lifted off diamond films, CN films and also in the carbon
implanted quartz.

### 5.3 Future Work

Whilst HRTEM has confirmed that ion tracks were not formed when diamond was irradiated with low doses of medium energy ions, the tracks could still form with high energy ions. Hence, Xe ions of 10MeV or higher (similar to the conditions for formation of ion tracks observed by other authors) may still produce the desired ion tracks. Although it has been confirmed that the ion tracks do not take part at all in conductivity activities, the understanding of the formation (if any) of such tracks will help in exploiting such tracks together with diamond’s electrical properties to produce some special electronic devices. On top of that, to address the problem of ion beam thinning damage to the samples, focused ion beam thinning technique may be a better approach than the conventional ion beam thinning technique.

A lower energy implantation may help to produce, without the aid of ion beam thinning, a much thinner lifted off diamond films having more electron transparent regions. While the lift-off technique has still to be perfected such that the top cap can be lifted off in a large very thin piece for cross-sectional analysis, the microstructure of the films due to high energy irradiation and subsequent annealing showed some interesting features. Further studies of such films would help to understand the formation of such “onion”-like layered structures. Cross-sectional studies of the lifted off films would be able to assist in identifying sp$^2$ and sp$^3$ regions. This could be done by sandwiching the lifted off film between Si and thinning it mechanically for TEM analysis. However, the film fragments are very brittle and small in size and this sample preparation will require much care and patience.

Because of the “destructive” nature of the high-energy plasma deposition method, where the substrates are ablated and then redeposited during deposition, another deposition method like CVD should be tried. Due to the high plasma shock pressure experienced by the substrates, only quartz glass could be used as substrates. However, the quartz glass observed in this study were found to contain impurities elements like Ca and Fe. Using methods like CVD, substrates such as Si or even pure quartz could be used as substrates. This would eliminate possibilities of impurities being incorporated into the deposited films. Furthermore, a more detailed study on the structural and chemical properties of Si$_3$N$_4$ would assist in the understanding of the formation of C$_3$N$_4$ films.

A more thorough study on the diamond nanocrystals formed in the fused quartz should be performed. HRTEM imaging has indicated the presence of some compound which has lattice separation of 7.5Å which has yet to be identified. Moreover migration of the nano-clusters, although expected, was found to be very large. Most of the clusters were found to have formed very close to the surface. A more detail study of the annealing and subsequent migration of carbon will have
to be undertaken.

As said previously, tiny regions of $i$-C phase was detected in the various forms of irradiated carbon. It is most likely formed in a mixture of sp$^2$ and sp$^3$-type of amorphous diamondlike carbon. This phase was observed in the heavily irradiated diamond and also in amongst nano-crystalline diamond. To understand the effects of ion irradiation on diamond or any form of carbon, it is of importance to study this phase in depth. This phase has only so far been observed in electron diffraction. It is difficult to co-relate this phase with ion irradiated defects formed in diamond/carbon due to the lack of ability to isolate such tiny areas. To further characterize such a phase a large enough region must be obtained so that Raman spectroscopy and EELS can be performed on it. Therefore, one of the challenges is to synthesize such a material.