Chapter 6

Conclusion

Outlined below is a summary of the results which bear upon the principal themes of this thesis.

6.1 Identification of crystalline carbon nitride

The unambiguous identification of crystalline carbon nitride remains ever elusive, as discussed at length in Chapters 1, 3 and 5. A higher degree of standardisation and a more rigorous approach to experimental analysis is required. For instance, any claim to have "found" crystalline carbon nitride should (for example) be accompanied by diffraction data which includes at least the first two Higher Order Laue Zones (HOLZ), and a comparison to a multislice calculation of the identified structure. While SEM crystal morphologies may be interesting, the presentation of some "semi-quantitative" data could be deemed almost misleading. As shown in the preceeding chapter, the use of EELS for microanalysis is a valuable tool both for quantitative elemental analysis and phase identification of solid carbon nitride.

6.2 Structure of $a-$C:N

In this thesis the experimental characterisation of carbon nitride has been described. Experimentally, I have analysed amorphous carbon nitride prepared by the techniques of cathodic arc deposition, nitrogen implantation into glassy carbon, reactively sputtered carbon nitride and plasma-assisted CVD. The analysis has shown that the structure of these materials is essentially identical. The $a-$C:N is predominantly sp^2 carbon bonded with the nitrogen atoms incorporated into the carbon network. The structure is similar to $a-$C but has a shorter average bond-length, and more ordering of graphitic sp^2-C:N planes. It is also proposed that the amount of nitrogen present in the amorphous carbon network reaches a saturation level for these deposition techniques caused by both the formation of N_2 and subsequent out-gassing and the limitation of only two nitrogen atoms per aromatic ring. A general structural model for $a-$C:N has been developed. It has been shown, that $a-$C:N deposited by several methods is essentially identical, with similar bonding environments for carbon and nitrogen atoms.

An investigation of the effects of annealing on the structure of cathodic arc deposited amorphous carbon nitride films showed that there was a significant portion of the nitrogen in loosely-bound states. No evidence for the presence of crystallites containing more nitrogen than the a-C:N matrix was found. Annealing the carbon nitride films results in the graphitisation of the film structure which drives nitrogen out of the network.

Ab initio molecular dynamics have been used to study the structure and bonding of amorphous carbon nitride at a range of densities and nitrogen concentrations. It was found that the most common form of nitrogen bonding was an uncharged pyramidal N_3^0 site. Addition of nitrogen causes a decrease in the sp^3 fraction of carbon, and this effect is most severe at high densities. Four fold coordination of nitrogen atoms were rare, with only one such site observed. This may explain the low doping efficiency of nitrogen in *ta*-C seen experimentally. At a low density of 2.00 g/cm^3 and 30 % nitrogen concentration, N_2 dimers were observed to form. A 2.45 g/cm^3 simulation showed clear planes at a 11 % nitrogen level.

The molecular dynamics simulation of the removal of electrons from the a-C:N networks showed that the structural changes caused could explain the two-state conductivity in ta-C:N memory devices.

ELNES calculated using multiple scattering theory provides good agreement with experiment for materials including diamond and graphite, cubic and hexagonal boron nitride and silicon nitride. The multiple scattering calculation for the carbon and nitrogen K-edges in $\beta - C_3N_4$ was not similar to that of cathodic arc deposited CN_x, supporting previous work that the structure of this material is not consistent at all with that expected from $\beta - C_3N_4$. The MS calculated C K and N K ELNES could be useful in identification of hexagonal crystalline phases of β-C_3N_4. The C K ELNES is predicted to be similar to diamond, while the N K ELNES should be similar to nitrogen in c-BN.

6.3 Future Outlook

The search for crystalline carbon nitride continues, almost unabated, as new and (perhaps) more exotic techniques are used in the hunt for any materials harder than or comparable to diamond. A coherent approach to characterisation of crystalline carbon nitride is required. Researchers should be more forthcoming with experimental data to enable the true structure and composition of samples to be determined.

Recent developments in Reverse Monte Carlo (RMC) modelling have enabled voids in amorphous structures to be used in fits to experimental data, as shown by Pikunic *et al.* in [1]. The simulation of amorphous carbon nitrides at various densities including the voids would enable a clearer idea of the structure to be elucidated, especially at low densities.

Bibliography

[1] J. Pikunic, R. J. M. Pellenq, K. T. Thomson, J. N. Pouzaud, P. Levitz, and K. E. Gubbins, in *Studies in Surface Science and Catalysis*, Y. Iwasaw, N. Oyama, and H. Kunieda, eds., (Elseview Science, B. V., 2001), Vol. 132.