# An investigation of carbon nitride

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*at the University of Sydney*
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*To Tanya. For truth, beauty, freedom and above all things, love.*

Suddenly the world seems
Such a perfect place,
Suddenly it moves with
Such a perfect grace ...
Sing out this song,
I'll be there by your side.
Storm clouds may gather
And stars may collide.
But I love you, until
The end of time.
— "Come What May",
*Written by David Baerwald.*

# Declaration of originality

Chapter 3 of this thesis is based on two papers by the author, D. G. McCulloch, D. R. McKenzie, Y. Yin, L. Hall, and E. G. Gerstner[1] and D. G. McCulloch and the author[2]. The IR spectra in Section 3.2.9 were collected with the assistance of Y. Yin. The Raman spectra were collected by D. G. McCulloch. The HF-CVD samples were deposited with the assistance of D. Barbara and L. Kostidis from the University of Melbourne. The SEM image of nitrogen implanted glassy carbon was taken by D. G. McCulloch. The plasma-assisted CVD deposited carbon nitride sample was provided by H. Grüger from Institut für Festkörper- und Werkstofforschung, Dresden. The reactively sputtered carbon nitride was provided by H. K. M. S. Chowdhury from the School of Electronic Engineering, Dublin City University, Glasnevin, Dublin. The HF CVD carbon nitride sample was provided through Y. Chen from Chinese Academy of Sciences.

With these exceptions, this thesis contains no material which has been presented for a degree at this or any other university and, to the best of my knowledge and belief, contains no copy or paraphrase of work published by another person, except where duly acknowledged in the text.

Alexander R. Merchant

[1] A. R. Merchant, D. G. McCulloch, D. R. McKenzie, Y. Yin, L. Hall,and E. G. Gerstner, "Structural investigation of two carbon nitride solids produced by cathodic arc deposition and nitrogen implantation," J. Appl. Phys. **79**, (1996), pp6914–6919.

[2] D. G. McCulloch and A. R. Merchant " The effect of annealing on the structure of cathodic arc deposited amorphous carbon nitride films " Thin Solid Films **290-291**, (1996), pp91–102.

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"To he who fears his fate to much
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who fears to put it to the test
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— Montrose Toast.

# Author's Publications

1. A. R. Merchant, D. R. McKenzie and D. G. McCulloch, "*ab initio* simulations of amorphous carbon nitrides", Physical Review B, 024209 (2002).

2. S. H. N. Lim, D. G. McCulloch, A. R. Merchant, N. A. Marks, M. M. M. Bilek and D. R. McKenzie, "Wannier function analysis for understanding disordered structures generated using Car-Parrinello Molecular Dynamics", submitted to Molecular Simulations (2001).

3. D. R. McKenzie, W. T. Li, E. G. Gerstner, A. R. Merchant, D. G. McCulloch, N. A. Marks and M. M. M. Bilek. "Applications of tetrahedral amorphous carbon in limited volatility memory and in field programmable gate arrays", Diamond and Related Materials, **10**, pp230-233, (2001).

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5. A. R. Merchant, D. G. McCulloch, and R. Brydson "A comparison of experimental and calculated electron-energy loss near-edge structure of carbon, and the nitrides of boron, carbon and silicon using multiple scattering theory" Diamond & Related Materials **7**, (1998), p1303–1307.

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2. R. Brydson, A. V. K. Westwood, S. J. Bowen, B. Rand, A. R. Merchant and D. G. McCulloch, in Proceedings of Eurem-11, edited by Committee of European Societies of Microscopy (Comm. of Eur.Soc. of Microsc., Brussels, 1998).

3. A. R. Merchant, D. G. McCulloch, and D. R. McKenzie, "First principles Car-Parrinello Molecular Dynamics simulations of bonding in amorphous carbon-nitrides" in Proc. 14th International Congress on Electron Microscopy, eds. H. Benavides and M. Yacaman (Institute of Physics, Bristol) p791-792 (1998).

4. D. G. McCulloch, C. M. Goringe, A. R. Merchant and D. R. McKenzie, "First-Principles Quantum Molecular Dynamics of Amorphous Carbon-Nitrides." 10th NTA and 4th VSA Conference, Australian National University ACT, Australia, 23-26 November 1997.

5. A. R. Merchant, D. G. McCulloch, D. R. McKenzie and E. G. Gerstner. 9th NTA and 3rd VSA Conference, The University of Newcastle NSW, Australia, 27–29 November 1995.

# Abstract

This thesis employs experimental and theoretical methods to characterise carbon nitride solids and proposes a general structural model for amorphous carbon nitride ($a-$C:N). It finds that $a-$C:N deposited by several methods is essentially identical, with similar bonding environments for carbon and nitrogen atoms. Using evidence from several techniques, the saturation of nitrogen in an $sp^2$ carbon matrix is discussed. The experimental studies on a range of carbon nitride solids show no evidence for a crystalline form of carbon nitride. In addition to the experimental characterisation of $a-$C:N, *ab initio* molecular dynamics were used to investigate bonding and structure in carbon nitride. These simulations show that the most common form of nitrogen bonding was three-fold sites with a lone pair of electrons. Two-fold nitrogen sites were also found in agreement with experimental findings. An increase of nitrogen in $a-$C:N decreases the $sp^3$-carbon fraction, but this is not localised on the nitrogen and the effect is most severe at high densities. A simulation of a low density/high nitrogen content network shows that the nitrogen saturation seen experimentally may be due to the formation of $N_2$ dimers and C-N molecules which are easily driven out of the structure. The *ab initio* simulations also explore the nature of charged nitrogen and carbon sites in $a-$C:N. An analysis based on Wannier Function centres provided further information about the bonding and allowed for a detailed classification of these sites. The removal of electrons from the networks caused structural changes that could explain the two-state conductivity in ta-C:N memory devices. Finally, a theoretical study of the electron energy-loss near-edge structure (ELNES) calculated using multiple scattering theory is presented. The calculated ELNES of diamond, graphite and boron, silicon and carbon nitride structures compare well to experiment and supports the experimental finding that no crystalline carbon nitride had (or has) been produced. These ELNES calculations will however, provide a means of identifying crystalline $\beta$-$C_3N_4$ should it be synthesised.

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