Chapter 1

Introduction

> "The central challenge to modern materials science is the rational design and synthesis of new materials with exceptional properties."
> *David M. Teter (MRS Bulletin January 1998)*

Modern globalised industry is moving towards an agile and "green" manufacturing processing environment with greatly reduced industrial waste. This has prompted the development of "dry" machining systems such as chemical vapour deposition (CVD) diamond coated tooling. However, while such processes achieve the required reduction in waste, they are currently limited by the the high costs and energy intensive nature of CVD [1]. Unfortunately, the cost of CVD diamond coating tools remains high and the process is very energy intensive. By the year 2001 the CVD diamond industry is expected to top US$1 Billion as shown in Table 1.1 [2]. New materials with excellent mechanical properties which are cheaper to produce than diamond are in demand.

This thesis focusses on solid carbon nitride as a promising new material. Traditionally, when new materials are found, their properties and structure are explored and studied. In contrast, the existence of crystalline carbon nitride has been predicted from theoretical calculations but has never been found naturally. From these predictions, the challenge is thrown down for experimentalists around the world to attempt to syn-

	1996	**2001**	AAGR[1]
Thin Films (PVD, VCVD, epitaxy, etc)	905	1426	(9.5%)
Diamond, diamond-like products	125	210	(11%)

Table 1.1: The predicted growth of thin films and diamond, diamond-like film materials. All figures are in US $Million. Source: Business Communications, Inc.

-thesise it. The unambiguous evidence for synthesis of crystalline carbon nitride is still controversial, although some evidence exists for minute (nano- or micro-) crystals of the material. The search for crystalline carbon nitride has resulted in the discovery and characterisation of new and interesting forms of amorphous carbon nitrides ($a-$C:N).

In this chapter a review of the recent history of crystalline phases of carbon nitride and attempts at their synthesis will be presented.

1.1 What is a hard material ?

Since the dawn of human history, we have searched for materials which can be used as tools. Diamond for example, coming from the greek word *adamas* meaning indestructible, is used in industry for drilling, grinding and polishing. Diamond and other hard materials form an essential part of our modern day life. But what is a hard material or hardness, and how is it measured ? Hardness is a quantity that is difficult to quantify - in simple metals and ionic substances, hardness is a function of extrinsic factors (eg. impurities and grain boundaries) of the material.

The experimentally measured value of hardness for a material will vary with the technique used - some techniques use indentation of a sphere or pyramid (Brinell, Vickers and Rockwell). More modern hardness tests involve micro-indenters. Hardness can also be described by tribological properties such as resistance to abrasion and scratching.

In covalent materials, however, as bonding is localised, hardness is an intrinsic property. An indicator of hardness in covalent materials is the energy difference between the energy of the lowest unoccupied molecular orbital (LUMO) and highest occupied

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[1] AAGR - Average Annual Growth Rate

molecular orbital (HOMO) [3]. This is because the energy gap will determine the strength of the chemical bond - intuitively a key factor in determining the strength of a material. It is therefore important to consider the electronic structure of any candidate ultrahard materials.

Some authors have argued that hardness for some materials, particularly diamond and zinc-blende semiconductors, can be quantified by the measurement of the bulk modulus – a measure of a material's resistance to isotropic pressure [4]. For example diamond, the hardest known material, also has the highest bulk modulus of 440GPa (4.4MBar), followed by cubic boron nitride (c-BN) at around 360GPa (3.6 MBar). A material with a bulk modulus exceeding diamond would be a revolution in materials technology.

1.2 What materials do carbon and nitrogen form ?

Carbon has four electrons in its outer shell ($1s^2$, $2s^2$, $2p^2$). When bonding, carbon is able to form molecular orbitals in one of three hybridisations: sp, sp^2 and sp^3 which are linear, trigonal and tetrahedral respectively. These different hybridisations are seen in liquid carbon (sp), graphite (sp^2) and diamond (sp^3) and are responsible for the remarkably different properties of these materials [5]. There are three naturally occurring allotropes of carbon - diamond, hexagonal diamond and graphite. In 1985 a new form of carbon known as buckminsterfullerene (C_{60}) and later the fullerenes (C_{70} and others) were discovered. Crystalline C_{60} has a face centred cubic structure.

At standard temperature and pressure graphite is the thermodynamically stable form of crystalline carbon. Diamond and graphite will be described further as they relate strongly to the production of carbon nitride.

Diamond consists of sp^3 bonded carbon tetrahedra. The cubic diamond structure consists of two overlapping face-centred cubic lattices offset by ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) [6] which is equivalent to the zinc blende structure. Hexagonal diamond also called Lonsdaelite is differentiated by the wurtzite packing of the sp^3 atomic layers. The C-C bond length in diamond is 1.54 Å longer than in graphite of 1.42 Å. Diamond is used as a valuable gemstone, industrial abrasive, hard coating, optical and semiconducting material. Diamond is hard because despite being of moderate mass density (3.52g/cm^3), contains densely packed planes in the same directions as the covalent C-C bonds.

Graphite consists of sp^2 bonded layers of six-membered carbon rings, with inter-layer bonding as a result of van der Waals forces. The accepted structure for graphite is the Bernal [7] structure which is hexagonal with symmetry P63/mmc (D46h). The C-C bond length is 1.42 Å with an inter-planar distance of 3.35 Å. Graphite is useful as a dry lubricant because of weak inter-layer (van derWaals) between adjacent layers. The C-C bond in graphite is stronger than in diamond, and this property is useful for carbon nanotubes, discovered by Sumio Iijima [8] in 1991. Nanotubes are related to the fullerenes, and are essentially a single plane of graphite wrapped to form a tube with an end-cap of pentagons.

Nitrogen comprises nearly 70% of the air we breathe, it naturally occurs as the dimer N_2. It has five electrons in its outer shell (1s^2, 2s^2, 2p^3) and so is able to bond in sp, sp^2 and sp^3 hybridisations, but tends to form lone-pairs (where one bond is doubly filled by two electrons). For example ammonia contains nitrogen bonded to three hydrogen atoms in a tetrahedral bonding configuration.

The hardest nitride known is cubic boron nitride (c-BN). In c-BN, the boron assumes control of one of the nitrogen's electrons by a process known as electron resonance transfer [9] making the boron and nitrogen isoelectronic with carbon. The structure of c-BN is almost identical to diamond, except the B-N bond is heteropolar (unlike diamond's homopolar bond) making it weaker.

Carbon and nitrogen co-exist in naturally occuring crystalline diamond, as nitrogen is the most common impurity in natural diamond types Ib and Ia. However, solubility of nitrogen in diamond is quite low, and although nitrogen is abundant, nitrogen is not able to dope diamond *n*-type to form a useful electronic material. Nitrogen can also form small platelets [10] in diamond and also (rarely) occurs in diamond as a single substitutional N^+ [11].

Other hard nitrides exist through the bonding of nitrogen with the transition metals (eg. titanium nitride), and although these are an important class of hard materials, they will not be considered further. In this thesis we are primarily interested in light element materials where the bonding is dominated by covalent bonds.

1.2.1 What is crystalline carbon nitride ?

An ultra-hard material made from carbon and nitrogen was first proposed in 1985 by Cohen [4] following his work relating the bulk modulus of diamond and zinc blende solids to their covalent or ionic radii. The empirical relation determined by Liu and Cohen [12] was:

$$B = \frac{(1971 - 220\lambda)}{d^{3.5}} \tag{1.1}$$

where B is the bulk modulus in GPa, λ is the ionicity of the bond and d the bond length in Å. For a carbon nitride covalent solid, the value of d lies between 1.47 and 1.49Å which suggests a bulk modulus between 461 and 483 GPa, significantly greater than diamond (443 GPa). Liu and Cohen [12, 13] also proposed a structure for crystalline carbon-nitride based on β-Si_3N_4. This new structure, termed "β-C_3N_4", contained 14 atoms (6 carbon and 8 nitrogen) in a hexagonal unit cell. The structure consisted of CN_4 tetrahedra linked on each corner as shown in fig (1.1)(a) topmost. By theoretically fitting the total energy as a function of lattice parameter (Murnaghan's equation) Liu and Cohen found a bulk modulus of 427GPa for β-C_3N_4 - comparable to, but not exceeding diamond. A measure of the cohesive energy using the first principles psuedo-potential total energy approach found a cohesive energy of 5.8eV per atom. This suggested the β structure was at least meta-stable as 5.8eV is comparable to the cohesive energy of carbon (in diamond) of 7.35eV and silicon of 4.63eV [15].

A provisional patent on β-C_3N_4, a "material harder than diamond" was awarded to Cohen and co-workers in the United States in 1993 following their reported successful synthesis of the material[2]. β-C_3N_4, a material with hardness comparable to diamond would be a viable alternative to natural or synthetic diamond if it were easier to form than diamond.

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[2] The work was not published until 1994, making Niu, Lu and Leiber's work in *Science* the "first", see Section 1.2.2

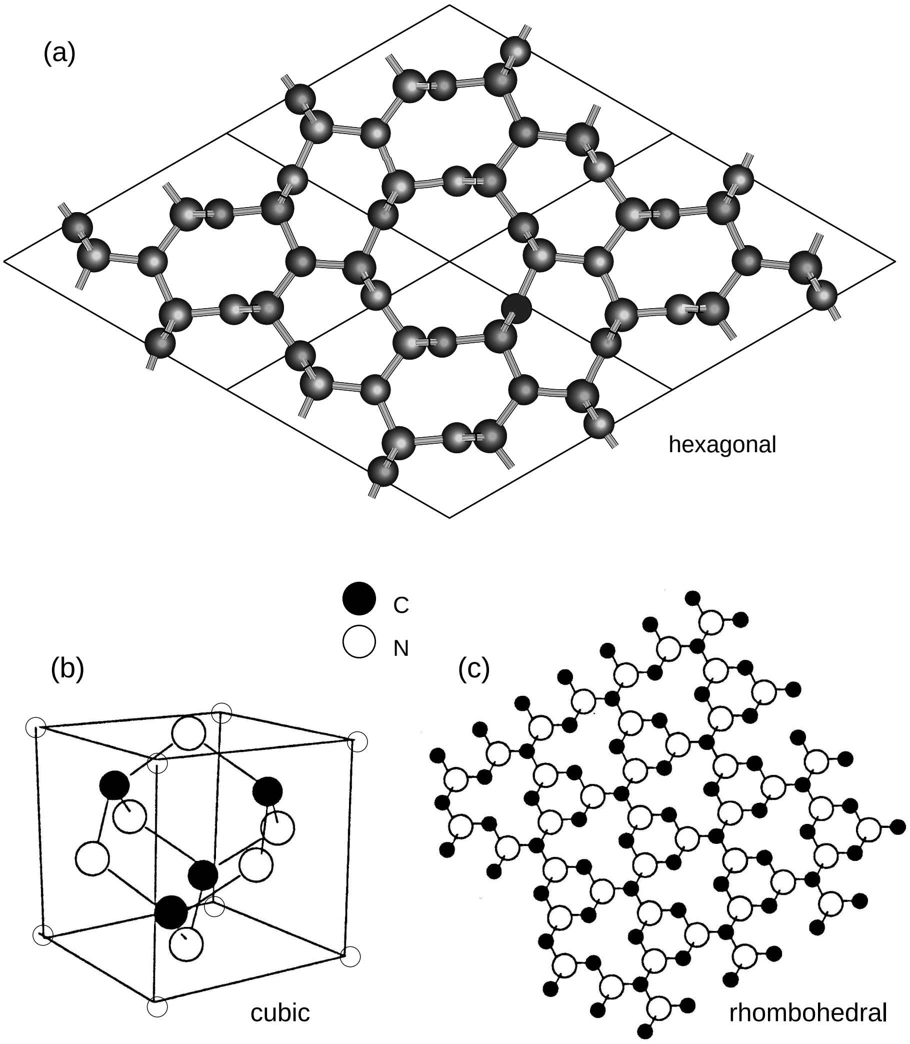

Figure 1.1: More than one C_3N_4 structure has been proposed, for example Liu and Wenzcovitch [14] suggested three structures: (a) β-C_3N_4, (b) a cubic C_3N_4 form with different symmetry and (c) a "graphitic" carbon nitride based on a defective graphite lattice. The small circles on the corners of the cubic lattice in (b) indicate vacant carbon sites.

Following Cohen's results, Liu (his then graduate student) continued the theoretical work with Wentzcovitch [14] and explored yet more C_3N_4 structures including cubic zinc-blende and rhombohedral forms, as shown in Figure (1.1)(b,c).

Later work by Teter and Hemley [16] refined these structures and suggested yet more based on the same stoichiometry. One form called "α-C_3N_4", is predicted to have a lower bulk modulus than β-C_3N_4, but fitted the existing experimental x-ray diffraction data with fewer errors.

Cohen and co-workers [17, 18] also explored different carbon nitrogen stoichiometry including 1:1. They were joined by Lowther [19] who investigated the effect of removing one nitrogen from each C_3N_4 unit (forming C_3N_3) on a cubic form of C_3N_4. Lowther's aim was to determine the effect of this slight 'amorphisation' on the bulk modulus of the structure. Lowther concluded that the lower bulk modulus of the 'defective' structure meant the number of C-N bonds formed experimentally would be crucial to reaching the optimal bulk modulus.

Meanwhile, a race was on to synthesise β-C_3N_4 in the laboratory, and since 1993 there have been 337 papers published with the words "C_3N_4" in the abstract, and more than 2000 with the words "carbon nitride" as shown in Figure (1.2).[3] At the time of writing this thesis, Cohen's original Physical Review B (1985) article has been cited 230 times[4], Liu and Cohen's article in Science (1989) has been cited almost 650 times, and their subsequent article in Physical Review B 440 times. It is clear that there has been intense interest in crystalline phases of carbon nitride.

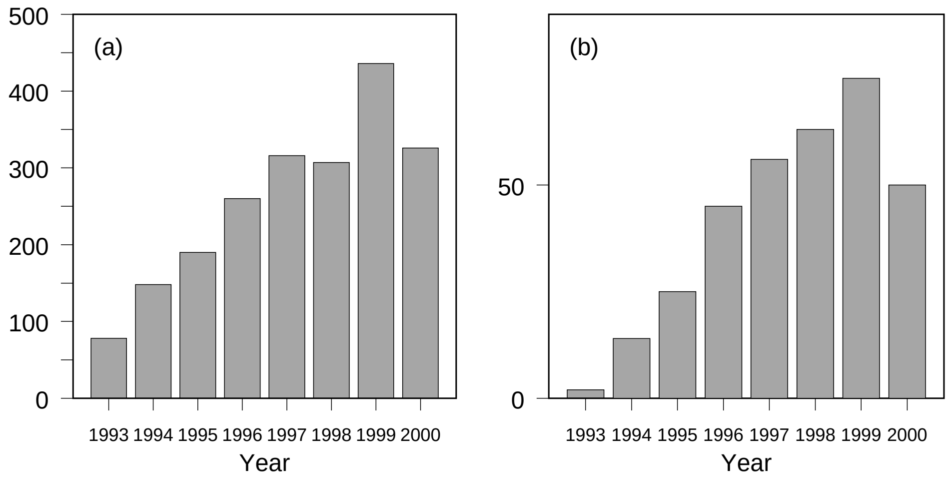

Figure 1.2: The number of publications using (a) "carbon nitride" and (b) "C_3N_4" in title, keywords or abstract for the years Jan 1st 1993 – Jan 1st 2001, showing a steady rise in the number of published papers, peaking in 1999.

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[3] Figures compiled from Current Contents database, Institute for Scientific Information.

[4] Figures compiled from Science Citation Index

1.2.2 Synthesis of β-C_3N_4

As explained in a recent review of carbon nitride by Muhl and Méndez [20], the first solid carbon nitride to be studied was probably paracyanogen by Guy-Lussac, who studied a "hard-to-dissolve" by-product of experiments using cyanogen (C_2N_2). The original attempt to make a carbon nitride thin-film is attributed to Cuomo [21] who used radio-frequency (rf) magnetron sputtering to produce a material he termed $-(CN)_n-$ referring to paracyanogen. The physical structure of this material was not studied, although its infra-red spectrum was presented.

The first published report on synthesis of crystalline carbon nitride was published by Niu, Lu and Lieber at Harvard University [22] in 1993 who claimed to have found β-C_3N_4 based on a polycrystalline electron diffraction pattern. The diffraction pattern fit several lines (reflections) expected from β-C_3N_4 quite well, but several important lines were missing, while some weak reflections were listed as a "good fit". The difficulty in the claim was compounded because the film composition was not consistent with C_3N_4, and they were unable to isolate a single crystal of material large enough for further study. Niu *et al.* argued that crystals of β-C_3N_4 were scattered throughout an amorphous carbon nitride matrix of lower nitrogen content. Their work was later criticised by Marton *et al.* [23] for not providing sufficient experimental data such as x-ray photoelectron spectroscopy (XPS) measurements to elucidate how many phases of carbon nitride were present.

This work was followed soon after by Yu *et al.* [24] whose boldly titled paper "*Observation of crystalline* C_3N_4" indexed an electron diffraction pattern to β-C_3N_4 from carbon nitride deposited using a r.f. diode-sputtering and a substrate temperature 400-600°C. The electron diffraction pattern and indexing was inconclusive, and the samples contained between 5-10% oxygen and a nitrogen content of 0–50%.

A large number of papers over the next few years claimed to identify nano- or micro-crystals of β-C_3N_4 in an amorphous matrix - for example Yen *et al.* [25], who used plasma jet chemical vapour deposition. It was Su *et al.* [26] who observed "β-C_3N_4 grains" using TEM, but only measured the nitrogen composition (59%) using energy dispersive spectroscopy (EDS). EDS is not a sensitive technique for the measurement of low-atomic number elements like carbon and nitrogen, and any measurement of nitrogen in a carbon matrix would be strongly affected by absorption of nitrogen x-rays by the carbon matrix.

In 1996, Chen, Guo and Wang presented observations of β-C_3N_4 single crystals [27] grown on nickel substrates using hot-filament chemical-vapour deposition (HFCVD), and presented transmission electron micrographs of single crystal diffraction patterns from single crystals of β-C_3N_4 shown in fig(1.3). To compare with these I have calculated the diffraction patterns simulated using multislice[5]. Multislice is a technique pioneered by Cowley and Moodie [28] for calculating the high-resolution images or diffraction patterns by predicting the electron wavefunction from successive thin “slices” of crystal. Multislice was used to calculate the diffraction patterns for β-C_3N_4 structure at the same orientations as quoted by Chen *et al.* [29]. It is clear the simulated diffraction pattern does not match the observed for the microscope and structure parameters given. [6]

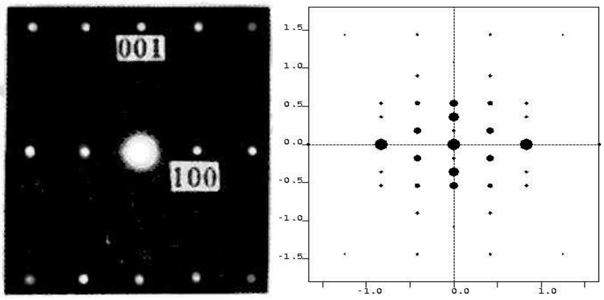

Figure 1.3: Many authors claim to have found the elusive β-C_3N_4, in this example an electron micrograph and diffraction pattern from Chen *et al.* [27] is shown. This is compared to my multislice calculation of the β-C_3N_4 under the same experimental conditions.

Since the work of Chen *et al.* there has been a several more papers claiming to have found evidence of β-C_3N_4, but none are any more conclusive or definitive than the

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[5] implementation on Cerius^2 by MSI Inc.

[6] Interestingly, in a later review of of carbon nitride research by E. G. Wang [30], the same figure appears with an altered caption.

results already mentioned. In the past year (2000), several authors have published results from deposition techniques including microwave plasma chemical vapour deposition (CVD), and electron cyclotron resonance (ECR) sputtering, but the analysis is still inconclusive. A review of mostly-crystalline carbon nitride research can be found in Wang [30], although perhaps a more balanced view of can be found in Muhl & Méndez [20]. A review questioning the validity of formation of crystalline carbon nitrides by Matsumoto *et al.* [31] presents the idea that most X-ray diffraction (XRD) data of crystalline "C_3N_4" is due to polytypic diamond. Matsumoto *et al.* also mentions the work of Chen *et al.* [29, 32, 27] commenting that several important reflections are absent in XRD data of α-C_3N_4 and in their conclusion noted:

> "[We] conclude that no definite evidence for the existence of C_3N_4 with the predicted structures has *ever* been presented ...

Historically it has been difficult to say with certainty that crystalline carbon nitride has been successfully synthesised. From relatively early days, as De Vries [33] wrote in his article "β-C_3N_4 *or bust*" that several attempts to synthesise β-C_3N_4 were "In all cases where chemical analyses are given, the material is woefully non-stoichiometric".

So does crystalline carbon nitride truly exist ? Some authors have questioned the theoretical basis of β-C_3N_4, for example Hughbanks [34] argued that the stability of C_3N_4 was optimised against lattice parameter alone, whereas if the repulsion between lone-pair electrons on the nitrogens are considered their destabilising influence leads to the development of a more energetically favourable C_4N_3 structure.

Is β-Si_3N_4 a valid basis structure for β-C_3N_4 ? This was discussed at length by Malkow [35] who explored important issue of nitrogen bonding to silicon and carbon, being as they are, on different rows of the periodic table. An issue somewhat overlooked is that there are two different nitrogen bonding sites in β-C_3N_4, leading to what could be two different bonding states.

Malkow also pointed out that in Si_3N_4, the nitrogen atoms form planar NSi_3 polyhedra. That is the N could form either sp^2 sites with p_z lone-pairs, or sp^3 sites with lone-pairs. In comparing the bond angles of molecular counterparts trisilyl-$(SiH_3)_3N$ and trimethylamines $(CH_3)_3N$ the N in the formed is sp^2 while the latter sp^3. Some simulations discussed by Malkow showed that for an extreme hardness carbon nitride in an cubic form, nitrogen atoms had to be planar.

Was crystalline carbon nitride as hard as theoretically claimed ? Teter [36] challenged the idea that the bulk modulus was the best indicator of the hardness of a material. In fact, he argues, there is a clear dependence between shear modulus and hardness. Under this scheme, the defect[7] zinc-blende structure of C_3N_4 would exhibit the highest hardness, not hexagonal β-C_3N_4. Another concern about the β-C_3N_4 structure is that some theoretical calculations constrained the nature of the nitrogen atoms. The least energetic structure for the nitrogen atoms may be pyramidal or planar. BelBruno [37] showed that linear C_3N_4 molecules with sp^2 bonded N was more stable those containing pyrimidal nitrogen atoms.

In summary, crystalline carbon nitride is an exciting possible new material, but there is no conclusive evidence for its synthesis. The most optimistic interpretation of results is that small nano- or micro-crystallites of some phase of carbon nitride can form in an amorphous carbon nitride ($a-$C:N or CN_x) matrix, but experimentalists have been unable to synthesise (or isolate) sufficient crystalline material for a conclusive analysis. This leads us to the next section of this chapter - the synthesis of amorphous carbon nitride.

1.3 Amorphous Carbon Nitride.

Amorphous carbon nitride ($a-$C:N) is far from being a by-product of crystalline carbon nitride deposition, instead it is a useful and complex material in its own right, that could have applications as an electronic material, an electrode in electro-chemical processing, an industrial lubricant or as a hard-yet-flexible coating. These properties can be considered an enhancement to the usefulness of the forms of carbon known

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[7] In the zinc-blende structure each atom is four-fold coordinated. The ‘defect’ structure of Teter (1998) contains three-fold coordinated atoms and is therefore missing some atoms, hence the term ‘defect’.

as amorphous carbon ($a-$C) and tetrahedral amorphous carbon ($ta-$C). To describe $a-$C:N and $ta-$C:N – the nitrogen doped forms of these amorphous carbons fully, $a-$C and tetrahedral amorphous carbon ($ta-$C) will first be explained.

1.3.1 What is amorphous carbon ?

Non-crystalline or poly-crystalline forms of carbon include glassy carbon (GC), amorphous carbon ($a-$C) and tetrahedral amorphous carbon ($ta-$C), also known as amorphous diamond (a-Dia). Glassy carbon is a turbostratic form of graphite-like carbon material created by the pyrolysis of hydrocarbon precursors. It is distinct from graphite because of the lack of registration between sp^2 bonded carbon layers. Amorphous carbon is a solid containing a mixture of predominantly sp^2 hybridised carbon with amounts of sp and sp^3 carbon hybrids with densities between 2.0-2.6 g/cm^3. Tetrahedral amorphous carbon is an optically transparent solid containing up to 95% sp^3 hybridised carbon with a theoretical density as high as 3.2 g/cm^3. A review of tetrahedral bonding in amorphous carbon can be found in McKenzie [38].

Amorphous carbon is generally deposited as a thin film under non-equilibrium conditions which prevents the formation of lower energy crystalline structures. One example, the thermal evaporation of graphite under vacuum, produces a film with an sp^3 content of between 10-12%, with the remainder mostly sp^2 bonded and a small percentage of sp bonded carbon. If the sp^3 fraction of amorphous carbon is increased it gains some of the properties that make diamond a superior material (eg. large optical band-gap, hardness, chemical inertness). Therefore to promote sp^3 bonding in amorphous carbon researchers deposited the material with hydrogen to form $a-$C:H. This material was not optimal because of the relatively low density of the resulting material, and a review of the material may be found in Robertson [39]. A more successful approach to increase the amount of sp^3 bonded carbon in $a-$C, was pioneered by Aisenberg and Chabot [40] who used an energetic condensation technique with ion energies above 1keV. A revolution in the deposition of dense carbon films was made by Askenov *et al.* [41] who used a vacuum cathodic arc. The first systematic diffraction analysis of the structure of these films [42, 43] led to the conclusion that the energy of deposition lead to development of compressive stress. This stress made the formation of sp^3 bonded carbon energetically favourable. The technique of cathodic arc deposition of $a-$C and $ta-$C will be discussed further in Chapter 2.

Tetrahedral amorphous carbon has a band gap of $\approx$2.5eV which in relation to other semiconductors, is a "wide" band gap. This means $ta-$C could be useful in semiconductor devices which utilise materials with a range of band gaps [44], as well as exhibiting useful material properties, for example low coefficient of friction, chemical inertness, and hardness.

In this thesis amorphous carbon nitride ($a-$C:N) will be divided into two categories. The term $a-$C:N will be used to refer to predominantly sp^2 carbon bonded $a-$C:N, while the term $ta-$C:N will refer to predominantly sp^3 carbon bonded material.

1.3.2 Synthesis of amorphous carbon nitride $a-$C:N

Potentially, any deposition technique used for the production of $a-$C as a thin film can be adapted to synthesise $a-$C:N thin films. This is because nitrogen is readily available as a gas and both precursors are non-toxic, also there are many organic carbon nitride compounds. The deposition processes used for carbon nitride include [20, 35, 30] chemical processes (eg. pyrolysis[8] of carbon nitride precursors), ion-beam deposition or implantation, pulsed laser deposition, chemical vapour deposition and reactive sputtering.

While it is relatively simple to categorise the deposition techniques, it is more difficult to characterise the different materials produced. The analysis of amorphous carbon nitride has been analogous to trying to solve a puzzle without enough pieces. This is because no two authors use exactly the same structural or stoichiometric analysis technique and tend to focus on one or the other - for instance, while x-ray photoelectron spectroscopy (XPS) is indicative of shifts in bonding energies it does not provide definitive structural information due to difficulties in assigning energies and fitting peaks [20].

Therefore, for the discussion of deposition techniques a phase diagram for amorphous carbon nitride suggested by Kleinsorge *et al.* [45] will be followed, as shown in fig (1.4). Firstly the techniques employed to form principally carbon sp^3-bonded materials will be

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[8] heating in absence of oxygen

explained, then secondly, the formation of primarily carbon-sp^2 matrix structures will be discussed. Thirdly, the techniques employed to form fullerene-like carbon nitrides will be presented.

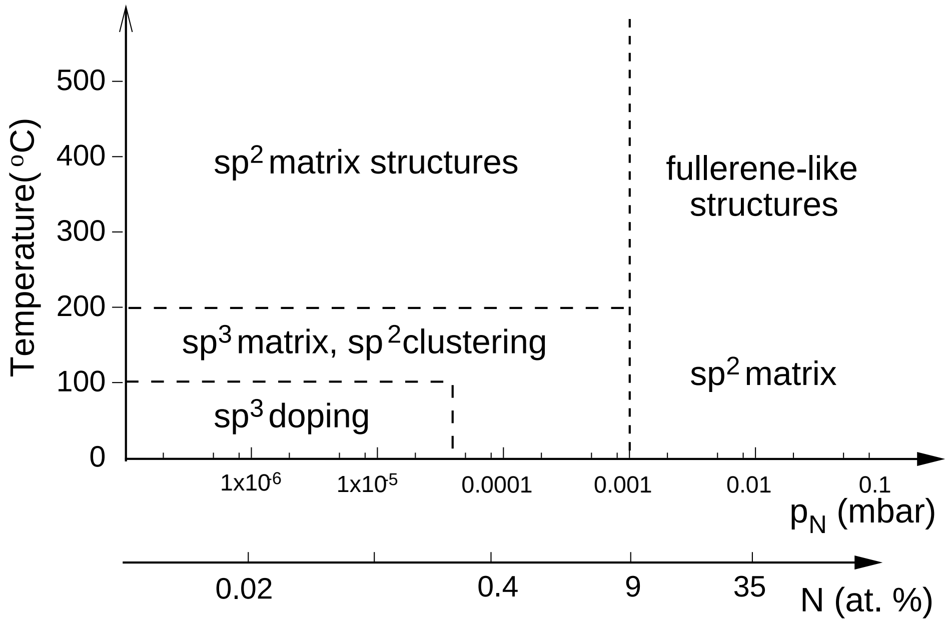

Figure 1.4: A phase diagram for amorphous carbon nitride following Kleinsorge *et al.* [45] and after Hellgren *et al.* [46]

1.3.3 Deposition of sp^3-doped $ta-$C:N or sp^3-matrix sp^2-clustering

Techniques which can be used to form $ta-$C:N include pulsed laser deposition (PLD), chemical vapour deposition (CVD), plasma enhanced CVD, filtered cathodic arc and ion implantation into diamond.

Pulsed Laser Deposition (PLD) or ablated (PLA) $ta-$C:N involves the vapourisation of a target material (generally graphite) in an atmosphere containing nitrogen containing gas [9] forming a plasma which condenses onto the substrate [47]. PLD is a useful technique because non-conducting target material can be used at low deposition temperatures [48]. Interestingly both the nitrogen content and carbon sp^3/sp^2 fraction are enhanced by increasing the deposition laser fluence.

The filtered cathodic arc is an efficient method of forming tetrahedral amorphous car-

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[9] for example nitrogen N_2 or ammonia NH_3

bon, and with the addition of a nitrogen atmosphere can be used to deposit hard films of *ta*−C:N as first described by Davis *et al.* [49]. The *ta*−C:N films deposited using the arc can have a density up to 3.0g/cm^3 and sp^3 fractions greater than 80%. An increase of nitrogen content will tend to reduce the carbon sp^3 fraction, although the sp^3 fraction can also be affected by the bias voltage, substrate temperature and deposition pressure.

In the N-doping of *ta*−C region, Robertson and Davis [50] presented a synopsis of experimental work using the filtered cathodic arc to deposit *ta*−C:N with a nitrogen content up to 28%. At 28% nitrogen, the network is no longer sp^3 but an sp^2 matrix. Davis *et al.* [49] found that increasing the partial pressure of nitrogen in the cathodic arc chamber increased the amount of nitrogen in the *a*−C:N films and decreased the C-sp^3 content. He concluded the C-sp^3 decrease was also linked to a decrease in the compressive stress of the film leading to formation of C-sp^2. The reduction in stress as the nitrogen increased resulted in a C-sp^2 fraction of around 80-90% in the deposited films.

Several research groups have used the technique of ion implantation into diamond to synthesise carbon nitrides and/or dope diamond for use as an electronic material. Ion implantation is used because diamond has a very high atomic density and therefore low solubility and diffusion coeffecients for impurity atoms. Ion implantation offers one way of doping diamond as discussed by Prawer [51].

Ion implantation of diamond generally involves high energy (typically MeV) ions penetrating the diamond surface. The ion loses energy by breaking bonds until stopping at a depth determined by the ion type, target material and initial energy. The damage in some cases can be annealled out of the structure depending on the fluence and ion energy [52]. Some authors [53, 54] have claimed to have formed buried crystalline carbon nitride based on Raman spectroscopy results following N$^+$ implantation of diamond.

Chemical vapour deposition (CVD) and plasma enhanced CVD are techniques successfully used to synthesise thin-film diamond. A typical depositon arrangement can use either hot-filament or microwaves to form a plasma with feeder gases of methane

(CH_4). For the formation of carbon nitrides, gases such as and nitrogen (N_2) or ammonia (NH_3) are introduced to the deposition chamber. Nitrogen has a number of effects including the formation of N_2 dimers in diamond [55], or at low temperatures (< 450K) the formation of sp^2-carbon bonded $a-$C:N films [56].

1.3.4 Deposition of sp^2-matrix $a-$C:N

Techniques used for deposition of carbon-sp^2 matrix $a-$C:N include the cathodic arc, r.f. magnetron sputtering, and ion implantation into carbon. Kumar *et al.* [57] used low power r.f. reactive sputtering to produce films of high sp^2 content measured using Raman spectroscopy to detect relative amounts of disordered or D and graphitic or G vibrational modes in carbon, but remarkably almost 50% nitrogen was measured using Rutherford Back Scattering (RBS).

PLD can also be used to deposit sp^2-matrix $a-$C:N, for example Reido *et al.* [58] recently reported polycrystalline $a-$C:N films produced by PLD with a nitrogen content of 30–40 at.%. The films had densities in the range of 2.0-2.5g/cm^3 (measured using the plasmon energy in EEELS) and increased laser fluence increased the number of nitrogen atoms bonded to sp^3 carbon atoms. Reido *et al.* also reported that at constant pressure the increase of the laser fluence caused an increase in the nitrogen content.

Ion implantation into carbon, for example glassy carbon, graphite or amorphous carbon produces a primarily sp^2-bonded $a-$C:N, as will be discussed in Chapters 2 and 3.

1.3.5 Deposition of fullerene-like sp^2-matrix $a-$C:N

As the concentration of nitrogen exceeds 9% the sp^2 carbon matrix combines with nitrogen to become a form of $a-$C:N described by Sjöström *et al.* [59] as a fullerene-like microstructure with nitrogen containing rings (eg. pentagons and hexagons). If the rings formed extended sheets, the buckling induced by pentagons (etc) could form curved structures. Hellgren *et al.* [46] extended this idea by suggesting sp^3 carbon atoms could form cross-links between sheets.

1.4 Applications of $a-$C:N

The applications of $a-$C:N and its use as a material are increasing daily.

$A-$C:N can be used in the production of stripper[10] foils used in cyclotrons to form radionuclides. Sugai *et al.* [60] found the $a-$C:N foils to have longer lifetimes than commercially available amorphous carbon foils for certain applications. Foil lifetime is crucial to the management of a cyclotron in relation to beam down-time and assured delivery of substances including short half-life medical isotopes. In a review by Lu *et al* [61] it was noted that the $a-$C:N foils of Sugai *et al.* had the second highest lifetimes of all stripper foils studied.

During the course of this program of study $a-$C and $a-$C:N foils were deposited and supplied to the National Medical Cyclotron facility in Camperdown NSW, Australia. Preliminary tests showed that $a-$C foils deposited using an evaporative carbon source and coated with collodion (a clear, brushable organic compound) had a beam lifetime superior to commercially supplied foils. An investigation of the deposited stripper foil using Raman spectroscopy is shown in fig (1.5).

As an electronic material, $a-$C:N or $ta-$C:N was initally used by McKenzie *et al.* [62] who investigated simple heterojunctions with the structure silicon/$ta-$C:N/metal. McKenzie *et al.* found that the n-doped $ta-$C had resivitivy of $10^7\Omega$cm and the I-V characteristics were that of a diode.

Later (1997), another application of $a-$C:N was in the $ta-$C *non-volatile* memory cells pioneered by Gerstner [63] who found while studying the IV characteristics[11] of a metal/$ta-$C:N/metal device that a "kink" appeared in the positive bias current which was not present under a reverse sweep. Gerstner [63] found that the "kink" was a result of charges stored in deep traps within the mobility gap of the $ta-$C:N film. This prompted the idea that the $ta-$C:N film could be used as a basis for a medium-term, nonvolatile memory cell.

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[10] Stripper foils are used to "strip" electrons from a cyclotron beam.

[11] the study of which was to determine band structure and carrier concentration from the expected asymmetry of the characteristic.

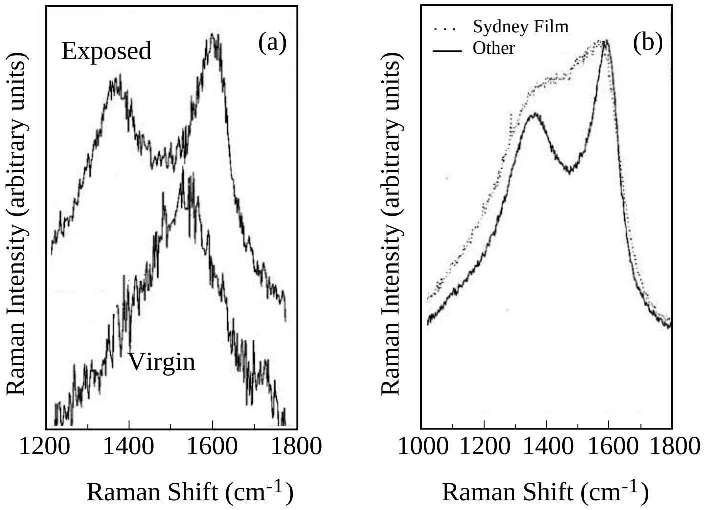

Figure 1.5: Raman spectroscopy of e-beam deposited $a-$C used as a stripped foil after being coated with collodian. The foil was remarkably stable and survived longer than any previous commercial foils, (a) shows the Raman spectra from the virgin and exposed films, while (b) shows the Raman spectra from a commercial; stripper foil and the e-beam deposited foil. The development of two peaks indicates a more graphitic structure.

A more recent (2000) development was by Maeng [64], who published a report describing N doped $ta-$C used to make a thin gate transistor as shown in fig(1.6). The active layer of the thin-film transistor is made from high sp^2-C content $a-$C:N deposited at room temperature using the cathodic arc. The device exhibits a threshold voltage of 15V and a field effect mobility[12] of 10^{-4}cm^{2}V^{-1}s^{-1}.

Probably the largest potential application of $a-$C:N is in low friction coatings, for example Zhang *et al.* [66] studied the thermal stability $a-$C:N films deposited by pulsed laser ablation and found that they exhibited a similar thermal conductivity to diamond, but had less residual stress than $ta-$C. $A-$C:N is being favoured over $a-$C in hard-disk overcoats [67, 68] where Scharf *et al.* [69] found that an $a-$C:N overcoat had the most wear resistance, least amount of plastic deformation and lowest kinetic friction coefficient of all hard-disk overcoats tested. Scharf suggests $a-$C:N will soon replace

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[12] mobility in a semiconductor is directly related to the mean free time between collisions. A good mobility is around 400 cm^{2}V^{-1}s^{-1} for laser annealed amorphous silicon[65].

$a-$C for applications because of its improved wear durability, lower friction coefficient, higher elasticity and compatibility with existing lubricants.

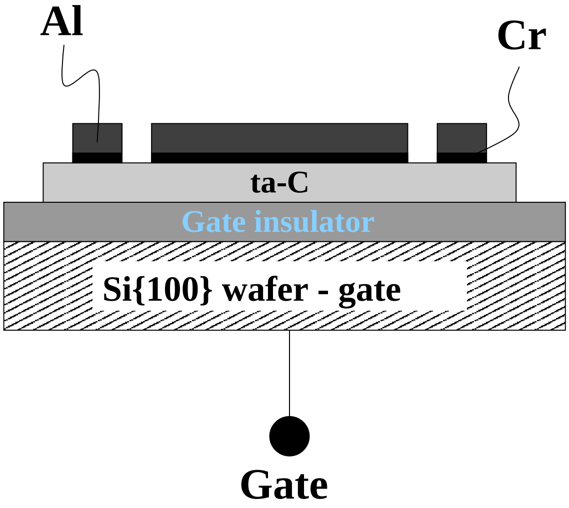

Figure 1.6: The use of $ta-$C or $ta-$C:N as doped wide-band-gap semiconductor has long been suggested, but rarely implemented. More recently, however, Maeng [64] published this schematic showing an inverted and staggered, bottom-gate and thin-film transistor (TFT).

1.5 Thesis Outline and Scope

This thesis is primarily concerned with characterising and understanding the structure and properties of carbon nitride solids. This thesis will be focussed on the following topics:

- To assess the evidence as to whether crystalline carbon nitride can be synthesised experimentally. To provide a means of identifying crystalline carbon nitride should it be synthesised.
- To pose a structural model for $a-$C:N deposited by different techniques.
- To compare the results of the experimental studies to molecular dynamics simulations of $a-$C:N.
- To explain the observed two-state conductivity in $a-$C:N memory devices.

Chapter 2 describes the synthesis and characterisation methods used throughout the thesis. The main synthesis methods were cathodic arc and Chemical Vapour Deposition (CVD). A wide range of characterisation techniques were employed to analyse the carbon nitride materials including Transmission Electron Microscopy(TEM), Energy Filtered Electron Diffraction, Electron Energy Loss Spectroscopy (EELS) and Infra-Red (IR) Spectroscopy.

Chapter 3 presents the experimental results of the characterisation of carbon nitride solids prepared using the techniques described in Chapter 2. In addition to this, several samples produced by a variety of methods in other laboratories are characterised. This chapter also includes a model for amorphous carbon nitride as deposited using physical vapour deposition methods.

The *ab initio* molecular dynamics study of structure and bonding in amorphous carbon nitride are presented in Chapter 4. The “liquid quench” method is used on 64 atom networks at a range of densities and nitrogen concentrations. This modelling provides a detailed view of the bonding in these materials.

Finally, Chapter 5 discusses the theoretical calculations of near edge fine structure from a variety of material structures including graphite, diamond, β-C_3N_4, h-BN, c-BN and β-Si_3N_4. The near edge structure is compared to experimentally measured energy-loss near-edge structure where possible, except for a calculation of β-C_3N_4. Near-edge fine structure as measured using electron energy loss spectroscopy or x-ray absorption spectroscopy probes the local electronic structure and therefore provides a means of identifying material phases.

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