

# Introduction 1 – Films and Materials

Carbon based materials have a diverse number of uses and have been acclaimed as the materials of the future. In this chapter, I will introduce several of these materials that have relevance to this thesis.

## 1.1 *Diamond and Graphite*

### 1.1.1 Introduction

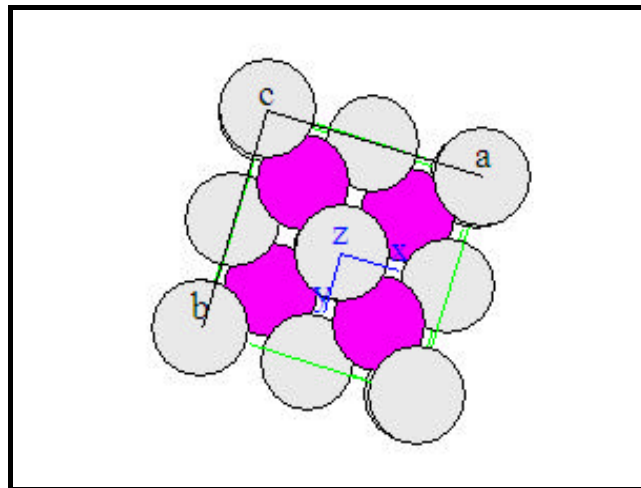
Diamond has long been known as a precious gem and for centuries has been sought after for its great beauty. But it is only relatively recently that its extreme properties and scientific usefulness have been noticed and studied.

Diamond has a cubic structure (shown in Figure 1.1) comprising of purely carbon-carbon  $sp^3$  bonds. This structure is extremely strong and rigid. This gives diamond two of its most extreme properties; its extreme hardness (a Knoop hardness of  $7000 \text{ kg mm}^{-2}$  and a Moh's hardness of 10) and its extreme thermal conductivity ( $1000 \text{ W m}^{-1} \text{ K}$  at  $273 \text{ K}$ )<sup>1</sup>, which is four times that of copper. Diamond is resistant to chemical attack; it does not react with concentrated acids and most strong oxidising agents. Pure diamond is electrically insulating and has a band gap of around  $5.4 \text{ eV}$ , but can be doped to become a semiconductor<sup>2</sup>.

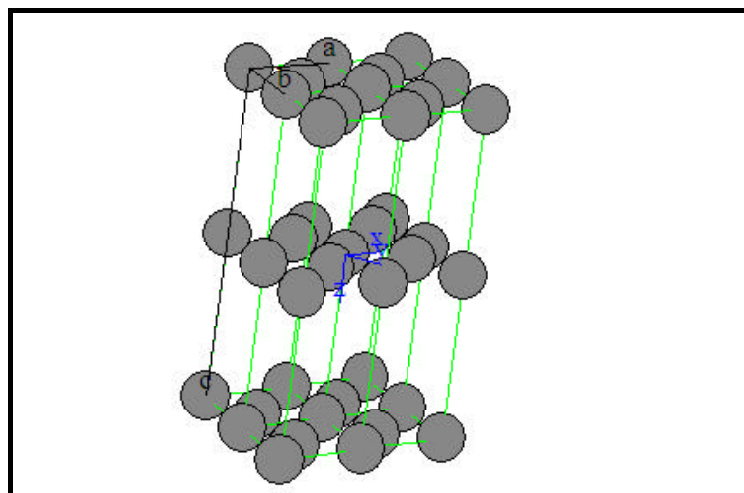
The other natural allotrope of carbon is graphite, which by comparison is very soft indeed (a Moh's hardness of  $0.5$ )<sup>1</sup> and electrically conducting. Its structure is

hexagonal (shown in Figure 1.2). The structure is layered. The graphite sheets are  $sp^2$  bonded and sheets bonded together with weak interlayer bonding (Van der Waals forces).

Interlayer bonding explains many of graphite's properties. For example, as the layers are weakly bonded, the sheets easily slide past each other. This allows graphite to act as a solid-state lubricant. The interlayer bonding is also responsible for graphite's electrical conductivity.



**Figure 1.1: Cubic structure of diamond, a, b, c, x, y and z are the axes, the grey and pink spheres represent different layers**



**Figure 1.2: Layered graphite structure**

Diamond and graphite have similar standard enthalpies (the difference between them is only  $2.9 \text{ kJ mol}^{-1}$ ), but the activation barrier between them is very large (see Figure 1.3). A survey of how nature produces diamonds shows how this barrier is overcome. Gemstone diamonds are usually mined from deep within the Earth, they are found in Kimberlitic deposits from ancient volcanic pipes. These occur mostly in the continent of Africa. Diamonds are also found on the ocean floor off the Cape of Good Hope. Microscopic diamonds are also found naturally in some meteorites that have landed on Earth<sup>3</sup>.

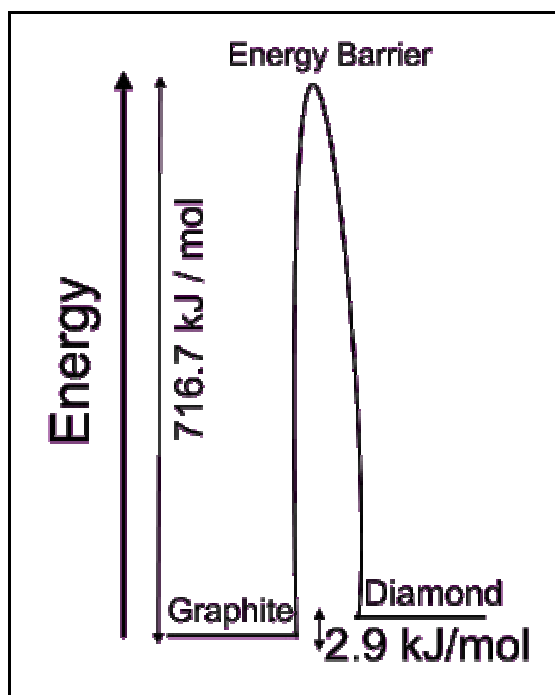


Figure 1.3: Energy level diagram for the transformation between graphite and diamond <sup>1</sup>

All these natural production methods are reliant on extreme conditions of temperature and pressure. The phase diagram in Figure 1.4 shows the extremes of temperature and pressure required to form diamond. When synthetic diamonds were first produced the process conditions mimicked the conditions under which diamond was made naturally. The General Electric Company developed the High Pressure, High

Temperature (HPHT) method of producing industrial diamonds and published it in the 1950s<sup>4</sup>. They used a hot hydraulic press, which compressed graphite to thousands of atmospheres and heated it to thousands of Kelvin in the presence of a metal catalyst.

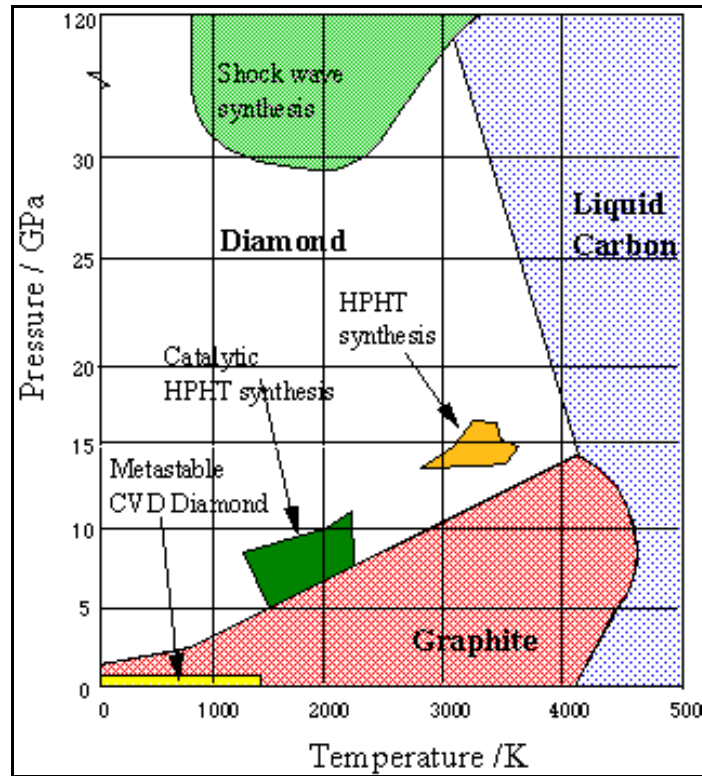


Figure 1.4: Phase diagram for carbon<sup>5</sup>

Recently Yang *et al*<sup>6-9</sup> developed a method of creating nanometre sized diamond crystals. A graphite target was ablated with a laser under various oxygen containing solvents. This method will be discussed in more detail in chapter 2.

The diamond produced by these methods consisted of single crystals with sizes ranging from nanometres to millimetres. Even though the larger sizes are suitable for applications such as cutting tool tips, applications are limited with diamond produced

by this method. Other methods include explosive detonation synthesis, which uses the products and conditions of a confined explosion to create diamond<sup>10</sup>.

In order to exploit some of the other properties of diamond, a way of making large single crystals or continuous films of polycrystalline diamond was needed. In order to do this the Chemical Vapour Deposition (CVD) of diamond was developed. In CVD, gas precursors are activated either by a hot filament or by a plasma. The diamond grows on a substrate such as silicon, or molybdenum. The diamond network is built up atom by atom, by surface species. The gas mixture is such that non-diamond (graphitic, or amorphous) carbon is preferentially etched away, this was first done by atomic hydrogen in  $\text{CH}_4 / \text{H}_2$  gas mixtures. Several gas mixtures have been developed in order to make good quality diamond ( $\text{CH}_4/\text{H}_2$ ,  $\text{CH}_4/\text{CO}_2$ , for example), yet maintain a reasonable growth rate. A schematic diagram of the CVD deposition of diamond is shown in Figure 1.5.

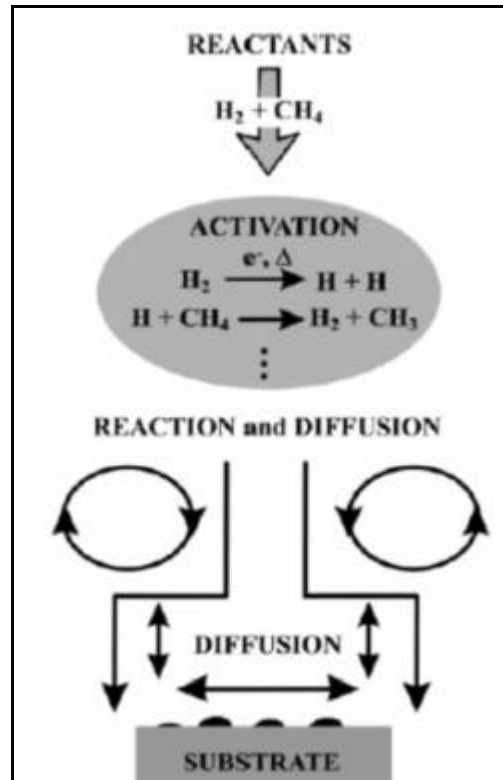
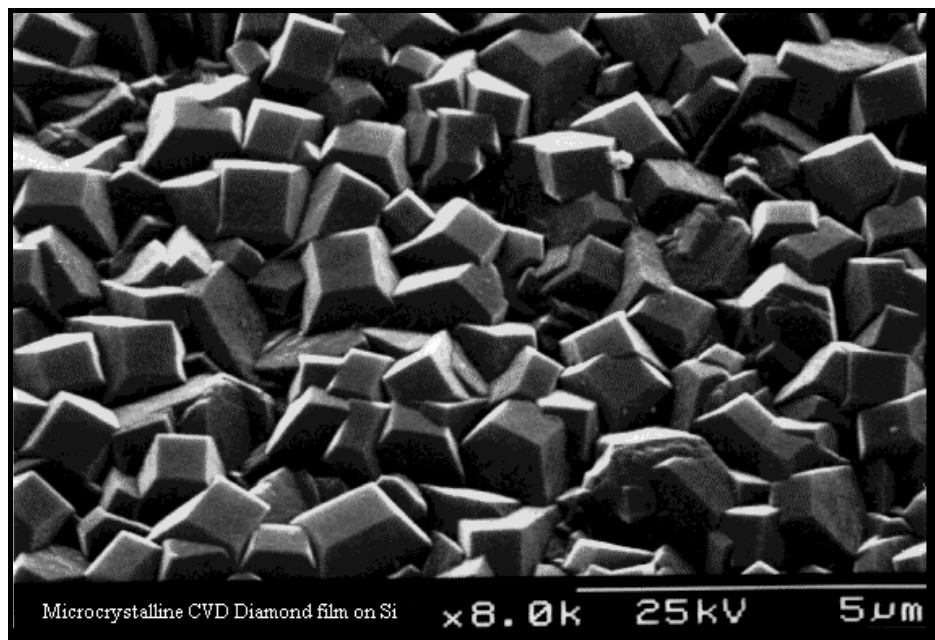


Figure 1.5: A schematic diagram of the CVD process<sup>11</sup>.

The substrate temperature is also important, as the high surface mobility of incoming species is essential, growth requires a high temperature that allows the surface chemistry that creates diamond to occur. Currently the limit to good quality diamond growth temperature is  $>500\text{ }^{\circ}\text{C}$ , which determines the materials onto which it can be deposited. The substrate material is also very important, for good film adhesion a thin carbide layer must be formed, but the carbide layer must be thin and must not diffuse into the substrate material. The substrate material must also have a high enough melting point, so that the substrate can survive the high temperatures required to grow diamond films.

Diamond films grown by this method are usually polycrystalline (heteroepitaxial growth), but under certain conditions they may be grown on existing crystals of diamond and add to the single crystal of diamond (homoepitaxial growth).

A photo of a typical CVD diamond film is shown in Figure 1.6. The crystal facet size can be adjusted with gas mixture, for example addition of small amount of nitrogen to the gas mixture increases crystal facet sizes dramatically, but too much nitrogen causes rapid degradation of the quality of the diamond grown.



**Figure 1.6: A typical CVD diamond film<sup>5</sup>.**

### **1.1.2 Uses of Diamond**

The extreme properties of diamond mean that it has many uses and potential uses. The most obvious property is diamond's hardness. For years diamonds have been used in specialist machining applications, as the cutting edge of specialist drills and used as blades in ultramicrotomy. Diamond grit is also used as an abrasive.

The high thermal conductivity of diamond means that it can be used in heat sink components. A more lucrative property of diamond is its ability to act as a

semiconductor when doped. Diamond-based electronics could potentially offer everything that silicon currently offers as well as excellent heat conduction. This could potentially mean that CPUs in computers could become faster as one of the major limiting factors in CPU speed is the heat transport problem.

The high thermal conductivity of diamond has already seen use in several specialist applications, Element Six (previously De Beers Industrial Diamond Division) have developed a range of diamond windows that have seen a number of uses including in an experimental fusion reactor.<sup>12</sup>

Diamond also has effectively a negative electron affinity value, which means that electrons are readily emitted from diamond if it is biased negatively in a vacuum. This means that diamond may be an effective field emission material and may have potential uses in display devices.<sup>13</sup>

### **1.1.3 The Doping of Diamond**

In order for diamond to be used for electronic and optoelectronic applications it must be suitably doped. The *p*-type doping of diamond is relatively simple, boron is usually used as the dopant. Boron acts as an effective acceptor and fits well into the diamond lattice<sup>14</sup>.

The *n*-type doping of diamond has been found to be more problematic. Several attempts have been made to *n*-type dope diamond, but they have had limited success. The dopants either donate into too deep a level, or do not fit well into the diamond lattice. Donors that have been tried have included nitrogen<sup>15-23</sup>, phosphorus<sup>24-31</sup> and



sulfur<sup>32-37</sup>. Doping with nitrogen creates a donor level that is too deep. Sulfur and phosphorus are not easily incorporated into the diamond lattice and cause distortions. Recently the co-doping of diamond with boron and sulfur has been investigated<sup>38</sup>.

Even though difficulties exist there have been some effective electronic devices fabricated based on diamond. Butler *et al* have fabricated Schottky Diodes<sup>39</sup> and Koizumi *et al* have fabricated a light emitting diode from a phosphorus/boron doped diamond *pn*-junction<sup>40</sup>.

## **1.2 Diamond Like Carbon**

### **1.2.1 Introduction**

The name Diamond Like Carbon (DLC) describes a group of materials that are amorphous carbon networks with structures and properties resembling that of diamond. They can be hard films, with a high degree of  $sp^3$  bonding, or softer films with less  $sp^3$  bonding.

There are three main types of DLC that have been classified:<sup>41</sup> Firstly tetrahedral amorphous carbon (ta-C). This classification describes a carbon film that has a very high degree of  $sp^3$  bonding. Secondly hydrogenated tetrahedral amorphous carbon (ta-C:H). This classification describes a carbon film as above, but including hydrogen in the structure. Finally hydrogenated amorphous carbon (a-C:H) is as above, but with a much lower degree of  $sp^3$  bonding. Figure 1.7 shows the relationship between

the degrees of  $sp^3$  bonding,  $sp^2$  bonding and hydrogen content against the classification.

There are several practical advantages of DLC over diamond. For example DLC can be smooth on the nanometre scale, but can have a hardness approaching that of diamond. It can be deposited at room temperature, which means that the range of materials it can coat is greatly increased. By controlling the deposition conditions the optical properties of DLC can be changed.

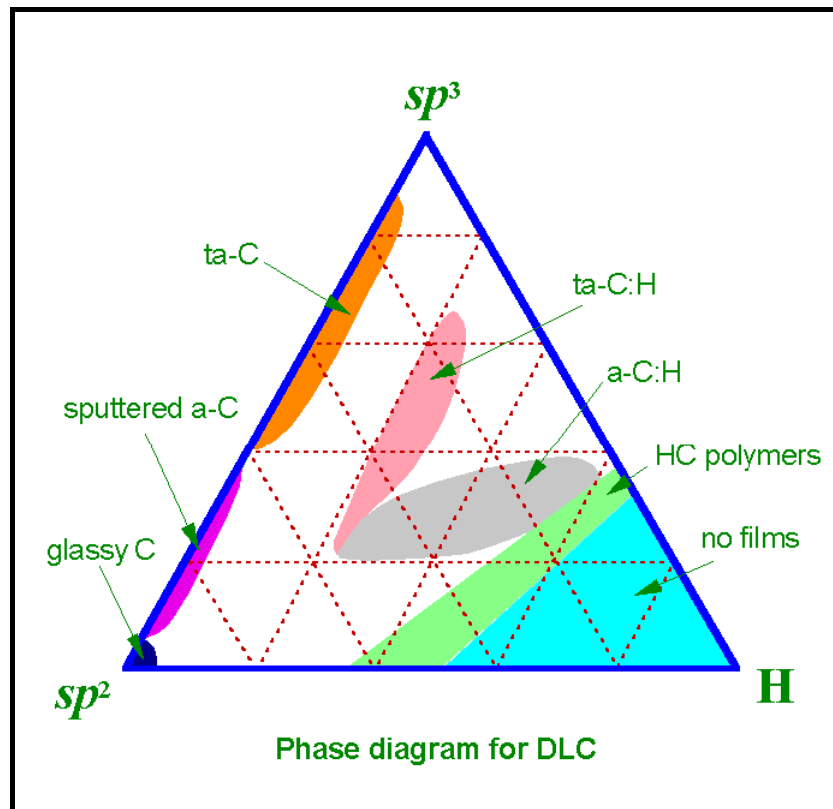


Figure 1.7: The phase diagram for the classification of DLC <sup>42</sup>.

### 1.2.2 Uses of DLC

Currently DLC is used commercially in wear resistant coatings. For example DLC coated hard disk read/write heads have been developed<sup>43</sup> and Gillette have used DLC coatings to improve the performance of razor blades. Recent cutting edge

developments take advantage of the high degree of biocompatibility that this material exhibits. DLC has seen use in medical implants such as prosthetic heart valves<sup>44</sup> and as wear resistant coatings for joint replacements<sup>45,46</sup>.

Currently applications are also being developed for using DLC in electronic devices, but in order to do that DLC must first be doped.

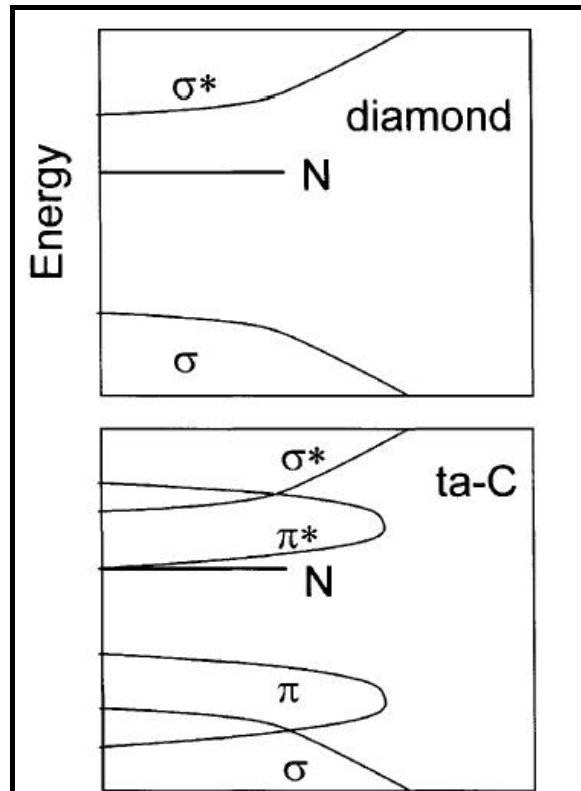
### 1.2.3 The Doping of DLC

Due to its attractive properties it has long been thought that DLC may be a useful electronic material. In order for it to be used electronically it must be doped as both *p*-type and *n*-type. Whilst *p*-type doping has been found to be relatively easy, *n*-type doping is proving a lot more troublesome.

*p*-type doping is usually carried out with boron<sup>47</sup>. Boron acts as a good acceptor and is well incorporated into the structure of DLC, analogous with the case in diamond. It is also well known that ta-C is slightly *p*-type in character<sup>48</sup>. It is thought that this is due to the high density of defects within the material which create vacancies.

Again, like diamond the *n*-type doping of DLC is more troublesome. There have been many studies of nitrogen as an *n*-type dopant<sup>49-51</sup>. In theory, the donor level should not be so deep as in diamond as DLC has a significantly smaller band gap than diamond (ta-C has a maximum band gap of around 2.2 eV compared to diamond which has a band gap of around 5.4 eV), illustrated in Figure 1.8. This means that the nitrogen donor level would lie closer to the conduction band. However as with all amorphous semiconductors, there is no rigid structure in the “lattice” and dopants are

free to exhibit preferred modes of chemical bonding that may not aid in semi-conduction. For example, in the case of nitrogen, it is energetically favourable to form trivalent bonds that do not contribute to the film semiconduction.



**Figure 1.8:** Schematic of levels in nitrogen doped diamond and ta-C <sup>41</sup>. The levels marked with N are the donor level that is created by doping with nitrogen

One of the main driving forces behind the study of nitrogen incorporation into DLC is because it is thought that this may be a possible way of making carbon nitride (see Section 1.3).

Phosphorus is another possible *n*-type dopant for DLC that has been studied, but, to date, there have been few reports published. In 1993 Veerasamy *et al*<sup>52</sup> incorporated up to 1% P into DLC (ta-C) films produced by a filtered cathodic arc method using a red phosphorus-doped carbon cathode. They found that P addition reduced the

resistivity of the films by 6–7 orders of magnitude, with no apparent change to the amorphous nature of the carbon films.

Capacitively-coupled radio frequency (RF) plasma deposition has been used to produce P-doped DLC films using  $\text{PH}_3$  as a dopant gas, producing films with P contents estimated to be ~11 %<sup>53,54</sup>. These films also showed increases in room temperature conductivity of nearly five orders of magnitude. Golzan *et al.*<sup>55</sup> showed that when films were doped with ~3% P, the dopant destabilised the tetrahedral network in favour of an  $\text{sp}^2$  bonded network.

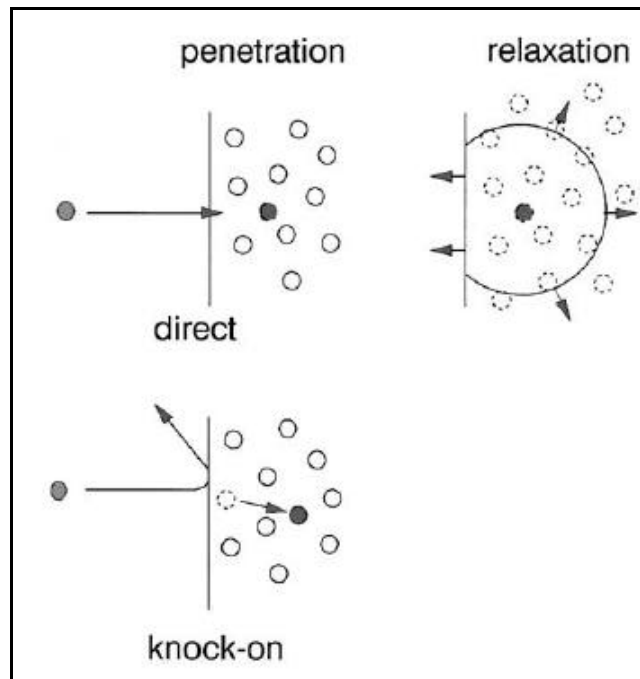
Kuo *et al.*<sup>56</sup> in the University of Bristol CVD Diamond Group studied the effect of doping DLC with larger amounts of phosphorus. He found that more phosphorus was being incorporated into the DLC as more phosphorus containing gas was added to the process gas mixture. He analysed the optical and chemical nature of the films and it was found that the films contained large amounts of phosphorus. This study is discussed in more detail in Section 1.3.

Recently the *n*-type doping of DLC with sulfur has started to be investigated<sup>32</sup>, but to date no conclusive reports of how successful this is have been published.

#### **1.2.4 The Deposition of DLC**

The methods by which DLC can be deposited are wide and varied. They all have one thing in common deposition is a physical rather than a chemical process (as is the case for CVD diamond deposition). Good quality DLC is grown using medium energy ions (~100 eV)<sup>57,58</sup>, building up the film by sub-surface implantation (subplantation)

either by the ion penetrating through the surface of the film, or by an ion knocking a surface atom into a subsurface layer. This causes a thermal spike that lasts significantly longer than the vibrational period of a molecule, allowing bonding to occur. Then a relaxation of this thermally excited state occurs<sup>42,59</sup> favouring the diamond-like structure. This process is illustrated in Figure 1.9.



**Figure 1.9: An illustration of the subplantation process<sup>41</sup>**

If the ion energy is too low, polymeric films are formed which are of very poor quality. If the energy is too high, deposited material is sputtered from the film and the growth mechanism cannot occur effectively. Figure 1.10 shows the quality of the DLC produced (measured by the density of the film) against the ion energy of the incoming growth species, showing that an impact energy of ~100 eV is optimum for producing the best DLC films.

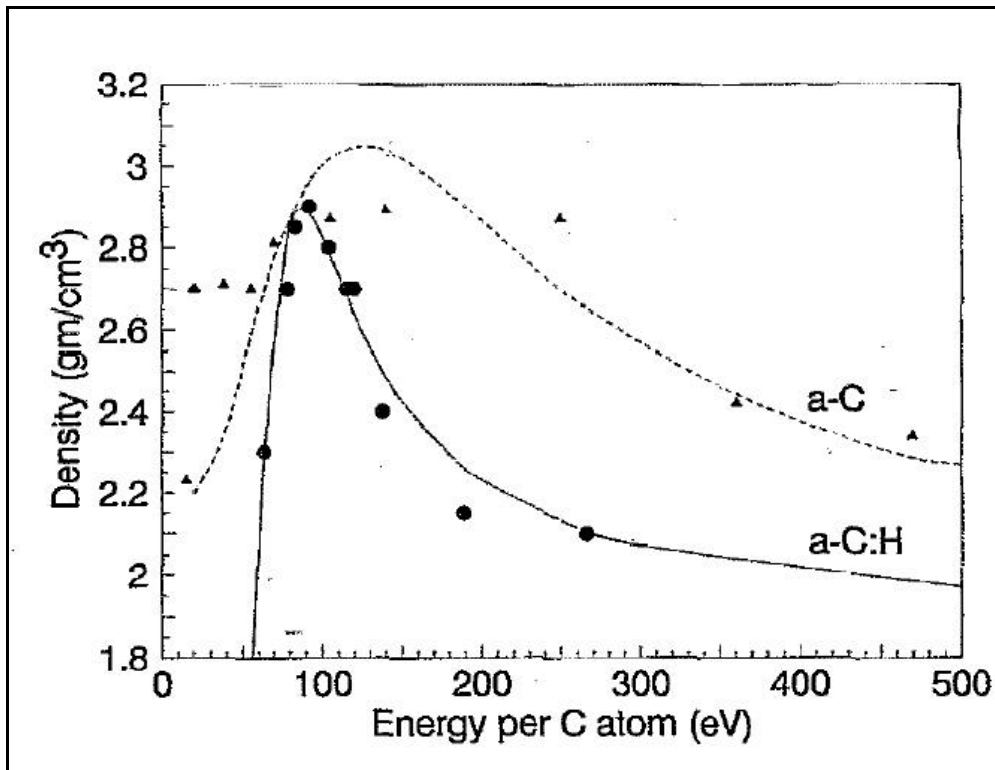


Figure 1.10: Graph showing the quality of DLC against the growth species ion energy<sup>58</sup>.

The most popular deposition techniques can be categorised into five groups; ion beam methods, pulsed laser ablation deposition, plasma enhanced deposition, cathodic arc deposition and sputtering. The final use of the DLC films determines which method is used for deposition. Figure 1.11 illustrates a number of these deposition methods.

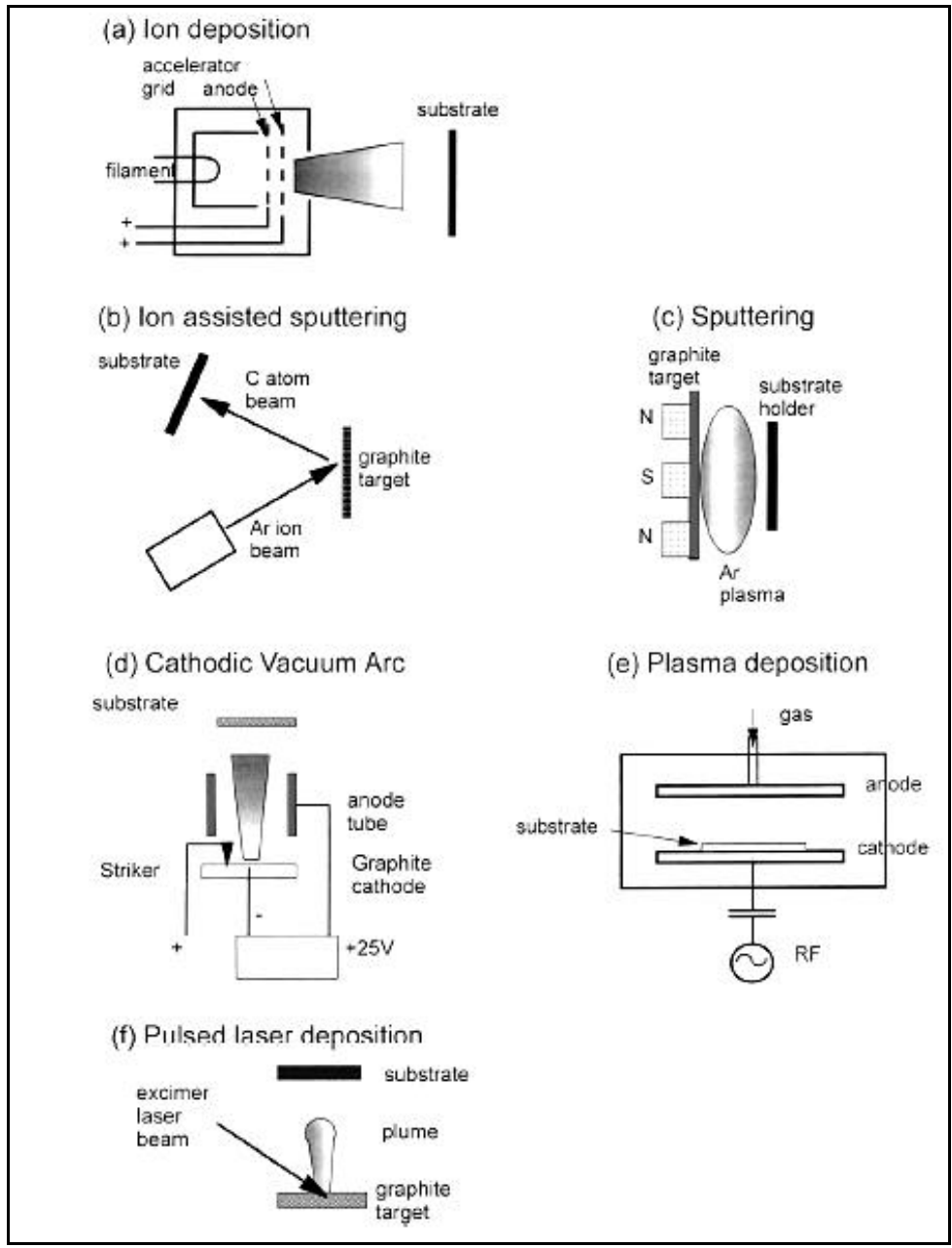


Figure 1.11: The most common systems used to deposit DLC<sup>41</sup>.

**1.2.4.1 Ion Beam Deposition Methods (Ion Deposition and Ion Assisted Sputtering)**

The first ever DLC films were deposited using the ion beam deposition method by Aisenberg *et al* in 1971<sup>60</sup>.



In ion beam deposition there are two methods that use different ion sources, those made in the gas phase and those created by the sputtering of a solid target. In the case of DLC a suitable gas phase ion source would be from the ionisation of methane. Under a bias the ions are then extracted into a beam. A suitable solid phase ion source would be a graphite target. The ions are liberated by collision with argon ions. The ions are then extracted into a beam, which is then accelerated onto a substrate surface to deposit the DLC film.

Ion beams are of great use for growing films with a great deal of control of process parameters. A variation of this method is the Mass Selected Ion Beam, where the beam is passed through a magnetic field and only ions within a certain mass and energy range are used for deposition. Ion beam deposition is usually used for research purposes as deposition is slow and apparatus is expensive.

#### **1.2.4.2 Sputtering**

In sputtering, a graphite or other carbon containing target is sputtered (material knocked off from it – usually atoms, but also larger clusters) using a plasma (usually argon) and this material is deposited directly onto the substrate<sup>61</sup> (unlike the similar ion beam method where ions are extracted into a beam). To improve the sputtering rate from graphite, magnets are placed behind the target. This causes electrons to spiral and increases their path length and hence the degree of ionisation. Applying a DC bias to the substrate controls the ion energy.

This method does not offer the precise control that an ion beam offers, but deposition is fast and can be scaled up to cover large substrates. This makes it ideal for use in industry.

### **1.2.4.3 Cathodic Vacuum Arc**

In this method an arc is struck between a graphite cathode and a striker. When the arc is initiated the striker is withdrawn, but the plasma remains stable. This plasma generates ions that can be used for deposition. It also produces clusters and particulates.

A variant of this method the Filtered Cathodic Vacuum Arc (FCVA) uses magnetic fields to direct charged materials (i.e. materials in the plasma) towards the substrate, but this magnetic field does not direct the particulates towards the substrate, effectively filtering them out.<sup>62</sup>

FCVA is used industrially as it has high growth rates and also as the plasma beam is neutral, so deposition onto insulating substrates is easy.

### **1.2.4.4 Plasma Enhanced Deposition**

In this method, deposition is achieved from the products of a plasma produced by the ionisation of a gas flowing between two electrodes that have Radio Frequency (RF) power applied to them. In sheath regions close to the electrodes (which have a net negative charge compared to the rest of the plasma) positive ions are accelerated towards the substrate. Most deposition systems have unequal electrode sizes, this

creates a negative DC-bias. The negative DC-bias accelerates positive ions towards the substrate<sup>63</sup>.

This method is used extensively to grow *a-C:H*, *ta-C:H* and type films. *a-C* films can be grown if the ion energy is large enough to sputter away light hydrogen atoms in the DLC structure.

This method is discussed much more extensively in chapter 2.

#### **1.2.4.5 Pulsed Laser Deposition**

In pulsed laser deposition a solid target such as graphite is heated with a pulsed laser beam. This causes the material to evaporate and expand rapidly into an 'ablation plume'. This ablation plume contains ionised material from the solid target. This then impinges onto the substrate and deposits<sup>64</sup>. This method is useful in research as its conditions can be precisely controlled, but it is limited commercially as the growth rates are low and the deposition area is low.

An emerging technique is the pulsed laser deposition under a hydrocarbon liquid such as cyclohexane<sup>65,66</sup>. This method is discussed in more detail in chapter 2.

In conclusion DLC is a unique and versatile material, with many everyday applications that have already been realised, but it is still having new potential uses exploited.

## 1.3 Carbon Nitride

### 1.3.1 The Properties of Carbon Nitride

In 1989 Liu *et al* conducted a set of calculations that concluded that carbon nitride may have similar or superior properties to diamond<sup>67</sup>. They calculated that the bulk modulus of one of the possible crystalline forms of this material might be similar to or harder than diamond. They also calculated that as the structure was rigid, as in diamond, it might have similar or superior heat conducting properties to diamond<sup>68</sup>. In 1994 Lui *et al* then calculated what the stable form of carbon nitride would be<sup>69</sup>. They found that the  $\beta$ -C<sub>3</sub>N<sub>4</sub> structure and the graphite-like rhombohedral C<sub>3</sub>N<sub>4</sub> structures (shown in Figure 1.12 and Figure 1.13 respectively) were most energetically favourable.

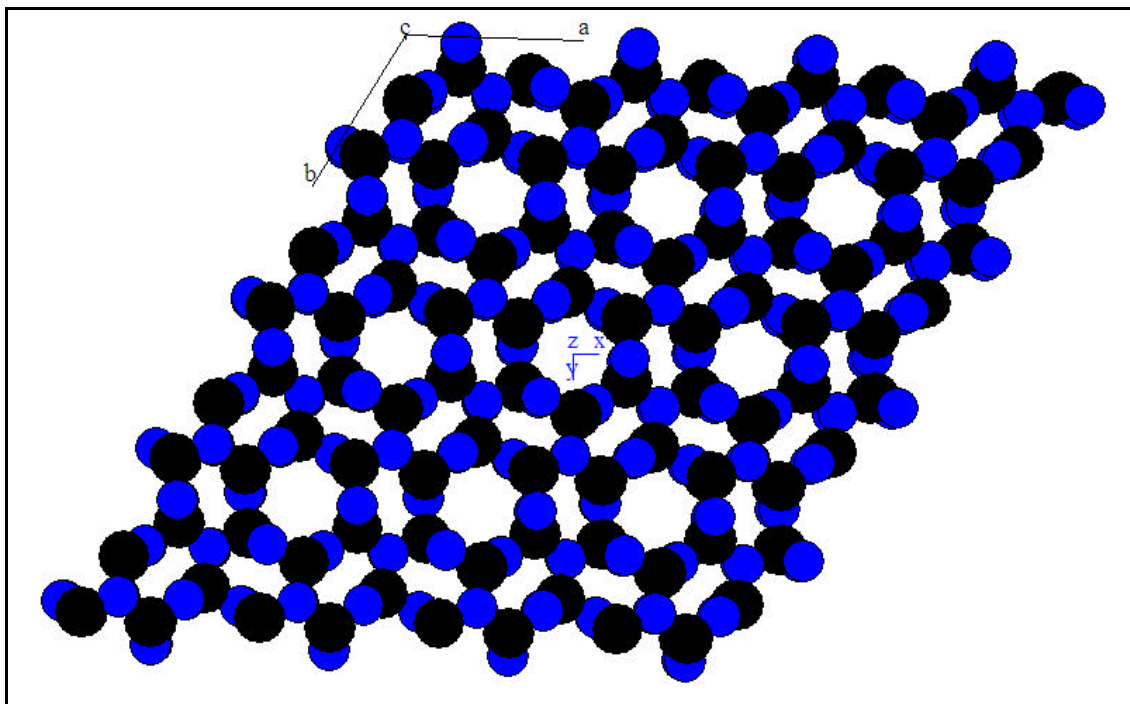
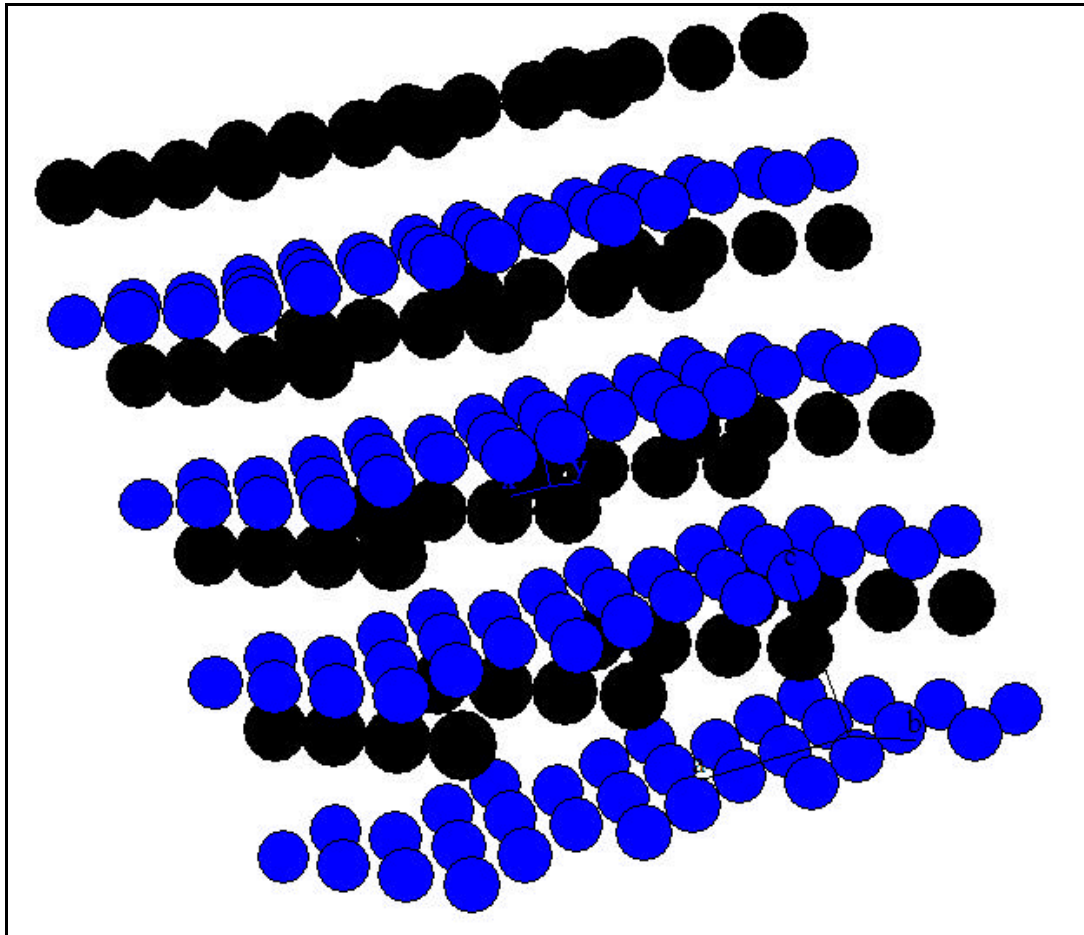


Figure 1.12: The structure of  $\beta$ -C<sub>3</sub>N<sub>4</sub> suggested by Lui *et al*<sup>69</sup>. The black spheres represent carbon atoms, the blue spheres represent nitrogen atoms.  $x$ ,  $y$  and  $z$  are the axes,  $a$ ,  $b$  and  $c$  represent the dimensions of one unit cell.



**Figure 1.13:** The graphite-like rhombohedral phases of  $C_3N_4$  calculated by Liu *et al*<sup>69</sup>. The black spheres represent carbon atoms, the blue spheres represent nitrogen atoms.  $x$ ,  $y$  and  $z$  are the axes,  $a$ ,  $b$  and  $c$  represent the dimensions of one unit cell.

A zinc-blende type structure was also suggested, but it was not found to be as energetically stable as the above.

In 1996 Teter *et al* calculated an  $\alpha$ - $C_3N_4$  structure and found it to be more stable than  $\beta$ - $C_3N_4$ , it was also found that the graphitic form shown above was more energetically favourable than  $\beta$ - $C_3N_4$ . A cubic structure (which was energetically stable at high pressures) was also calculated and it had a bulk modulus exceeding that of diamond.<sup>70</sup>

More recently several other structures of carbon nitride have been studied; monoclinic, triclinic and paracyanogen-like forms of CN, rhombohedral  $C_5N_4$  graphite-like  $C_5N$ , cubic and monoclinic  $C_4N_2$  and nanotubes.

### 1.3.2 Production of Carbon Nitride

The first report of a compound containing only carbon and nitrogen was by Guy-Lussac who discovered the existence of paracyanogen ( $C_2N_2$ ). It was described as 'a troublesome by-product'<sup>68</sup> of several reactions involving cyanogen. It was a polymeric solid that was very difficult to dissolve.

In 1979 Cuomo *et al* produced amorphous carbon nitride films with a polymeric structure by sputtering a carbon target in an atmosphere of nitrogen<sup>71</sup>. The films that were produced had approximately a 1:1 ratio of N:C.

It was not until Liu *et al*'s publication in 1989 that the production of carbon nitride films became a widely studied area of science<sup>67</sup>. Since then many groups have attempted to prepare crystalline carbon nitride with varying degrees of success.

The first report of crystalline carbon nitride was from Chen *et al* in 1992<sup>72,73</sup>. They produced nanometre crystals of carbon nitride ( $C_3N_4$ ) by reactive magnetron sputtering. The films had a N:C ratio of up to 0.4:1. The films were found to be smooth, they had a high resistance to wear and a coefficient of friction comparable to diamond. Unfortunately the crystals were dispersed in an amorphous matrix. There were no crystal structure details due to "rapid amorphization of these crystallites

under a focused electron beam". In 1994 Yu *et al* reported the production of  $\beta$ -C<sub>3</sub>N<sub>4</sub> by RF-sputtering (the plasma was produced by an RF discharge in N<sub>2</sub>, this sputtered from a graphite target above the substrate)<sup>74</sup>. They reported and presented selected area electron diffractions patterns that supported this claim. Again the nanocrystals were dispersed within a large amount of amorphous material. Since then there have been several other reports of nanocrystalline carbon nitride materials with various structures. All reports are of amorphous material with small nanocrystals dispersed within them. Recently Yang *et al* have claimed to produce carbon nitride crystals by the laser ablation of graphite under ammonia solution<sup>75</sup>.

In conclusion whilst there has been a lot of recent research the most significant result is that some nanocrystals of carbon nitride have been produced, but they are not large enough, or have not been produced in a large enough quantity to be of any significant use.

Theoretical studies have shown that there are many potentially stable forms of carbon nitride. Experimentalists must make bulk materials for the full potential of carbon nitride to be realised.

## **1.4 Carbon Phosphide**

### **1.4.1 Introduction**

The production of and study of carbon phosphide is new, but it may be a material with interesting and lucrative properties.

### **1.4.2 The Properties of Carbon Phosphide**

A survey of the most useful or potentially useful materials around today shows many of them are binary compounds made from two elements in the same area of the periodic table. For example, gallium arsenide (GaAs) has been used for many years in light emitting diodes (LEDs) as the material that emits red light. Gallium nitride (GaN) is a relatively new material that has allowed the manufacture of blue and white LEDs. Boron nitride ( $B_4N$ ) is an extremely hard material that sees use as a component in aircraft gyroscopes. Silicon nitride ( $Si_3N_4$ ) is used as an etch resistant layer in integrated circuit (IC) fabrication. Carbon nitride as discussed in the previous section has several interesting properties. Indium phosphide (InP) is used in ultra-fast computer chips.

From looking at the properties of these materials and other similar materials an idea of the properties of carbon phosphide may be estimated. Figure 1.14 shows the estimated band gap and hardness of carbon phosphide if it followed the trend of other similar materials. It was indeed these estimates of properties that motivated this research.



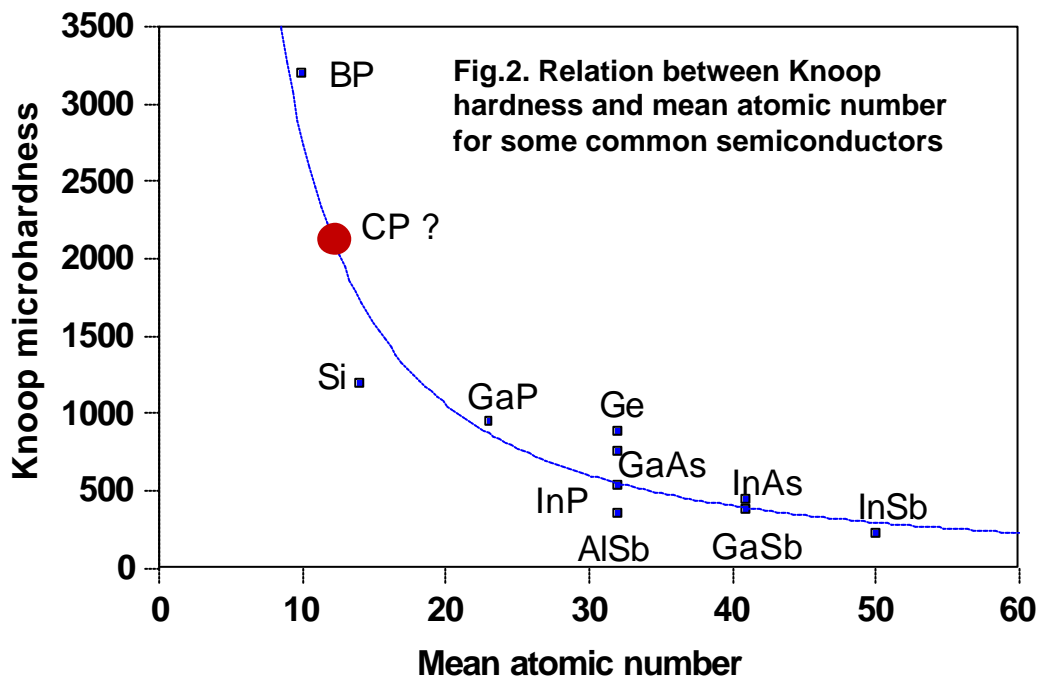
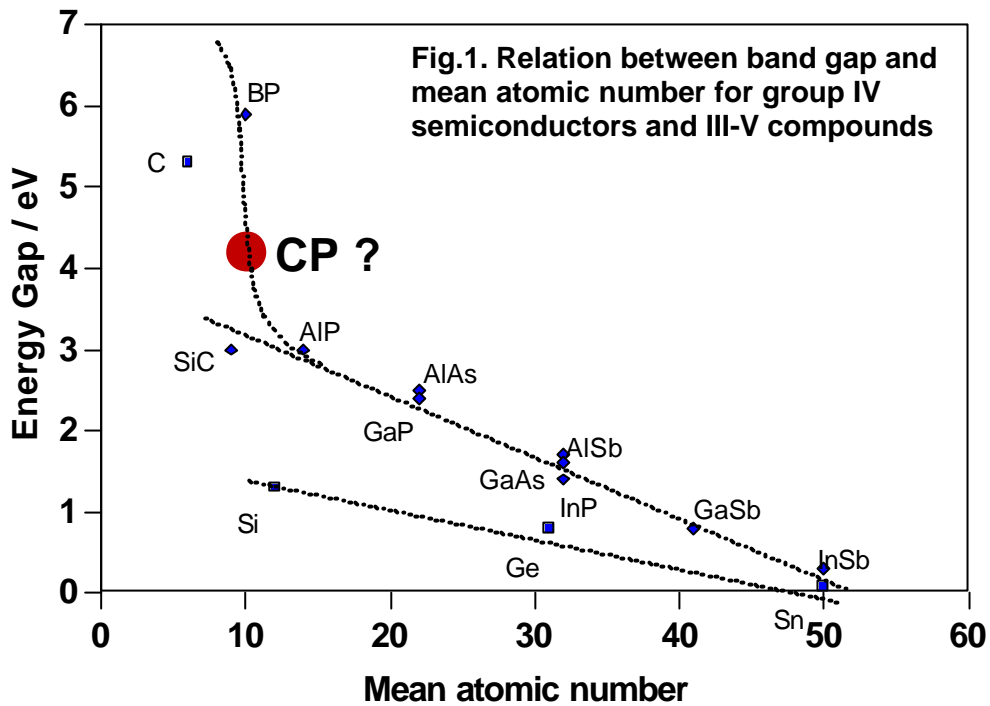
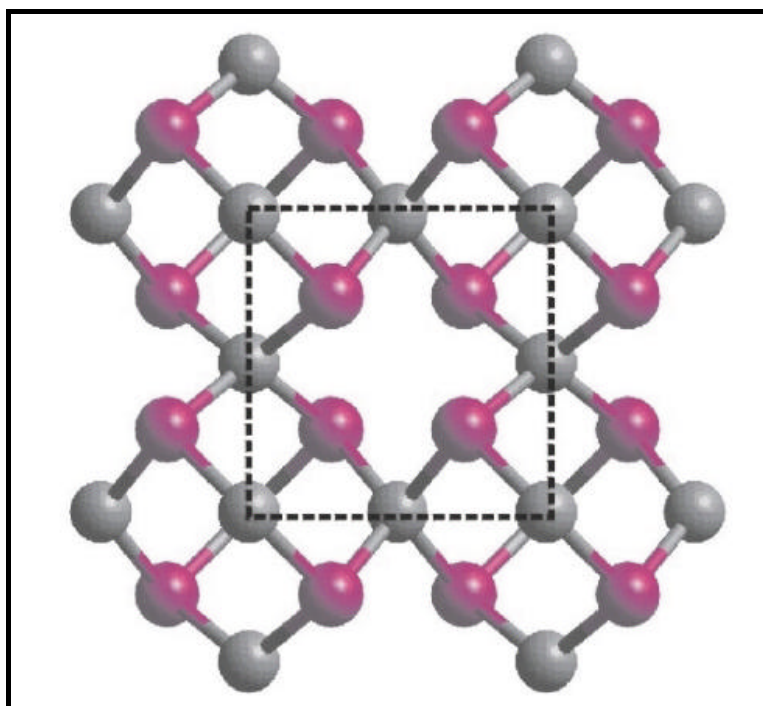


Figure 1.14: Estimate of the hardness and band gap that crystalline carbon phosphide may exhibit<sup>76</sup>.

So it can be seen that carbon phosphide may exhibit useful properties, but to date there have only been four theoretical studies published on this subject (two of which were carried out by this group during the course of this project). Claeysens *et al*<sup>77</sup> have calculated by density functional theory (DFT) that a stable form of carbon phosphide will have a cubic defect zinc-blende structure and will have the formula  $C_3P_4$ . The suggested structure is shown in Figure 1.15. They also calculated the bulk modulus and found it to be 158-161 GPa. This is approximately the same bulk modulus as for steel and is much lower than that for diamond (442 GPa) or that calculated for carbon nitride (448 GPa).

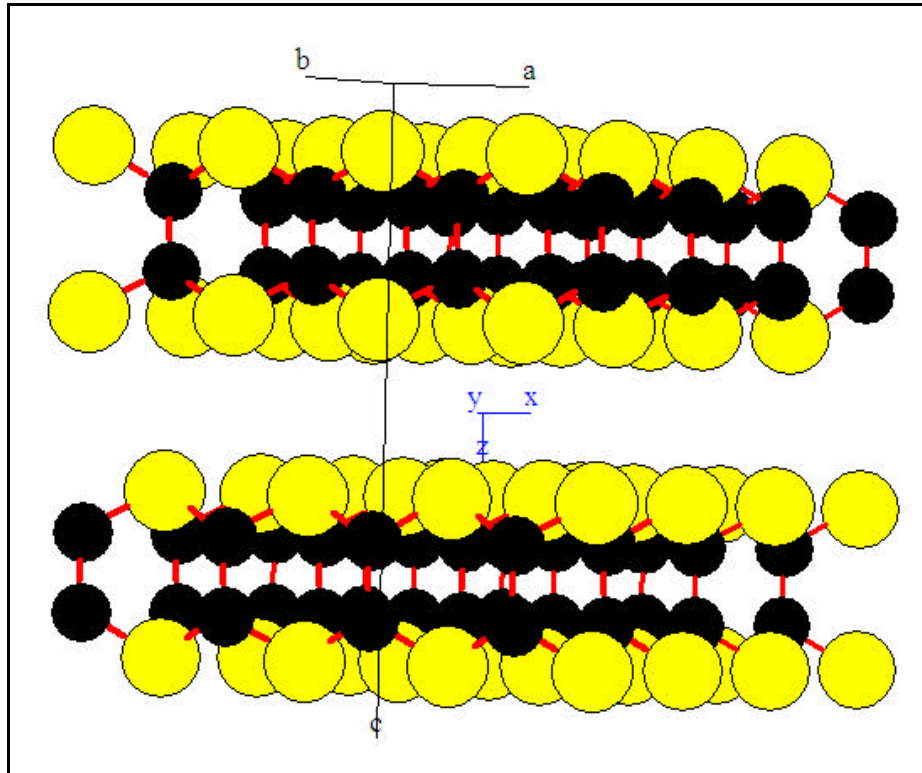


**Figure 1.15: The structure of carbon phosphide suggested by Claeysens *et al*<sup>77</sup>. The purple spheres are phosphorus atoms, the grey spheres are carbon atoms. The dotted line represents one unit cell.**

They also reported that the band gap of this material estimated by DFT was metallic. But when estimated by Hartree-Fock calculations even though the minimum energy structure agreed with the DFT calculations, the band gap calculations indicated an insulating state. They also called it phosphorus carbide; this was due to calculation of the Mulliken populations that showed that the electron density was attracted towards the carbon atom. In this experimental study the experimental group have always called it carbon phosphide. This is because the group are approaching it from the carbon based materials route.

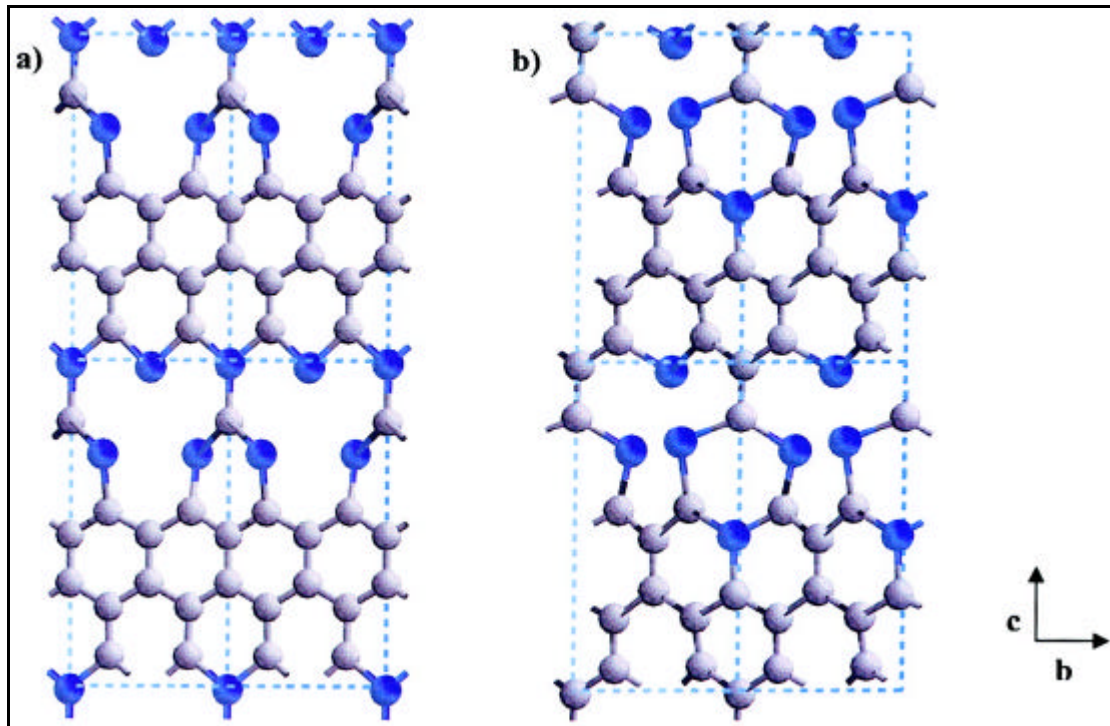
Lim *et al*<sup>78</sup> also calculated that the pseudo-cubic structure above was the most stable. They estimated that carbon phosphide would be a metallic conductor, although this study was not as extensive as the Claeysens *et al* study.

Zheng *et al*<sup>79</sup> have recently published a paper assuming that carbon phosphide would have the molecular formula CP. They found that in this stoichiometry a GaSe hexagonal type structure would be the low energy structure and it would have semiconductor properties with a direct band gap of 1.60 eV. They have estimated that the band gap of this form of CP (if it can be synthesised) may be slightly larger as it is well known that the method by which it was calculated underestimates the band gap.



**Figure 1.16: The GaSe like structure of CP proposed by Zheng *et al*<sup>79</sup>, the black atoms are carbon and the yellow atoms are phosphorus.**

Claeyssens *et al*<sup>80</sup> have recently published a study which investigates the structure of periodic phases of carbon phosphide (that is, carbon phosphide with the molecular formula  $P_4C_{3+8n}$ ). They found that unlike in their previous work with  $C_3P_4$ , the structures they calculated favoured a defect-graphite structure as opposed to a defect-zinc blende structure. A figure of this is shown in Figure 1.17.



**Figure 1.17: Two graphitic like phases of carbon phosphide periodic phases from Claeysens *et al*<sup>80</sup>. The grey spheres are carbon atoms and the blue spheres are phosphorus atoms. The dotted blue lines represent a unit cell.**

There is a lot of further theoretical research that is ongoing. But in conclusion carbon phosphide is predicted to exist in many low energy phases and have a number of interesting and useful properties.

### 1.4.3 Experimental Reports of carbon phosphide materials

In 1921 de Mahler *et al.* reported the synthesis of a new polymer<sup>81</sup>. This polymer was the first chemical compound to contain just carbon and phosphorus. The compound was reported to be a waxy solid that reacted violently in air and with hydrochloric acid. It was insoluble in the solvents available. It was produced by adding phosphorus trichloride to acetylene di-magnesium bromide. Since then there have been no reports of any stable compounds containing only phosphorus and carbon.

This result is controversial as there have been no reported successful confirmations of this experiment.

In 1997 Fisher *et al* reported the observation of stable carbon/phosphorus (for example  $CP^-$ ,  $C_2P^-$ ,  $C_3P^-$ , etc) cluster anions in the mass spectrometry of the gaseous products of a laser ablation<sup>82</sup>.

In 1999 Kuo *et al*<sup>56</sup> (in the University of Bristol CVD Diamond laboratory) doped DLC with large amounts of phosphorus. The films were produced using RF plasma enhanced deposition using  $CH_4$  and  $PH_3$  mixtures as the process gases, with  $PH_3$  concentrations of up to 21% by volume. This resulted in films which had P:C ratios of up to 0.9:1 and with such high P content that it was no longer valid to call these films 'doped DLC' – instead, they were termed 'amorphous carbon phosphide'. Micro-combustion analysis showed that the films still contained ~10% H and Secondary Ion Mass Spectrometry (SIMS) indicated that this H was distributed throughout the bulk of the film. Auger Electron Spectroscopy showed that the surface contained a high proportion of oxygen, suggesting that these films were air sensitive. Laser Raman Spectroscopy (LRS) established that the long-range order of the films decreased with increasing P incorporation. The optical band gap (measured by the Tauc plot method<sup>83</sup>) was found to be a complicated function of the P content of the film, but had a range between 2.3-3.4 eV.

The aim of the current project therefore, was to try to extend the work of Kuo *et al* and to produce DLC films with even higher P:C ratios. The ultimate hope was that if a stable stoichiometry for a C:P compound could be predicted (by the theoretical

group working alongside the experimental group) it might be possible to make a crystalline version of carbon phosphide and to analyse its mechanical and electronic properties.

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