Electronic properties of hydrogenated amorphous carbon thin films

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Abstract

This thesis is concerned with the growth, electronic properties and modification of hydrogenated amorphous carbon films of a thickness range of 50-300 nm, which have been deposited using rf plasma-enhanced chemical vapour deposition. These films may be subdivided into two types according to the electrode on which they are grown and the resulting film properties. These are polymer-like amorphous carbon or PAC, and diamond-like amorphous carbon or DAC.

PAC possesses a wide optical band gap (2.7 eV), high resistivity ($10^{14} - 10^{15} \, \Omega \, \text{cm}$) and low density of paramagnetic defects ($\sim 10^{17} \, \text{spins cm}^{-3}$). The dominant current transport mechanism at room temperature has been observed to be hopping conduction at low electric fields and space-charge-limited current at high electric fields. The addition of nitrogen gas to the plasma to incorporate nitrogen within the film has been shown to move the Fermi level by 1 eV, towards midgap. A mechanism of doping due to the introduction of aromatic nitrogen-containing sites has been postulated.

The boron, carbon and nitrogen ion implantation of PAC has resulted in the controllable increase in conductivity from $10^{15}$ to $10^{6} \, \Omega \, \text{cm}$ as a function of ion dose, from $2 \times 10^{12}$ to $2 \times 10^{15} \, \text{ions cm}^{-2}$. At low ion doses (up to $6 \times 10^{14} \, \text{ions cm}^{-2}$) this occurs without any change in band gap; however, at higher doses the band gap collapses as a result of graphitisation. The dependence on the implant ion shows that it is possible to move the Fermi level towards the valence band with the implantation of boron, and towards midgap with the implantation of nitrogen. A hysteresis effect is observed at intermediate ion doses, which is attributed to the trapping of holes resulting in an increase in electron current. Implanting part of the thickness of the film at this ion dose has resulted in rectification, which has not previously been reported for this type of structure in amorphous carbon.

DAC has been shown to possess a smaller band gap (0.7 eV), higher density of defects ($\sim 10^{20} \, \text{spins cm}^{-3}$) and lower resistivity ($\sim 10^{13} \, \Omega \, \text{cm}$) than PAC. The room-temperature current transport is governed by band-tail conduction at fields below $10^{5} \, \text{V cm}^{-1}$, and the Poole-Frenkel effect at higher fields. The addition of nitrogen of up to 8 at. % has been observed to increase the band gap from 0.7 to 1.0 eV and therefore decrease the magnitude of the Poole-Frenkel conductivity. The Fermi level remains pinned at midgap, however. Therefore, it appears that PAC shows advantages over DAC in terms of future device applications.
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1. *Electron delocalization in amorphous carbon by ion implantation*

2. *A review of the effects of carbon self-implantation into amorphous carbon*

3. *Amorphous carbon antireflection coatings for solar cells*

4. *Influence of sp$^2$ clusters on the field emission properties of amorphous carbon films*

5. *Ion implantation in hydrogenated amorphous carbon films*

6. *Photoluminescence in low defect density a-C:H and a-C:H:N*

7. *Tailoring of the field emission properties of hydrogenated amorphous carbon thin films by nitrogen incorporation and thermal annealing*
8. Studies of carbon self-implantation into hydrogenated amorphous carbon
   2000, Vol. 9, No. 3-6, pp. 675-679

9. Electronic conduction in ion implanted amorphous carbon thin films

10. Growth and characterisation of amorphous carbon films doped with nitrogen
    Grötschel and W. Möller, *Nuclear Instruments and Methods in Physics Research B*,

11. A study of the effects of nitrogen incorporation on the electrical properties of
    hydrogenated amorphous carbon films
    *Carbon*, 1999, Vol.37, No.5, pp.777-780

12. The microstructural dependence of the opto-electronic properties of nitrogenated
    hydrogenated amorphous carbon thin films
    1998, Vol.332, No.1-2, pp.118-123

13. Electron field emission from amorphous carbon thin films as a function of anneal­
    ing

Book Chapters

*Amorphous carbon thin films*

of Thin Films*, Academic Press, London (accepted for publication)
Chapter 1

Introduction

The most cited motivation within the semiconductor industry is the fabrication of smaller and faster silicon-based devices. Yet, there are several growing sectors which possess different objectives. A major economic concern within the semiconductor industry is the realisation of electronic materials which may be deposited over large areas. For comparison with the crystalline silicon industry, according to Intel, the largest silicon wafer size currently commonly in production is 300 mm in diameter. In the field of large area electronics, such diameters are easily and cheaply achievable in order to fabricate device arrays which are useful for a wide range of applications. At present several companies are processing 1 m² glass substrates for large area device applications.

There are several applications for which large area electronic materials are required, and probably the most potentially important is in the field of display technologies. Much of the current display market is based on the cathode-ray tube (CRT), which has existed for the past 70 years. Advantages include the brightness, contrast and comparatively low price of the CRT-based screen, however the technology is bulky and power inefficient. The existing competition is based on liquid crystal technology, which allows flat, thin panels to be produced. At present, for a display approaching the quality of a CRT, driver circuitry is required for each individual liquid crystal pixel which supplies a voltage in order to polarise them in one of two directions. Light would pass through the crystal according to its direction of polarisation. The driver circuitry would need to be deposited onto a glass substrate in order for the cell to be backlit.

The other application which is growing in importance is the thin-film photovoltaic solar cell, which requires light-absorbing and photoconductive materials which can be
1.1 Amorphous carbon as a semiconducting material

Amorphous carbon as a semiconducting material deposited onto glass substrates over areas in the range of m². The motivation behind this is the fact that global energy requirements are doubling every 25 years according to US Government sources, and the levels of carbon emissions caused by the burning of fossil fuels must be reduced in order to minimise the environmental impact due to global warming.

The current circuitry for both of these applications is based on a form of silicon which can be grown over large areas, namely hydrogenated amorphous silicon or a-Si:H. This is normally deposited using a process called radio-frequency plasma-enhanced chemical vapour deposition or rf-PECVD. This type of silicon is not cheap to produce as unstable and potentially hazardous precursors, namely silane (SiH₄), diborane (B₂H₆) and phosphine (PH₃) are required. Such materials must be manufactured from their naturally occurring sources and, following deposition, the exhaust emissions must be "scrubbed" in order to reduce the ecological impact. In an environmentally conscious sector such as the solar cell industry, such a high environmental pay-back may not be acceptable. The price of the precursors and handling also add to the cost of the product such that an a-Si:H thin-film-transistor (TFT)-based screen would cost significantly more than a screen which does not use this technology. A further disadvantage of a-Si:H-based technology is that in order to produce an electronic-grade material deposition must occur above a temperature of 250 °C which excludes substrate materials such as plastic. Therefore, there is a strong economic motivation for large-area semiconductors which may be deposited from cheap, non-toxic precursors at room temperature.

1.1 Amorphous carbon as a semiconducting material

A possible alternative to amorphous silicon is amorphous carbon (a-C) which may be deposited using a range of techniques. One of the most commonly investigated forms of a-C is hydrogenated a-C or a-C:H which is usually deposited using rf-PECVD. This has the specific advantage of using existing a-Si:H deposition procedures which would ensure industrial compatibility with the existing technology. In order to grow films using this method a carbonaceous precursor is required which permits the use of any hydrocarbon gas such as methane (CH₄), ethylene (C₂H₄) or cyclohexane (C₆H₁₂). These gases are inexpensive as they may be extracted from the fractional distillation of crude oil, and relatively non-toxic when compared with silane. Depositions may also be
performed at room temperature, which allows the utilisation of a range of substrates, including plastics. Should a carbon-based semiconducting thin-film be achieved, the potential market would be greatly enhanced through the wider range of applications and the reduced cost of the material.

A specific advantage of a-C-based materials is the ability to vary the properties of the film according to the deposition or post-deposition parameters. Carbon possesses three bonding hybridisations which give rise to the wide range of structures that may be created: $sp^3$ bonding as in diamond, $sp^2$ bonding which exists in graphite and fullerenes and $sp^1$ bonding which occurs in acetylene and cyanide. By varying the relative proportions of these configurations, the mechanical, optical and electronic properties may be greatly altered. Of special significance to this study is the ability to tune the band gap and resistivity, and hence the bulk electrical properties, of the material.

Other types of a-C are commonly studied, for example graphitic a-C and tetrahedral a-C or ta-C, which are also of interest in terms of their possible electronic applications. Graphitic a-C is commonly grown using sputtering which would ensure good compatibility with common industrial processes, but the material possesses a narrow band gap which would exclude its implementation as a semiconducting material. Ta-C requires elaborate deposition procedures such as pulsed laser ablation (PLA) or the filtered cathodic vacuum arc (FCVA), neither of which currently allow the deposition of thin films over large areas. Neither of these materials will be investigated in this study.

1.2 Project aim

The proposed aim of this study is to investigate the electronic properties of a-C:H as an electronic material, and to optimise these properties in order to produce a material suitable for the future production of electronic devices. This will be conducted by investigating various factors, such as deposition parameters and post-deposition processing, in order to determine their effect on the electronic properties of the material.

The method of investigation will be to fabricate simple a-C-based devices, for example metal-semiconductor-metal (MSM) structures, and to electrically test them in order to ascertain the important parameters in terms of carrier transport. This must be supported by other techniques in order to quantify other important properties of the
film. These include the film composition, thickness, optical band gap, refractive index, and defect density.

1.3 Outline of thesis

The preliminary part of this thesis will firstly review the theory of amorphous semiconductors in terms of the electrical properties. Much of the theory is derived from the well-researched fields of chalcogenide glasses, amorphous silicon and various dielectrics such as Al₂O₃ and SiO₂ but much would also be applicable to a—C. Secondly, the literature in the field of a—C will be reviewed, of which the majority of research has been performed on a—C:H and tetrahedral a—C (ta — C) thin films. As the doping of a—C is of paramount importance to any potential application as a semiconducting material, specific attention will be given to that topic. Following this chapter, an examination of the experimental techniques used in this study will be described. These include the methods of film growth, device fabrication, post deposition processing and film analysis.

The next three chapters will describe the electrical properties of a—C:H as deduced from this study. Chapter 5 will examine the electrical properties of the intrinsically grown material which is essential if the properties of the doped or ion-beam modified material are to be understood. Two forms of a—C:H will be examined in this study; polymeric a—C:H which will be denoted PAC and diamond-like a—C:H which will be denoted DAC. Both may be grown using the same deposition technique but there are very few studies in the literature which examine the electrical properties of PAC.

Chapter 6 will examine the effect of adding gaseous nitrogen into the plasma on the opto-electronic properties of the a—C:H films. This is of particular interest because nitrogen may have the effect of n—type doping a—C films. It is of paramount importance that this should be examined as there is some conjecture in the literature as to whether this is occurring or not in DAC films, or the effects are largely due to the graphitisation of the films. The effect of nitrogen addition on PAC has not previously been investigated.

Chapter 7 will investigate ion implantation as a method of doping and modifying PAC films. This well-established technique is utilised in the semiconductor industry to introduce dopants into a wide range of semiconducting materials. Its effect on the properties
of PAC films is of particular interest as the intrinsically grown material has the lowest
defect density of any form of amorphous carbon and therefore the effects of ion-beam
damage would be clearly observed.

Finally, Chapter 8 will draw the conclusions of this study into the electronic properties
of \( a-C \) and highlight the main findings. Some more avenues on which progress towards
devices which are useful to large area electronics will be identified.
Chapter 2

Theory

This chapter will outline the generalised theory of amorphous semiconductors. It has been shown that the disorder of an amorphous material results in deviations in the electronic properties when compared to the crystalline case. This allows a wide range of carrier transport mechanisms which apply to the amorphous but not the crystalline case. These may be divided into two regimes, namely low-field conduction and high-field conduction. Both regimes are of interest if the electrical properties of $a-C$ are to be understood and therefore both will be described in this chapter.

2.1 Electronic band structure of amorphous materials

Several texts describe the electronic structure and properties of amorphous semiconductors. The original models introduced by Mott and Davis [1] showed that amorphous materials exhibited short and medium range order but no long range order. Free electron theory shows that the band gap of a material is caused by its crystalline order [2]. Anderson described a model of the potential wells for an amorphous semiconductor, as shown in Figure 2.1 [1]. In general for a semiconductor the solution to the Schrödinger’s equation gives rise to a wavefunction for electronic states that is solved using the Bloch theorem. There is a constant phase difference between wavefunctions at different lattice sites due to the periodicity in crystalline semiconductors which have a $k$-space that extends throughout the crystal. Therefore, the wavefunction has a well-defined $k$ value defined by the $E - k$ relationship [2]. However, in the case of an amorphous material this relationship breaks down, as the potential of the lattice is non-periodic.
2.1. Electronic band structure of amorphous materials

For a crystalline semiconductor, there exists a band gap, caused by the broadening of the individual electronic states into well-defined bands, in other words an occupied valence band that is separated from an empty conduction band by a gap that is usually less than 3 eV. This is due to the formation of standing waves being set up in the periodic lattice, which results in the formation of allowed and forbidden bands in the $E - k$ diagram. However, in the case of an amorphous material, variations in the periodic potential due to variations in bond angle and length result in the sharp band edges found in crystalline semiconductors to be replaced by band tails, although as these bands are mostly influenced by short range order, amorphous materials do have a band gap [1].

In amorphous films there are states within the solid between the top of the valence band ($E_V$) and the bottom of the conduction band ($E_C$), as shown in Figure 2.2. However, these states are a consequence of the amorphous nature of the solid and hence are not extended throughout the solid. Therefore, states in the crystalline valence and conduction bands are known as extended states and states found within $E_C$ and $E_V$ in the amorphous material are known as tail states that are localised [1]. The mobility of carriers in localised states is much lower than in extended states [1]. The $E_C$ and $E_V$ lines shown in Figure 2.2 are known as the mobility edges. Also, the existence of trapping centres and defects introduce states within the band gap that can act to

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**Figure 2.1** Anderson model for the variation of the energy of potential wells in an amorphous material.
2.1. Electronic band structure of amorphous materials

pin the Fermi level. The tail states are crucial in the conduction process as even a small concentration will control the electronic properties due to them being closer to the Fermi level.

![Density of States plot for an amorphous material.](image)

**Figure 2.2** Density of States plot for an amorphous material.

In an amorphous material the Bloch theorem can only be used with a varying non-periodic potential function $V(r)$, whose disorder potential $\delta V$, though small, will tend to scatter electrons from one atom to another. Therefore, phase coherence is lost due to the disorder and as a result of the uncertainty principle there is a loss of momentum or $k$-conservation ($\Delta k \sim h/\Delta x \sim h/a_0 \sim k$) in electronic transitions due to the uncertainty in the interatomic ($\Delta x$) or scattering length $a_0$ [1]. The loss of $k$-conservation due to disorder gives rise to a number of very important properties in amorphous materials and emphasises the importance of the spatial location of the carriers which gives rise to the density of states. Electron and hole effective masses must be redefined as either tunnelling masses [3] obtained empirically or by simulation, as the usual curvature of the $E - k$ diagram cannot be used. Also, due to the disorder the carrier mobilities are decreased significantly due to frequent scattering which also causes localisation of the wavefunction. More importantly, due to the lack of momentum conservation, there is no distinction between direct and indirect band gaps in amorphous materials, with transitions allowed to occur whenever there is an overlap of states in real space.
2.2 Comparison with amorphous silicon

Amorphous silicon was first produced using evaporation or sputtering and it was found that the density of states (DOS) in the mobility gap was very high resulting in the pinning of the Fermi level. This prevented the doping of the material [4]. It was then found that amorphous silicon produced by the rf glow discharge of silane (SiH$_4$) had a reduced midgap DOS, allowing effective electronic doping by Group III or Group V elements [4]. It was suggested that hydrogen had the ability to bond to the dangling bonds and hence reduce the density of states in the middle of the gap [4]. However, the optimum atomic percentage of hydrogen was experimentally found to be 10%, which was at least two orders of magnitude higher than the amount required to satisfy all of the dangling bonds. Therefore, hydrogen also remained in molecular form in a–Si:H and the material was in fact an alloy. Disadvantages included instability problems due to the presence of hydrogen.

Intrinsic a–Si:H was found to be slightly n-type [4]. Therefore, the addition of boron to the film had the effect of initially lowering and then increasing the conductivity as the Fermi level moved through the middle of the band gap. Activation energy measurements showed an increase followed by a decrease for the same reason. The doping mechanism was not thought to be able to be simply substitutional because of the 8-N rule [1], which stated that all atoms (including dopants) in an amorphous network bond with their optimal valency. However, experimental evidence did show that substitutional doping was occurring for a–Si:H. Furthermore, the midgap DOS was shown by ultraviolet photoelectron spectroscopy (UPS) to increase with doping. It would be expected that light-induced EPR would also reveal the same result, but this was not the case as the movement of the Fermi level by doping caused defects to become doubly occupied and hence non-paramagnetic.
2.3 Low field conduction

Most authors use the measurements of conductivity and activation energy for describing the electrical characteristics of amorphous carbon [5]. These are commonly taken by measuring the resistance of the film by applying a voltage which results in a field strength of around $10^3$ V cm$^{-1}$. Generally, at this field the current is shown to vary linearly with voltage. Also, this magnitude of electric field is applicable for planar (gap-cell) contacts onto a thin film, as amorphous carbon is typically grown in the thickness range of 50-300 nm, which results in a higher electrical field if the electrical characteristics are measured in a sandwich structure for any appreciable voltage.

![Figure 2.3 Schematic of the temperature dependence of conductivity expected for an amorphous semiconductor.](image)

Due to the presence of localised states around the Fermi level and the band tails, electronic transport may occur in three possible regions of the DOS, as described below [1, 6]. These correspond to conduction in four different regimes.

(a) Transport by carriers excited beyond the mobility edges into extended states at $E_C$ or $E_V$, leading to a straight-line dependence in the $\ln \sigma$ versus $1/T$ characteristic:

$$\sigma = \sigma_{\text{min}} \exp \left[ -\frac{E_C - E_F}{kT} \right]$$  \hspace{1cm} (2.1)

where $\sigma_{\text{min}}$ is related to the extended state mobility and the density of states at the conduction band edge by $\sigma_{\text{min}} = \mu_{\text{ext}} eN(E_C)kT$. 

2.3. Low field conduction

(b) Transport by carriers excited to localised states at the band edges, and then hopping at the band tail, also leading to a straight-line $\ln \sigma$ versus $1/T$ dependence:

$$\sigma = \sigma_1 \exp \left[ -\frac{E_A - E_F + \Delta_1}{kT} \right]$$  \hspace{1cm} (2.2)

where $\Delta_1$ is the hopping activation energy and $E_A$ is the band-tail energy of conduction. $\sigma_1$ is found to be considerably lower than $\sigma_{\min}$, due to the reduced density of states and also the much reduced mobility. Although the mobility term for the hopping process has been shown by Mott [1] to possess a temperature dependence as shown in (d), the thermally activated temperature dependence of the excitation of carriers to the band tail will dominate this, resulting in the observed dependence.

(c) Transport by the hopping of carriers excited between localised sites at around $E_F$:

$$\sigma = \sigma_2 \exp \left[ -\frac{\Delta_2}{kT} \right]$$  \hspace{1cm} (2.3)

where $\Delta_2$ is the hopping energy of activation. This also leads to a $\ln \sigma$ versus $1/T$ dependence.

(d) Finally, at lower temperatures, variable-range hopping (VRH) dominates for most materials, which can be expressed as:

$$\sigma = \sigma'_2 \exp \left[ -\frac{B}{T^{1/4}} \right]$$  \hspace{1cm} (2.4)

where $B = 2(\alpha^3/kN(E_F))^{1/4}$. $\alpha$ is a measure of the decay of the wavefunction on a single potential well, and $\sigma'_2 = \nu_{ph} e^2 N(E_F) R^2$ where $R$ is the average hopping distance and $\nu_{ph}$ depends on the phonon frequency. The curved nature of the $\ln J$ versus $1/T$ characteristic in the case of most forms of $a-C$ has led many authors to believe that VRH predominates up to room temperature and above [7]. However, others have disagreed by showing that the localisation factor derived in the case of $a-C$ is often unrealistic [8]. Finally, another form of hopping, known as nearest-neighbour hopping, is possible if the localisation is very strong, such that the electron jumps to the state nearest in space because the term $\exp(-2\alpha R)$ falls off rapidly. This leads to an $\exp(-W/kT)$ dependence [1], where $W$ is approximately $1/R_0^3 N(E_F)$, $R_0$ being the nearest neighbour hopping distance.
2.4 High-field conduction

This applies in the electric field range of $10^5 \text{ V cm}^{-1}$ - $10^6 \text{ V cm}^{-1}$. This would be achieved by performing electrical measurements through a thin film, using for example a metal-semiconductor-metal (MSM) or metal-semiconductor-silicon (MSS) structure. Normally, in this voltage region the current no longer varies linearly with voltage. The following mechanisms that describe these characteristics have been observed in amorphous semiconductors: space-charge-limited current (SCLC) [9, 10], Poole-Frenkel effect [11, 12], Schottky effect [13, 14, 15] and tunnelling [16, 3].

2.4.1 Space-charge-limited current

This applies in MSM- and MSS-type structures where two ohmic contacts separate a space charge, as shown in Figure 2.4. The reason that these contacts are ohmic is that the work function of the metal is less than that of the semiconductor resulting in an accumulation layer extending from the metal-semiconductor junction. This assumes in this case an n-doped semiconductor, which can be assumed to be trap-free and not contain surface states [10]. It can be seen below that the accumulation regions overlap for both contacts, and as a result the bottom of the conduction band is curved throughout its length. Therefore, space charge must extend through the length the semiconductor to allow for the band bending. The result of this is that the conduction process is controlled by the extrinsic space charge rather than the bulk properties of the material. In other words, the conduction is space charge limited (SCL). The derivations of the equations governing SCLC are well outlined by Lamb [17], who in the most simple case, models the system as a parallel-plate capacitor with a transit time of carriers between the plates. For a trap-free semiconductor with single carriers the $J/E$ characteristic is:

$$J = \frac{9\mu \varepsilon_0 \varepsilon_r}{8d} E^2$$

where $\mu$ is the carrier mobility, $\varepsilon_r$ is the relative permittivity, $\varepsilon_0$ is the permittivity of free space and $d$ is the film thickness [17]. When the semiconductor contains shallow traps, a large fraction of injected space charge is trapped, resulting in a reduced density
2.4. High-field conduction

Figure 2.4 Energy diagram for two ohmic contacts on an insulator (assumed trap free).

of free charge. The free charge to trapped charge ratio \( Q \) can be calculated by applying a simple Arrhenius dependence:

\[
Q = \frac{N_c}{N_t} \exp \left( \frac{E_t}{kT} \right)
\]

(2.6)

where \( N_t \) is the number of shallow traps, and \( E_t \) is the energy distance between the trap and the conduction band edge [9]. For deep traps, \( Q \) is no longer a constant but depends on the depth and distribution of traps in the density of states. Therefore, it is possible to extract some measure of the density of states at the Fermi level, from the current versus voltage data. This has been carried out in the case of DAC [18] and ta–C [19].

The following scaling law has been predicted [20], assuming field-independent mobility.

\[
\frac{J}{I} = f \left( \frac{V}{I^2} \right)
\]

(2.7)

2.4.2 Poole-Frenkel effect

This mechanism is bulk-controlled, and so occurs due to the intrinsic properties of the semiconductor and is not a contact-limited effect, and is therefore detrimental to device performance. Conduction in the bulk is governed by the manner in which the carrier leaves its originally occupied state at the Fermi level. These states are as a
result of defects, which exist due to the amorphous nature of the material. Some of these defects will be charged and hence contain carriers which are trapped by the electrostatic potential due to the charge. Hence, these trapping centres can be modelled as Coulombic potential wells. The carrier can leave this well by a reduction of the well height caused by the application of an electric field, namely the Poole-Frenkel effect, which was first discussed in the 1930s [11] and modified in the 1970s by Hill [12]. Figure 2.5 shows the model diagramatically.

![Diagram of the Poole-Frenkel effect](image)

**Figure 2.5** Single-centre Poole-Frenkel Effect.

The resulting $J$ versus $E$ characteristic, as shown by Hill [12], is given by:

$$J = E e\mu N_c \exp \left[ \frac{E_\theta}{2kT} \right] \exp \left[ \beta \sqrt{E} \right]$$  \hspace{1cm} (2.8)

where

$$\beta = \frac{1}{kT} \sqrt{\frac{e^3}{\pi \varepsilon_0 \varepsilon_r}}$$  \hspace{1cm} (2.9)

and $A^*$ is Richardson's constant, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $e$ is $1.6 \times 10^{-19} C$, $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is the relative permittivity. Therefore, by plotting $\ln J/E$ versus $E^{1/2}$, values of relative permittivity can be calculated. The trap density $N_C$ may also be estimated.
2.4.3 Schottky effect

At intermediate electric fields ($10^4 - 10^5$ V cm$^{-1}$), the Schottky effect is the dominant process controlling the current versus voltage characteristic in several materials, for example silicon nitride [13, 14]. The standard Schottky equations describe the process where the barrier height is reduced due to the application of an electric field. The Schottky effect only occurs at fields at which the metal-to-semiconductor barrier height is reduced due to image forces attracting the electron to the surface of the metal, which is shown in Figure 2.6. When an electron is at a certain distance from the metal surface, a positive charge is induced onto that surface. The force of attraction between the electron and the induced charge is equivalent to the force that would exist between the electron and an equal positive charge on the other side and equidistant from the metal surface. The resulting current density is given by:

$$J = A^* T^2 \exp \left[ \frac{\Phi_0}{kT} + \frac{\beta}{2} \sqrt{E} \right]$$  \hspace{1cm} (2.10)

where $\beta$ describes the same quantity as in Section 2.4.2. The dielectric constant and barrier height at zero voltage, $\Phi_0$, can therefore be calculated from the above equation by plotting $\ln J$ versus $E^{1/2}$. In the case of a-C, this type of analysis is relatively rare and there has been no proof as yet of a Schottky barrier on this material according to a fit to barrier lowering.
2.4.4 Tunnelling

At higher fields the electron can tunnel through the barrier, with or without thermionic assistance, as shown in Figure 2.7. The derivation of thermionic tunnelling assuming thermionic field emission is outlined by Shannon [3]. For small carrier effective masses the total current is described by the following equation:

\[ J = A^* T^2 \exp \left[ \frac{-(\Phi_0 + aE_s)}{kT} \right] \]  \hspace{1cm} (2.11)

where \( E_s \) is the surface electric field and \( \alpha = (kT)\delta \ln J/\delta E_s \) which is the tunnelling constant. Generally, this type of tunnelling only occurs at electric fields of higher than \( 10^6 \) V cm\(^{-1} \), and is characterised by a straight line in the log \( J \) versus \( E \) characteristic. The simplest case of the Fowler-Nordheim [16] process assumes a triangular potential barrier and obeys the following dependence:

\[ J = \frac{aV^2 \beta^2}{\Phi_0} \exp \left[ \frac{-b\Phi_0^{3/2}}{\beta V} \right] \]  \hspace{1cm} (2.12)

where \( a \) and \( b \) are constants, \( \Phi_0 \) is the barrier height and \( \beta \) is a constant which depends on the localised field enhancement. It must be noted that this model applies to tunnelling at the Fermi level. A straight line \( \ln J/V^2 \) versus \( 1/V \) dependence is observed.

![Figure 2.7 Thermionic and Fowler-Nordheim tunnelling through a potential barrier.](image)
2.5 Summary

In particular, though, this analysis has greater relevance in the case of electron field emission, as Fowler-Nordheim tunnelling has often been cited as the process controlling the emission of electrons through the barrier to the vacuum level [21].

2.5 Summary

To conclude, in this Chapter we have reviewed some of the relevant mechanisms governing current transport. These are appropriate for the study of amorphous materials, including amorphous carbon in its various forms. Much of the work presented in this study will concentrate on high-field conduction, as MSM structures have been employed extensively which permit the measurement of these types of film in the high-field regime.
Chapter 3

Historical Perspective of the Electronic Properties of Amorphous Carbon

Amorphous carbon (a-C) has been studied as an electronic material for about 30 years. The electronic structure of a-C, and hence the electronic properties, are complicated by the fact that both π and σ states exist within the band gap, which contribute differently to the transport properties of the material. In Sections 3.1-3.4, the electronic properties of amorphous carbon in its undoped state will be described. This will be subdivided into its two most commonly researched forms: a-C:H as further subdivided into polymer-like (PAC), diamond-like (DAC), and graphitic (GAC); and ta-C. Sections 3.5-3.6 examine attempts to dope a-C using nitrogen addition and ion implantation. Finally, Section 3.7 reviews applications in terms of novel a-C-based devices.

3.1 Electronic structure

The early experimental data which describes the electronic structure of a-C is summarised by Robertson [5]. Using current/temperature measurements, Robertson has reviewed work which has shown that for sputtered and glassy a-C, conduction obeys variable-range hopping with an $\alpha^{-1}$ value of 1.2 nm and $N(E_F)$ of $10^{18}$ eV$^{-1}$ cm$^{-3}$. Robertson also showed that the temperature dependence of conductivity was curved and did not fit any law particularly satisfactorily. Above 400 K it was ascribed to band
3.1. Electronic structure

tail conduction. Chan et al. [22] showed that from a range of 300 to 500 K, it was not possible to ascribe any single conduction mechanism as the fits were similar to both band-tail and variable-range hopping. If band-tail hopping was assumed to be occurring, an activation energy of 0.34 eV could be obtained. This was much smaller than half the bandgap, which suggests that the Fermi level was not at midgap. This was attributed to the fact that in the case of a–C the dangling bond defect states possess a significant s content, as they consist of isolated sp\(^2\) sites which have not paired up as \(\pi\) bonds. Therefore, their energy levels are lowered, as s states lie deeper than \(p\) states [23]. This results in the \(p\)-type conductivity of the undoped forms of a–C [24].

The fact that hopping conduction occurs over a large range of temperatures suggests that the gap states of a–C are highly localised. The outcome of this is that in any form of amorphous carbon, conduction at room temperature will always occur by some hopping process between localised states. Higher temperatures are therefore required for conduction in the extended states to be realised.

In a–Si which only permits \(\sigma\) bonds, localisation only occurs at the midgap states and the tail states of both conduction and valence bands [6]. In the case of a–C where both \(\pi\) and \(\sigma\) bonds are present, as well as defect states the localisation present can extend through the gap. Chen et al. [25] performed atomistic calculations and showed that the entire \(\pi\) band is localised. The inverse participation ratio of the \(\pi\) states that control the conduction properties is very high. The simulation used a \(sp^2\) bonding concentration of 80%, which is well over the percolation limit, and despite this the conductivity within the material was low. In this case the disorder potential \(\delta V\) is expected to be small and so there must be another reason for the localisation of the wavefunction. This effect was found to be the interaction between \(\pi\) states which is controlled by the projected dihedral angle \(\phi\) of two bonds [25]. In most cases the planes involving \(\pi\) bonds ended up being close to orthogonal and so there was little or no interaction as \(V\), the potential well of each atom, tended to zero. This meant that \(\delta V(= V_0 - V)\) was of a similar magnitude to \(V\) so \(\delta V/V\) tended to be greater than 1 resulting in localisation over the whole wavefunction.

This result is completely different to a–Si as in that case all the bonds are tetrahedral \(\sigma\) bonds. Therefore, the nature of the tail states in a–C will differ greatly from those of a–Si. It also means that in the case of photoluminescence, it is likely that the generated electron-hole pair will remain within a delocalised cluster, which is isolated from the
remainder of the network, and give rise to a geminate pair. Another artefact of the localised tail states in $\alpha$–$\text{C}$ would be the room temperature intense PL as the carriers cannot diffuse apart easily and thereby get trapped into a non-radiative recombination path as seen by experiments [26].

### 3.2 Electronic properties: GAC films

The current versus temperature plots for GAC films were reported and investigated by Orzeszko et al. [7]. They evaporated GAC with or without a hydrogen atmosphere and compared the resulting current versus temperature curves. Non-hydrogenated films showed a reasonably close $T^{1/4}$ dependence, but the hydrogenated films showed a closer $T^{-1}$ relationship. This is shown in Figure 3.1. Therefore, assuming a reciprocal localisation length $\alpha$ as documented by Hill [12] of $7.5 \times 10^6$ cm$^{-1}$, the density of states at the Fermi level $N(E_F)$ was calculated using the equations for variable-range hopping. $N(E_F)$ was measured to be two orders of magnitude lower in the case of non-hydrogenated films than hydrogenated films.

![Figure 3.1](image)

**Figure 3.1** Variation of current versus temperature for hydrogenated and unhydrogenated GAC films, reproduced from Orzeszko et al. [7]: (a) $I$ versus $1000/T$, (b) $I$ versus $1/T^{1/4}$. 
Measurements on similar types of film were carried out in more detail by Dasgupta et al. [8], who looked into the electronic properties of hydrogenated and non-hydrogenated GAC. Both types of film were grown using rf sputtering. Firstly, the conductivities of both forms were found to be similar, implying that the optical gap and conductivity were governed by the size and concentrations of sp² islands rather than the hydrogen content. Secondly, in the case for films where the sp²:sp³ proportion was below the percolation threshold, the conduction at high temperatures appeared to follow some type of activated (band tail) hopping process at higher temperatures and some type of $T^{1/4}$ relationship at room temperature, implying variable-range hopping. This was in accordance with the behaviour cited by Orzeszko et al. However, the calculations of $\alpha$ and $N(E_F)$ yielded unrealistic values ($\alpha < 10^{-7}$ cm$^{-1}$ and $N(E_F) > 10^{45}$ cm$^{-3}$ eV$^{-1}$ in one case). However, by fitting an Arrhenius-like relationship for the conduction at room temperature, and assuming a process of hopping between neighbouring sp² islands using a model from Mott [1], a good fit was obtained to the equation

$$\sigma = (2e^2 R^2/kT) \nu_{ph} N_\pi T \exp(-w/kT - 2\alpha R)$$

(3.1)

The term $R$, which refers to the distance between adjacent sp² clusters, was crucial in calculating the conductivity variation of the material. For conduction at higher temperatures, hopping in the band tails was observed. For films with an sp²:sp³ proportion above the percolation threshold, hopping in the band tails appeared to be the only effective model. This has been contradicted by Helmbold et al. [27], a reason being that the values of thermopower generally found in the case of GAC (and DAC) were very small, in the order of 10-30 $\mu$V K$^{-1}$. Conduction in band tails should result in thermopowers several orders of magnitude higher due to an appreciable activation energy. Therefore, an alternative mechanism based on a multiphonon tunnelling model with weak electron-lattice coupling was postulated. A hopping process between sp² clusters was also assumed and the electron - phonon coupling was related to the mean lattice spacing and the localisation length. Activation energies in the order of 0.015 eV were derived, which would account for the small thermopowers.
3.3 Electronic properties: DAC films

Robertson [5] cites that the optical absorption data suggests that most forms of $a-C$ possess broad tails and hence a narrow band gap (0.4-0.7 eV). However, DAC possesses a wider band gap, due to the reduction of the band tail density of states as a result of the increase in $sp^3$ bonding. These highly localised midgap states can dictate the conduction properties. They are formed as a result of the breaking of $\pi$ bonds, since $\pi$ bonding is weaker than the $\sigma$ bonding. If the $\pi$ defect is on a conjugated system (for example an aromatic ring), it can conjugate with the ring. Any system with a half-filled $\pi$ bonded site, including odd-membered rings, such as azulenes, as well as odd-numbered clusters, introduce states around $E_p$ and are referred to as $\pi$ defects. Dangling bonds are also classified as $\pi$ defects, as the unpaired electron will preferentially occupy a $\pi$ orbital.

3.3.1 Deposition parameters

The DC self-bias voltage during deposition plays a critical role in determining the optoelectronic properties of the $a-C$ films. The variation of optical band gap with DC bias voltage, according to Rusli et al. [28], Ristein et al. [30] and Tamor et al. [29], is

![Graph showing variation in optical band gap of DAC films as a function of DC bias voltage.](image)

Figure 3.2 Variation in optical band gap of DAC films as a function of DC bias voltage, as reported by Rusli et al. [28], Tamor et al. [29] and Ristein et al. [30].
shown in Figure 3.2. At bias voltages close to zero, the films possess a band gap of approximately 4 eV, and are polymer-like in nature (PAC). As the DC bias voltage is increased, the band gap shows a corresponding decrease as the film passes through a diamond-like (DAC) phase. Eventually, above DC bias voltages of 600 V, the film becomes graphitic in nature (GAC).

However, relatively few studies have been carried out which refer to the effects on the electronic properties of DAC. Stenzel et al. [31] cites the effect of dc conductivity on the optical band gap, as referred from earlier work. This variation is shown in Figure 3.3. This can be therefore be correlated to the effect of DC self-bias on optical band gap, as documented by Silva et al. [32] and Ristein et al. [33]. It is commonly observed that an increase in the DC self bias results in a decrease in optical band gap. At low bias voltages, such as those which exist on the earthed substrate table of a PECVD process.

![Figure 3.3](image-url) Variation in refractive index and room temperature conductivity as a function of optical band gap, reproduced from Stenzel et al. [31].
3.3. Electronic properties: DAC films

the films are polymeric in nature and possess a Tauc optical band gap of 2.5 - 3 eV. At higher DC voltages the films become increasingly diamond-like and then graphitic in nature with the optical band gap falling to eventual closure at the highest voltages. Stenzel et al. found that the room temperature conductivity showed an approximately exponential decrease with the increase in optical band gap, corresponding to values of $10^{-2}$ Ω⁻¹ cm⁻¹ with an optical band gap of 0.3 eV (a GAC film grown with a DC bias of higher than 500V), to $10^{-10}$ Ω⁻¹ cm⁻¹ with an optical band gap of 1.8 eV (a DAC film grown with a DC bias of less than 100V). Thus, the resistivity can be varied greatly by changing the optical band gap of the material.

The effect of deposition temperature on the opto-electronic properties was documented by Jones and Stewart [34] who also grew films using an rf plasma. Firstly, they found that the optical band gap of DAC decreased with increasing deposition temperature, from a value of 1.2 eV at a deposition temperature of 175 °C to 0.7 eV at 350 °C, and the activation energy showed a concomitant decrease from 0.6 to 0.1 eV. This could be explained by the increase in $sp^2$ content resulting in a narrowing of the band gap and hence the reduction in activation energy. However, they found that the difference between optical band gap and activation energy remained constant at approximately 0.6 eV as the deposition temperature was changed, even though both were dependent on the deposition temperature. This indicated that the position of the Fermi level remained fixed relative to the valence band.

The effect of thermal annealing on the optical band gap of DAC is shown in Figure 3.4, which describes the variation according to Burden et al. [35] (in this case for DAC films grown using magnetically confined PECVD), Bounouh et al. [36] (direct vapour deposition) and Koidl et al. [37] (PECVD). What is generally found is an increase in $sp^2$ content above a graphitisation threshold, commonly around 350 °C, which has been correlated with the decrease in optical band gap at this temperature, as well as a decrease in resistivity of around 5 orders of magnitude. However, Burden et al. [35] found that the optical band gap increased greater than could be accounted for by errors of measurement, at the anneal temperature of 125 °C. It was suggested that the passivation of dangling bonds due to the movement of hydrogen during the anneal had sharpened the band tail and hence increased the band gap.
3.3. Electronic properties: DAC films

3.3.2 $I/V$ characteristics

An understanding of the current versus voltage characteristic is essential in order to ascertain the dominant high-field conduction mechanism which is taking place in these films. In the most simple case, DAC films grown on different metal substrates show a symmetrical $J/E$ characteristic [38, 39] suggesting that conduction is bulk limited and not ruled by the differences in barrier heights at either contact. Adkins et al. [40] showed thirty years ago that high-field conduction was likely to be governed by the Poole-Frenkel effect with a range of trap depths and a large effective dielectric constant. This was verified by Egret et al. [38] and has also been shown by others [41, 42, 39]. This appeared to hold even as the self-bias voltage was increased. As a test of PF conduction, films were grown with a range of refractive indices of 1.8-2.3. This corresponded to an optical band gap range of 1.2 to 2.2 eV. The dependence of the PF $\beta$ factor with the refractive index was observed. $\beta$ was found to vary approximately with $1/\sqrt{\varepsilon_r}$ which suggested that the PF equation was applicable. Furthermore, it was found that as the optical band gap increased over this range, the current density at zero voltage $J_0$ decreased from $10^{-7}$ to $10^{-12}$ A cm$^{-2}$ and the PF activation energy at high temperature increased from 0.4 to 0.6 eV between band gaps of 1.3 and 1.5 eV. At lower temperature the temperature dependence of current was non-linear.

According to these results, conduction in these films at high electric fields is bulk-limited.
3.3. Electronic properties: DAC films

and as the optical band gap is increased, the energy of excitation required to promote a trapped electron to the extended states increases, causing a decrease in $J_0$. It has been stated that $p$-type conductivity is likely in the case of DAC and this suggests that the PF activation energy is to the valence band via hole conduction.

A study to investigate the effect of contact material on the $I/V$ characteristics was carried out by Konofaos et al. [43]. The films were grown on silicon substrates using a mixture of CH$_4$ and H$_2$ in a standard $rf$–PECVD system, and substantial differences were observed in the $I/V$ characteristics between using gold and aluminium top contacts. This was explained by the presence of a Schottky barrier, which resulted in a different barrier height for the two materials. Also, it was found that by growing films of different thicknesses, the $J/E$ characteristics did not overlap, suggesting contact-limited conduction.

However, Allon-Alaluf et al. [44] grew DAC films on aluminium substrates using a similar process and found that the $I/V$ characteristics were symmetrical using gold or copper top contacts, indicating an ohmic contact. There appeared to be a low field asymmetry using aluminium top contacts, which was investigated using $C/V$ measurements. This indicated an interfacial barrier between the film and the top contact. This was further justified using Auger electron spectroscopy (AES) which showed a substantial concentration (20%) of oxygen at the interface. It is possible that this result may explain those of Konofaos et al.

However, others, such as Silva et al. [18] have discussed these properties of DAC films in terms of space-charge-limited current. From such measurements, using the analysis outlined previously and described in Lampert and Mark [20], an approximation of the density of states at the Fermi level has been derived, the value being of the order of $10^{18}$ eV$^{-1}$ cm$^{-3}$. This can be compared to a spin density as derived from EPR of the order of $10^{20}$ cm$^{-3}$ [33]. Using this reference, an extracted correlation energy from photoelectron yield experiments is of the order of 1 eV, thus giving a density of states at the Fermi level of $\sim 10^{20}$ eV$^{-1}$ cm$^{-3}$. However, DAC films with a higher band gap were also measured by Silva [45] and were found to obey Poole or Poole-Frenkel conduction. Therefore, it can be ascertained that most forms of DAC follow this type of conduction, and hence the density of defects dictate the conduction properties of the material.
3.3.3 DAC heterojunctions

There has been much work which has provided evidence for a DAC/Si heterojunction. This was first reported by Amaratunga et al. [46] who showed that the $I/V$ characteristic of the metal-carbon-silicon structure displayed rectifying behaviour. This suggested an a-C / silicon junction, and has been shown by others [22, 47, 48]. Chan et al. [22] found that the forward to reverse rectification ratio was 6 orders of magnitude, by growing a band gap-modulated DAC superlattice film, as shown in Figure 3.5.

![Figure 3.5](image)

**Figure 3.5** $I/V$ characteristic of a band gap-modulated DAC superlattice /Si heterojunction showing 6 orders of magnitude of rectification, reproduced from Chan et al. [22].

Capacitance-versus-voltage ($C/V$) measurements were performed by Chan et al. [22, 49], following investigations carried out on sputtered a-C by Khan et al. [50, 51]. Chan showed that the observed frequency dependence of the $C/V$ characteristic was as a result of interface traps. This was modelled and the interface trap density was found to be of the order of $10^{10}$ cm$^{-2}$ eV$^{-1}$, and was comparable to that reported by Khan et al. [50]. This value was also far lower than the areal spin density as derived from EPR which obtained a value of $10^{12}$ cm$^{-2}$ [30], or deep level capacitance profiling [52] in ta-C, which suggested that the dangling bonds in a-C films were not acting as trap centres. In comparison, Mandel et al. [53] carried out similar measurements and found that the gap state density of states was in the order of $10^{16}$ cm$^{-3}$ eV$^{-1}$. In the case of PAC which was grown using an inductively coupled plasma, Munindradasa et al. [47] correlated the $C/V$ properties as a function of frequency with the field emission properties of the material. In this case, the amount of hysteresis was low and the flat band voltage was zero, suggesting an absence of fixed charges.
3.4 Electronic properties: ta–C films

Even though ta–C possesses a high $sp^3$ content of around 80%, there will always be a significant proportion of $sp^2$ bonds that will introduce $\pi$ states into the band gap [54]. These will hence dictate the electronic properties of the material, by being closer to the Fermi level.

3.4.1 Effect of $sp^2$ / $sp^3$ bonding

The $sp^2$ content of ta–C, and its subsequent effect on the electronic properties of the material, is of paramount importance when discussing the conduction within the material. Surprisingly, relatively few studies which concentrate on the electrical properties have been carried out. Fallon et al. [54] reported on ta–C films which were deposited using a filtered cathodic vacuum arc (FCVA), and varied the bias voltage of deposition, in order to see if there was an optimum ion energy for the promotion of $sp^3$ bonding. This was found at a bias voltage of 100 V, which related to an ion energy of approximately 140 eV, and corresponded to the maximum in resistivity, along with other factors such as compressive stress and plasmon energy. It was suggested that this was because the band gap was at its widest at this energy. Another explanation which may be proposed is the decrease in conduction (variable-range or band-tail hopping) between $sp^2$ clusters, should the density of these clusters within an $sp^2$ matrix be reduced. Similar trends on optical and mechanical properties have been shown by Xu et al. [55], Chhowalla et al. [56] and Waidmann et al. [57]. Figure 3.6 shows the variation in optical band gap and conductivity with ion energy, according to various authors [56, 54, 57]. It can be seen that Fallon et al. and Chhowalla et al. concur with the conductivity measurement, but the ion energy at which the optical band gap is at its widest is 220 eV in the case of Waidmann et al. as opposed to 100 eV or less for Chhowalla et al. This illustrates the point that different groups have measured different energies at which the peak in $sp^3$ content occurs. This could be due to differences in the degree of ionisation, or varying monochromacities of the ion beam.

The effect of varying the deposition temperature on the conductivity and optical band gap has also been measured, and is illustrated in Figure 3.7 as derived by Chhowalla et al. [56], Sattel et al. [58] and Kleinsorge et al. [59]. It is observed that the optical band gap shows a decrease from 2-2.5 eV to 0-1 eV as the deposition temperature is
increased, and the conductivity shows an accompanying rise of 7-10 orders of magnitude over the temperature range. In the study by Chhowalla et al. [56], the sharp decrease in resistivity at higher deposition temperatures was explained by the increase in disorder of the film due to energetic ion bombardment leading to gap states. It could be explained similarly to the above result, though, which is an increase in the hopping probability between $sp^2$ clusters, as the $sp^2$ content is increased. Chhowalla et al. also measured the conductivity as a function of inverse temperature and found a linear dependence. This suggested band-tail conduction, and as the activation energy was 0.45 eV the Fermi level was not at midgap.
3.4. Electronic properties: \textit{ta–C} films

3.4.2 Annealing of \textit{ta–C}

The only significant studies into the effects of annealing on the electronic properties of \textit{ta–C} were carried out by Sullivan \textit{et al.} [60] and Ferrari \textit{et al.} [61]. This is shown in Figure 3.8. In addition, the annealing data for the case of \textit{ta–C}:H as derived by Conway \textit{et al.} is shown and will be discussed at a later stage. In the case of \textit{ta–C}, a stress relaxation occurred around 600 °C. Sullivan \textit{et al.} modelled this stress relaxation as a small change in $sp^2$ content, of up to 6.5 at. %. Therefore, the variation in conductivity was compared with this change in $sp^2$ content. In particular, the conductivity appeared to be exponentially dependent on the $sp^2$ concentration of the film. It was postulated by the data that the enhancement of conductivity was governed by variable-range hopping with a term for the variable separation between $sp^2$ sites, assuming they occur in chains.
rather than rings. A typical chain length was estimated to consist of 13 carbon atoms. Therefore, the conduction was thought to be governed by the length of \( sp^2 \) chains, which were lengthened through annealing (though only from 13 to 14), coupled with chain-to-chain tunnelling. Ferrari et al. also showed that the \( E_{04} \) optical gap stayed between 2.7 to 3.0 eV until 600 °C, and therefore, the change in \( sp^2 \) content was likely to be low. They also concluded that the decrease of resistivity of almost three orders of magnitude (initially \( \sim 10^7 \Omega \text{ cm} \) ) over this temperature range could be accounted for by the slight increase in hopping centres. Above 600 °C, though, the resistivity decrease was much greater and coincided with a fall in the optical band gap, though the \( sp^3 \) percentage remained unchanged until 1200 °C where it fell from 85 % to 20 %. This coincided with complete
3.4. Electronic properties: ta—C films

stress relief within the films. It was likely that this final transition was triggered by the formation of SiC, which may trigger a large-scale graphitisation of the material.

3.4.3 ta—C heterojunctions

Tetrahedral amorphous carbon has been shown to form a heterojunction with silicon [62, 63], and it has also been shown that ta—C forms a highly sp$^2$-rich 1-2 nm thick surface layer as a consequence of the likely subplantation process which results in a densification below the film surface [64]. These heterojunctions possess strongly rectifying $I/V$ characteristics and breakdown strengths above 100 V. From the ta—C/Si heterojunction characteristic, it was shown that the current flow was space-charge-limited [19]. The turn-on voltages were 1.6 V for the ta—C/n—Si heterojunction and 0.4 V for the ta—C/p—Si heterojunction, suggesting that the material was p—type. Using the differential method, the density of states derived from the valence band was of the order of $10^{21}$ cm$^{-3}$ eV$^{-1}$. Furthermore, Palinginis et al. [52] carried out junction capacitance measurements on ta—C in order to derive the defect density. Using the drive level capacitance profiling technique, a defect density of $6 \times 10^{17}$ cm$^{-3}$ was determined. The value as derived from EPR was at least two orders of magnitude higher; this was explained by the fact that this technique used only would detect the $D^+$ or positively charged defect centre, whilst EPR would detect all unpaired spins which lie at or near the Fermi level.

3.4.4 Photoconductivity of ta—C

Photoconductivity in the case of ta—C was first reported by Amaratunga et al. [65]. It was found that the resistivity decreased from $10^7$ to $10^5$ $\Omega$ cm when the films were illuminated under light of AM1 intensity. The spectral response was then observed and it was found to show a peak at around 750-800 nm, corresponding to a photon energy of around 1.7 eV, which was close to the optical band gap. The quantum efficiency of the film was between 10 and 12.5 % over the 450-800 nm range and then decreased at longer wavelengths. Also, it was found that the variation of photoconductivity was independent of temperature, indicating that the conductivity under light illumination was dominated by carrier generation.

McKenzie et al. [66] found that photoconductivity decreased with increasing nitrogen
content. Following this, Cheah et al. [67] fabricated nitrogenated ta—C/ p—Si heterojunctions and also observed that the optical absorption increased as a function of nitrogen content. Also ta—C(:N) films were grown on p—Si substrates and the resulting reverse characteristic of the ta—C:N/Si heterojunction was found to increase by 3 orders of magnitude under light illumination.

The latest and most detailed studies on the photoconductivity of ta—C and ta—C:H have been carried out by Ilie et al. [68, 69]. They investigated the photoconductivity of the undoped forms. Above 200 K the photoconductivity decreased with temperature, and below 200 K it was independent of temperature. It was found that ta—C was a low-mobility solid with μτ products in the order of $10^{-11} - 10^{-12} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ due to the high defect density. The main recombination centres were deep defects but tail states also caused recombination, and at 200 K there was a peak in conductivity corresponding to competitive recombination between two classes of centre. A later study showed that in the case of ta—C:H, the photoconductivity was increased by nitrogen doping, as the material was doped n—type. The photosensitivity obtained was approximately 200 under 35 mW cm$^{-2}$. The addition of nitrogen did not create extra charged defect recombination centres.

3.4.5 Hydrogenated ta—C (ta—C:H)

A study was carried out by Davis et al. [70] who measured the properties of ta—C deposited in the presence of varying flow rates of hydrogen, and it was found that there existed a certain threshold at approximately 0.05 sccm H$_2$. Below this threshold, the $sp^3$ fraction increased from 82 to 86 % and the plasmon energy increased from 29.8 to 30.5 eV, suggesting in increase in density with some hydrogen incorporation. Also, the optical band gap increased from 1.9 to 2.1 eV and the trap density decreased. Using a SCLC analysis as in the case of Veerasamy et al. [19] the current injection was at its sharpest at 0.05 sccm. These measurements suggested that at these low hydrogen contents, there was a reduction in the band tail density due to the increased $sp^3$ content, effectively as hydrogen would favour $sp^3$ bonding. This would result in a reduction in defect states below the Fermi level, and hence a movement of the Fermi level towards midband, causing an increase in activation energy. This increased from 0.22 eV in the undoped case to 0.36 eV at a flow rate of 5 sccm H$_2$ with a concurrent increase in resistivity from $\sim 10^7 \Omega \text{ cm}$ to $\sim 3 \times 10^7 \Omega \text{ cm}$. However, above 0.05 sccm H$_2$, the trap
density increased, and the \( sp^3 \) content decreased down from 83 % to 77 % at 5 sccm \( \text{H}_2 \). It was postulated that this was due to an increase in the number of isolated \( sp^2 \) sites as the carbon-carbon coordination number decreased.

In the case of \( ta-C:H \) grown using a plasma beam source, a variation in resistivity with ion energy similar to the case of \( ta-C \) was found [71]. At an ion energy of 200 keV, the resistivity reached its maximum value of \( 2.5 \times 10^7 \ \Omega \ \text{cm} \), and it was suggested that this was also the energy at which the peak in the \( sp^3 \) content occurred. There has also been evidence of a reduction in the defect density by annealing, as reported by Conway et al. [48], from \( 6 \times 10^{20} \ \text{cm}^{-3} \) to \( 2 \times 10^{19} \ \text{cm}^{-3} \) at an annealing temperature of 300 °C. This has been correlated to a decrease in conductivity and increase in both activation energy and band gap around the same annealing temperature, as shown previously in Figure 3.8. This is similar to the trend described by Burden et al. [35] as shown in Figure 3.4, which had previously demonstrated that annealing at 250 °C increased the optical band gap of DAC. However, the study into the annealing of \( ta-C:H \) was carried out in more detail, and showed that these films conducted via hopping at the band tails rather than at the Fermi level, as the \( \ln J \) versus \( 1000/T \) plot showed a straight line from 250 K to 500 K. Therefore, the decrease in conductivity and increase in activation energy as bought about by annealing was attributed to the sharpening of the \( \pi \) tails. This was later corroborated [72] by evaluating the reciprocal Urbach slope, which is proportional to the slope of the band tails in the energy range just below the \( E_{g04} \) gap. This value was found to increase from \( 3.7 \ \text{eV}^{-1} \) to \( 4.4 \ \text{eV}^{-1} \) from the unannealed sample to the sample annealed at 300 °C, implying a reduction in the density of band-tail hopping sites. The postulated explanation for this was a redistribution of H atoms causing a passivation of dangling bonds by moving along the atomic network. These films contained an as-deposited hydrogen content of 30 at.%. Therefore, there is likely to be sufficient hydrogen within the films to allow this type of process.
3.5 Electronic modification of amorphous carbon

A significant proportion of the work in a–C is related to attempting to electronically modify or “dope” the material. The most commonly used method is to add gaseous nitrogen as an in-situ dopant during deposition. This is performed for two reasons. Firstly, nitrogen has been shown to be an n-type donor in the case of diamond, albeit a deep one, so one of the major objectives is to dope the material n-type. This is of interest, as has already been mentioned, a–C is thought to be intrinsically p-type due to the existence of s-orbital character in the dangling bond defects [24]. The second reason is that nitrogen is a cheap, non-hazardous precursor which would ensure low cost and ease of manufacture should a working a–C-based device be realised.

3.5.1 In-situ Doping of a–C:H: DAC, GAC and ta–C:H

Several authors have reported the electronic doping of DAC by the addition of gaseous precursors into the deposition chamber during growth. The first reports of n- and p-type doping were reported by Meyerson and Smith [73]. Films were grown using the dc glow discharge of acetylene at 150 °C and 250 °C and the gaseous addition of PH3 and B2H6 was investigated. It was found that in the case of boron addition for films grown at 250 °C, the activation energy showed a small rise from 0.6 to 0.65 eV for a diborane flow of 0.1 %, followed by a fall to 0.3 eV at diborane flow rates of up to 10 %. The conductivity measurements showed the contrary, with a decrease from $10^{-11} \ \Omega \ cm$ to $10^{-12} \ \Omega \ cm$ at 0.1 % diborane, followed by an increase of up to $10^{-7} \ \Omega \ cm$. This indicated that the DAC films were intrinsically n-type and could be doped p-type by the addition of boron. Conversely, the films grown with increasing amounts of PH3 showed only increases in conductivity ($10^{-11} \ \Omega \ cm$ to $10^{-7} \ \Omega \ cm$) and decreases in activation energy (0.6 to 0.3 eV), further substantiating this claim. A later report [74] showed that the thermopower for B-doped films was positive and for P-doped films was negative, further indicating that doping was taking place. However, the magnitude of thermopower was small, and conductivity versus temperature measurements fitted a $T^{1/4}$ relationship, indicating a variable-range hopping mechanism. The most important point to note, though, was that no band gap data was discussed in the study. It was later found that the incorporation of a range of dopants would have the effect of increasing the $sp^2$ content of the films, thus narrowing the band gap, decreasing the activation
energy and increasing the conductivity though not necessarily as a result of electronic doping.

Jones and Stewart [34] reported on the effects of nitrogen, phosphine and diborane doping into DAC. Both diborane and phosphine were found to increase film conductivity. The effect of increasing the nitrogen content was to decrease the optical band gap from 1.2 eV to 1.0 eV at a nitrogen flow ratio of 10\% , increase the conductivity at 227 K from $10^{-7}$ to $10^{-4}$ Ω$^{-1}$ cm$^{-1}$, and decrease the activation energy from 0.6 to 0.3 eV. However, the difference between optical band gap and activation energy remained constant as the doping level was changed. This indicated that the position of the Fermi level remained fixed relative to the valence band irrespective of the doping level. Similar studies on the effects of nitrogen modification were carried out by Amir et al. [75] and Stenzel et al. [31]. They reported similar trends in terms of conductivity, activation energy and optical band gap. Amir et al. performed thermopower measurements which showed a positive sign for films containing less than 1 at. \% N, indicating conduction in the valence band tail. Increasing the nitrogen content of the films resulted in a change to conduction around the Fermi level, as shown by the sharp reduction in the magnitude of the thermopower from 600 μV K$^{-1}$ (0.2 \% N) to −4μV K$^{-1}$ (3 \% N). The change of sign indicated $n$–type conduction; however, the doping effect was very weak and at still higher flow rates, the thermopower sign was once more positive. Stenzel et al. suggested that the enhancement of conductivity was due to a greater interconnectivity between existing clusters resulting in enhanced hopping conduction.

In light of these contradictory findings, Helmbold et al. [27] investigated the addition of phosphine into the deposition chamber during DAC growth. They found that their current versus temperature measurements showed a $T^{1/4}$ dependence which was observed at and above room temperature. Therefore, a model based on variable-range hopping was postulated; however, conduction appeared to be dictated by a "characteristic temperature" at which all samples possessed the same conductivity. All other parameters could be explained by such factors such as cluster diameter and lattice spacing. With this type of model, a shift in the Fermi level was excluded as changes in medium-range order could account for the variations in conductivity.

Silva et al. [76, 77] grew films on the driven electrode of a magnetically confined rfp-PECVD source, with a low DC self bias of around 60 V and varying flow rates of
nitrogen. It was found that the optical band gap increased from 1.65 to 2.1 eV and the Tauc B constant increased concomitantly, as the flow rate of nitrogen was increased from 0 to 7 at. %, which was attributed to defect passivation. At higher levels of nitrogen (up to 13 at. %), the optical band gap lowered to less than 2.0 eV, which was likely to be as a result of $sp^2$ re-ordering. Activation energy measurements showed that there were two regimes of conduction, one at temperatures above 100 °C which was reported to be extended state conduction, and at temperatures between 40 °C and 100 °C which was likely to be band-tail hopping. It was found that the activation energy of the high temperature mechanism appeared to increase from 0.5 eV to 0.92 eV and then decrease to 0.45 eV as the flow rate of nitrogen was increased, the peak coinciding at 7 at.% N once more. It was assumed that DAC is intrinsically $p$-type, which agreed with the initial activation energy value and band gap. This value appeared to increase to half of the optical band gap, suggesting that the Fermi level had moved to the centre of the band gap, possibly due to the compensation of defects which led to $p$-type properties. At higher nitrogen levels, the activation energy decrease suggested $n$-type doping of the material. A later study [78] showed from electron energy-loss spectroscopy (EELS) measurements that the point at which the Fermi level was suggested to be in the centre of the band gap coincided with the point at which the $sp^3$ fraction of the C and N atoms was its highest. This point occurred at 7% atomic nitrogen, which appeared to be a turning point.

This work could be compared to other studies, for example by Schwan et al. [79] who deposited GAC films using a plasma beam source (PBS). These films possessed a low hydrogen content of around 10%, which increased due to the addition of nitrogen, possibly because of the introduction of N-H bonds. Also observed was an increase followed by a decrease in the optical band gap, agreeing with the findings by Silva et al. However, it was found that the electrical conductivity simply increased and the activation energy decreased slightly as the nitrogen flow rate was increased. This meant that the Fermi level was only moving very slightly and other effects rather than doping were occurring. For example, carriers may have been thermally activated to a $\pi^*$ state, and the addition of nitrogen could have created N $\pi^*$ states which were situated below the C $\pi^*$ states, to which the carriers were being excited. Therefore, the $n$-type dopant site could have manifested itself as a mixed C-N $\pi^*$ state. In comparison to this, Conway et al. [71] also grew films using a PBS and measured the
optical band gap and conductivity as a function of nitrogen content. It was found that
the conductivity showed an increase with nitrogen content from \( \sim 10^{-8} \ \Omega^{-1} \ \text{cm}^{-1} \) to
\( \sim 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1} \), and the optical band gap showed a corresponding decrease from
2.0 eV to 1.0 eV \((E_0)\). No turning point in the conductivity data as predicted by
compensative doping was observed. The explanation for this was that the films were
grown using acetylene as the source gas, which contained a nitrogen contamination
corresponding to 4 at.
\% within the film. When methane was used, the polarity of
the \(ta-C:H/Si\) heterojunction was changed as the nitrogen concentration increased,
suggesting doping through a compensative state.

Figures 3.9-3.11 show the variations in optical band gap, room temperature conduc­
tivity and activation energy as reported by various groups [76, 79, 75, 71]. Only those
who have related these parameters to the atomic nitrogen content within the films have
been included. In order to interpret the variations it is necessary to understand the
variation in the properties of the undoped material, which depend on such factors as
self-bias voltage and deposition temperature. For example, there are large differences
in the reported magnitude of optical band gap, which could be related to differences in
film microstructure and \(sp^2\) content. Also, activation energy measurements are prob­
lematic as some groups observe a \( T^{1/4} \) relationship, some an Arrhenius relationship and
some two relationships depending on the measurement temperature.

Figure 3.9 Variation of room temperature conductivity of nitrogen-doped \( a-C:H\) films, as
reported by Schwan et al. [79], Amir et al. [75] and Conway et al. [71].
3.5. Electronic modification of amorphous carbon

Figure 3.10 Variation of activation energy of nitrogen-doped \(\alpha\)-C:H films, as reported by Silva \textit{et al.} \cite{76} and Schwan \textit{et al.} \cite{79}.

Figure 3.11 Variation of optical band gap of nitrogen-doped \(\alpha\)-C:H films, as reported by Silva \textit{et al.} \cite{76}, Schwan \textit{et al.} \cite{79}, Amir \textit{et al.} \cite{75} and Conway \textit{et al.} \cite{71}.

However, the following may be surmised. Firstly, nitrogen has the effect of increasing the conductivity. This could be either due to doping or an increase in the \(sp^2\) content. Secondly, different groups have seen different trends in terms of optical band gap and activation energy. Some have observed a decrease in optical band gap \cite{71, 75} which may be explained by graphitisation, and some have seen an increase in optical band gap with nitrogen content \cite{78, 79}. This could equate to a sharpening of the band tail...
(passivation) and hence a reduction in the defect density of the material from $\sim 10^{20}$ cm$^{-3}$ to $\sim 10^{18}$ cm$^{-3}$ [75]. Therefore, it suffices to say that there is evidence for electronic doping of DAC according to some groups, and also evidence for either defect passivation or graphitisation according to others.

3.5.2 *In-situ* doping of $ta-C$

The first reported case of the electronic doping of $ta-C$ was shown by Veerasamy *et al.* [80]. Phosphorus was incorporated into the films by use of a graphite / red phosphorus mixed cathode. It was found that with an increase in cathodic phosphorus percentage, the conductivity was found to rise and the activation energy fall, although no initial increase in activation energy was reported. However, electrical measurements of undoped and P-doped $ta-C$ // $n$-Si heterojunctions showed a reversal in polarity, suggesting that an $n$-type heterojunction had been formed with the doped sample.

A later study [81, 82] documented successful $n$-type doping of $ta-C$, this time by injecting nitrogen gas into the bend region of the filtered cathodic vacuum arc system. The evidence for $n$-type of doping of $ta-C$ was firstly a change in sign of thermopower from positive to negative. Secondly, the resistivity and activation energy of the films showed an increase followed by a decrease, which assuming intrinsically doped $ta-C$ was $p$-type, placed the undoped Fermi level at 0.3 V above the valence band edge. The compensative case at which the Fermi level was found to be midgap corresponded to approximately 0.45 atomic % nitrogen. With a further increase in the nitrogen content the Fermi level was thought to move to within 0.2 eV of the conduction band edge on the addition of nitrogen. The optical band gap was also observed to fall, indicating $sp^2$ re-ordering. EELS analysis suggested that at low nitrogen levels there was little $sp^2$ re-ordering of the material, which was evident at higher nitrogen levels.

A similar study was reported soon afterwards by Davis *et al.* [66, 83]. Similar trends in terms of variations of resistivity and activation energy were reported. However, in this case, a rectifying $p-n$ junction consisting of nitrogen-doped $ta-C$ on undoped $ta-C$ was also found, although the forward to reverse rectification ratio was only around 6. These trends have been reproduced elsewhere [84, 85]. However, other studies [59, 86, 42] have seen only an increase in conductivity and a decrease in optical band gap as the nitrogen content is increased. This is evidence only for $sp^2$ re-ordering.
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In the case of Ronning *et al.* [86, 42], the fact that *n*-type doping of *ta*-C was not reported could be because the films were grown using mass-selected ion-beam deposition and nitrogen was added by alternating the ionic species layer-by-layer during deposition. This may have had an effect on the doping efficiency or controllability of activated dopant. However, it was found that the *I/V* characteristics were linear at low fields, suggesting hopping conduction, and at higher fields could be explained by Poole-Frenkel conduction between two trap states, one around *E_F* and one at the conduction band edge, at high fields. The addition of nitrogen or boron had the effect of modifying the *I/V* characteristics such that the density of one trap-state increased far more than the density of the other state. This led to a kink in the *I/V* characteristic. This suggested that the addition of the dopant had the effect of vastly increasing the density of states at the Fermi level. However, no change in activation energy was observed, suggesting no shift in the Fermi level. Also, *p-i-n* diodes were fabricated and were not found to rectify, suggesting no doping effect, or a pinned Fermi level. With the MSS structures, heterojunction rectification was observed, but the polarity did not appear to change with respect to the doping of the film.

Figures 3.12–3.14 show the variations in conductivity, activation energy and optical band gap as a function of nitrogen, as reported by various groups [59, 70, 81, 85]. The atomic percentage of nitrogen content as a function of nitrogen flow rate is taken from

![Figure 3.12](image-url)  
**Figure 3.12** Variation of room temperature conductivity of nitrogen-doped *ta*-C films, as reported by Davis *et al.* [70], Veerasamy *et al.* [81], Liu *et al.* [85] and Kleinsorge *et al.* [59].
other studies where necessary [66, 84]. What can be noted is that at moderately high nitrogen contents (1 %), the optical band gap closes, which is attributed to an increase in the \( sp^2 \) content. Secondly, the resulting variations differ significantly in terms of conductivity. This could be related to the relative fraction of \( sp^2 \) bonding which is also controlled by such factors as the incident ion energy, as mentioned earlier, or the monochromacity of the ion beam. Thirdly, in terms of the evidence for doping, the
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compensated state varies considerably according to the different groups. This could be related to the method of nitrogen inclusion into the plasma, as Xu et al. [84] injected nitrogen gas directly into the cathodic plume, resulting in a large degree of ionisation. Liu et al. used an ion beam source, and the others added nitrogen simply into the deposition chamber or the torus. Finally, not all groups see a turning point in the values of conductivity and activation energy corresponding to the compensated state. This also suggests that the reactor configuration has a large role in determining whether doping is occurring or not.

![Diagram](image)

**Figure 3.15** Possible configurations of nitrogen in $a-C: H: N$. The lines represent bonds, dots are unpaired electrons; the items within the dotted box are the doping configurations; after Silva et al. [78].

Robertson [87] attempted to ascertain the role of N in the doping process. Figure 3.15 shows possible doping and non-doping structures diagrammatically, as documented by Silva et al. [78]. In the case of diamond, the donor level was about 1.7 eV from the conduction band edge. In the case of $ta-C$, the substitutional N site was now shallow when compared to the $\pi^*$ edge. However, the doping efficiency was likely to be poor as most N would adopt its trivalent bonding configurations (see (a) in Figure 3.15), so the substitutional $N^+_4$ site (b) was less likely. Alternatively, the $N_4$ site could compensate existing midgap defects leading to the $N^+_4C^-_3$ state (c), which would result in a full C defect state and an empty N donor level, and hence a weak doping effect. However, in the case of a predominately aromatically bonded $sp^2$ material as in the case of higher nitrogen doping levels, $N_4$ could still substitute a C atom in an aromatic ring, contribute an electron into an $N\pi^*$ state, and weakly dope it (e). However, it would be
far more likely in this case that non-doping pyridine- or pyrrole-like structures would be formed (f). For an olefinic $sp^2$-bonded region, once again a weak bonding effect could be brought about (h) in spite of other more likely configurations (g) or even $sp^1$ sites (i).

3.6 Ion implantation of $a-C$

Implantation of diamond has been carried out as a route to electronic doping of the material. Boron has successfully doped diamond $p$-type [88], and, more recently, there has been evidence for the $n$-type doping of diamond using phosphorus [89]. The damage effects of ion-implantation in diamond have also been widely reported. These include the onset of hopping conduction [90], and also the onset of $sp^2$ re-ordering [91]. There appears to be a threshold ion dose in both cases, above which the film re-orders into an $sp^2$-rich state and the electrical conductivity increases dramatically. This has been related to the eventual overlap of damage cascades. However, at lower doses, it was found that diamond transforms into an amorphous $sp^3$-bonded phase, in a similar way to silicon.

One of the earliest reports of the effect of ion-implantation into DAC films was conducted by Prawer et al. [92]. This study used a novel experimental technique where the resistivity of the film was measured in-situ during ion irradiation. It was found that there was a threshold dose below which no changes were evident, and above which the resistivity collapsed by as much as 6 orders of magnitude. The band gap showed a concomitant decrease, as did the hydrogen content. This suggested that the reduction of hydrogen content from 35 to 4 at.% resulted in a depassivation of dangling bonds and a rise in the number of inter-gap states. This caused the increase in conductivity at a dose of approx. $10^{15}$ ions cm$^{-2}$ (which was thought to be of the type of variable-range hopping in this case) and reduction in band gap due to the broadening of the band tails. Graphitization was thought not to occur until higher doses, when the damage cascades were thought to overlap, as in the case of diamond, and the films underwent macroscopic graphitisation. Adel et al. [93] supplemented this study with EPR data and found that the paramagnetic density increased from $2 \times 10^{20}$ cm$^{-3}$ to $8 \times 10^{20}$ cm$^{-3}$ at the same dose threshold. This was concomitant with a decrease in the peak-to-peak linewidth from 0.4 to 0.1 mT. This was consistent with a motional narrowing of the
linewidth as a result of increased exchange or hopping between paramagnetic spins. This was similar to results found by Ingram et al. [94] and Doll et al. [95], who also reported on $n$-type conductivity after DAC was implanted with nitrogen ions. Whether this was a doping effect, or a consequence of defect addition, was not ascertained. Wang et al. [96] found an initial increase in resistivity with an implantation dose of $10^{15}$ ions cm$^{-2}$. IR measurements suggested that at this dose the C-H $sp^3$ concentration had increased, which would result in a decrease in the density of hopping centres and hence higher resistivity.

McCulloch et al. [97] implanted carbon and xenon ions into $ta-C$, and also performed in-situ resistance measurements. In this case, it was found that there was no threshold behaviour in the resistivity trend, which was mirrored in the optical band gap trend. This suggested that there was a regime at intermediate doses, in which a highly disordered $sp^2$-rich but non-graphitic material was being created. This was similar to the case in diamond and was corroborated using EELS measurements. For very high doses, it was thought that conduction was due to hopping between graphitic islands. It was also found, as by Doll et al. [95], that using Seebeck measurements undoped $ta-C$ was $p$-type and after nitrogen implantation the films became $n$-type. Therefore, it was suggested that $sp^2$-bonded material was being created, which contributed to the conductivity by acting as $n$-type dopants and also narrowed the band gap. A later study [98] showed that the effect of irradiation at elevated temperatures was to increase the $sp^2$ fraction at higher doses and also the degree of re-ordering. Therefore, a graphitic material was favoured at elevated temperatures, also as in the case of diamond.

### 3.7 $a-C$-based devices

A number of devices have been fabricated based on amorphous carbon. One of the simpler electronic devices is probably the $p-n$ junction. There has only been one reported case of this device; as documented by McKenzie et al. [66]. A graded film of $ta-C/ta-C:N$ was grown onto a plastic substrate. The resulting film was found to rectify by approximately one order of magnitude. However, it was reported that the defective surface layer may have hindered the device performance.

Various groups have attempted to fabricate thin film transistors (TFTs). The only documented transistor based on $a-C$ was reported by Clough et al. [99]. Here, a
thin-film transistor (TFT) was fabricated, and a coplanar design was chosen so that the ta-C surface $sp^2$ layer could be etched, using a nitrous oxide plasma. The channel length was 10-30 $\mu$m and the gate insulator was silicon nitride. The drain characteristic for this transistor is shown in Figure 3.16. It was found that the TFT operated in the $p$-channel enhancement mode, as would be predicted if undoped ta-C was $p$-type. The calculated field effect mobility was only in the order of $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the characteristic did not saturate, suggesting band-tail rather than extended state conduction. The high field conduction showed a near $V^2$ dependence which was attributed to space-charge-limited current.

![Figure 3.16](image)

**Figure 3.16** ta-C TFT drain characteristics as a function of gate bias, reproduced from Clough et al. [99].

Chan et al. [100] has demonstrated a working a-C-based heterojunction bipolar transistor (HBT). A 50 nm DAC film was used as the emitter, which was grown onto $p$-implanted Si which was contacted as the base. The underlying $n$-type Si substrate functioned as the collector. It was seen that the collector current increased with $I_E$ and $V_{CE}$. This was shown to be due to carrier injection from the DAC emitter and not due the leakage current across the reverse-biased junction. No current gain was observed, though, and it was surmised that current injection took place from trap states in the DAC film, which suggested a pinned Fermi level in a deep acceptor band centred around 0.3-0.35 eV from the valence band edge.

As reported by Diedrich et al. [101], nanostructured carbon films (NACs) have been investigated for use in supercapacitors. These are electrochemical double-layer capacitors
formed by two electrodes, a separator and electrolyte. The ions of the electrolyte are adsorbed onto the charged electrode, resulting in a “Helmholz layer”. As the surface area must be maximised in order to increase the capacitance of the device, and an inert material is required, NAC has been used for the electrode. Furthermore, NAC may be grown over large areas on a variety of substrates which further enhances its potential in this role. A capacitor with series resistance $R = 1.13 \ \Omega$, $C = 0.099 \ \text{F}$ and maximum power density of 506 kW kg$^{-1}$ was fabricated, which suggested that NAC was very attractive for this particular application.

Gerstner et al. [102] suggested that $ta-C$:N may have promise as a material for use in non-volatile memories. It was observed that these films showed switching, in that that after a negative bias was applied across the film, a kink was observed in the forward bias, and the small signal resistance of the forward bias was found to fall from an “OFF” state to an “ON” state. Hence, the film possessed a “memory” of whether the last bias was negative or not. This is shown diagrammatically in Figure 3.17.

This was explained by suggesting that the “OFF” state corresponded to conduction by hopping around the Fermi level, and the “ON” state corresponded to Poole-Frenkel conduction, according to $I/V$ and $I/V/T$ data. Therefore, it was suggested that the negative switching bias resulted in electrons being promoted from deep acceptor traps to shallow donor traps, where they could conduct according to Pool-Frenkel conduction. The switch from “ON” to “OFF” was as a result of the accumulation of electrons in

![Figure 3.17 I/V characteristic of non-volatile $ta-C$:N memory device, reproduced from Gerstner et al. [102].](image-url)
the conduction band enhancing the re-filling of electrons in the acceptor traps. This memory effect occurred with a write time down to 100 µs and the memory retention time was in the order of months.

An antifuse is a device which forms a state of low resistance when a threshold electric field is passed. a-C shows promise for such a device, such as low OFF-state leakage current, ON-state resistance, and low dielectric constant. Most importantly, a-C antifuses do not show ON-OFF switching. Liu et al. [103] fabricated and reported upon DAC and DAC:N:F antifuses using a sandwich structure and Al top contacts. It was found that the breakdown voltage was about $1.4 \times 10^6$ V cm$^{-1}$. The breakdown was attributed to the temperature effect of current heating resulting in hydrogen loss and hence $sp^2$ re-ordering. This resulted in a graphitic phase being formed, which caused the observed low-resistance state. However, it must be noted that DAC sandwich structures are notoriously difficult to measure as any particulate underneath a top contact would render the device unusable, by causing a short circuit between the top and bottom contact. The same would occur with excessive contact pressure resulting in punch-through of the film. Also, the short circuit may be only observed when a small voltage is applied. No information as to the reproducibility of these devices was documented, and therefore there may be some conjecture as to whether this was a true antifuse effect or not.

It has already been stated that DAC is a promising material as a switching element in metal-insulator-metal based LCDs, which was investigated by Egret et al. [38]. This is due to the fact that in present TFT-based technology the function of the transistor is to allow charge to flow into or out of the pixel. Two-terminal devices will perform a similar role at reduced cost, although the driver circuitry would be more complex. At high fields DAC exhibits Poole-Frenkel (PF) conduction which allows a sharp turn-on voltage and hence suitability for this application. In particular, the dielectric constant of DAC is of the order of 5-8 which results in a high value for the PF-$\beta$ factor, resulting in a sharper turn-on voltage than other materials (Ta$_2$O$_5$ for example).

ta-C:N shows promise as a photoconductive material according to Cheah et al. [67]. This due to its benefits in terms of photoconductivity and high optical absorbance. However, others such as Lee et al. [104] have also attempted to fabricate p-i-n solar cells using boron-doped DAC (DAC:B) as the $p$-layer. As the DAC:B layer was too resistive for it to make up the whole of the $p$-type contact, it was proposed to grow
an ultrathin carbon layer between the transparent conducting oxide (TCO) and $p$-$SiC$ layer, in order for it to add to the SiC layer and enhance the built-in potential of the cell. It was found that the collection efficiency of the cell was enhanced with the DAC:B layer. This was thought to be due to the reduction in band bending experienced by the holes flowing towards the TCO front contact.
Chapter 4

Experimental Details

In this section, the growth of amorphous carbon films and the fabrication of structures will be described. This entails the deposition of films onto various types of silicon substrate for ellipsometric analysis and the fabrication of metal-semiconductor-semiconductor (MSS) structures, metal-on-glass substrates for the construction of metal-semiconductor-metal (MSM) structures, and glass substrates for optical absorption analysis.

The a—C:H films used for this research were grown using radio-frequency plasma-enhanced chemical vapour deposition (rf-PECVD). The significance of this with reference to a future industrial implementation is that firstly film growth occurs at room temperature, and secondly, the technique permits film growth over large areas using cheap, non-toxic precursors such as methane and helium. This is important in the industrial environment as either glass or even plastic substrates can be used, which increases the range of products that may be offered and allows the production of a cost-effective device material.
4.1 Substrates and pre-deposition procedure

All substrates were kept below a size of 2 cm$^2$ for most of the experiments presented here, as will be explained later. Substrates used were $n$- and $p$-type silicon of resistivity 0.01 – 0.02 Ω cm, for electrical measurements and ellipsometric analysis. For electron paramagnetic resonance (EPR) spectroscopy and Fourier-transform infra-red (FTIR) spectroscopy, high resistivity (either $n$-type 60 Ω cm or $p$-type 100 Ω cm Si) was used. The reason for this was as in the case of EPR, a lower resistivity and hence more conductive substrate will attenuate the microwave signal within its skin depth [105] which would reduce the magnitude of the signal, and in the case of FTIR, the existence of a large concentration of dopants would result in high IR absorption which limits the signal and hence increases noise.

Corning 7059 glass was used for optical absorption measurements which were performed by uv-visible spectroscopy. This material is not ideal for uv-visible measurements as it absorbs heavily at wavelengths lower than approximately 300 nm. Quartz, in spite of its high price, would be a better candidate. However, the low concentration of contaminants in this type of substrate such as Na and Ba meant that the transmittance over the 300-900 nm region was relatively flat. This allowed the use of this material for optical absorption analysis.

The metal substrates consisted of chromium sputtered in a nitrogen atmosphere onto glass (CrN). The thickness of this metallic thin film was approximately 100 nm. The sputtering process was performed in Philips Research Laboratories, Redhill, and this substrate was chosen due to the fact that it was known not to form interfacial layers with amorphous silicon nitride. Also the conductivity and mechanical hardness of CrN has been shown to be superior to that of Cr.

All glass and silicon substrates underwent rigorous cleaning before deposition. This consisted of a three-stage clean using acetone, methanol and isopropanol. An ultrasonic bath was used for five minutes per solvent. Acetone was the first solvent to be used per clean owing to its powerful degreasing properties due to its ability to dissolve most large organic molecules. However, it would leave a residue which had to be removed by the following solvents, methanol and then isopropanol. Finally, the substrates were washed in deionised water and dried using a nitrogen gun.
4.2 Deposition

The sandwiching layer of $a$--C:H was grown using a standard Plasma Technology DP800 radio-frequency plasma-enhanced chemical vapour deposition system. This was conducted at room temperature and at a pressure of 200 mTorr, as measured using a capacitance manometer (Baratron), though other pressures were employed for other studies. The pressure was controlled by an automatic throttle valve, which was controlled using a feedback circuit from another capacitance manometer.

Films were deposited using a CH$_4$/He/(N$_2$) plasma which was formed using a 13.56MHz rf power source. There are two electrodes in this setup; a bottom earthed electrode, and a top powered electrode which is capacitively matched to the rf signal. Samples were placed on either electrode. The plasma was created due to dissociation brought about by the $rf$ power and consisted of ionised radicals, electrons and ions.

There exists a uniform electric field, which is known as the DC self-bias, between the plasma and both electrodes. Therefore, positively charged carbon and hydrocarbon species produced by the glow discharge are accelerated from the plasma towards the electrodes, where they come into contact with the sample. This ionic bombardment results in film formation. The region over which these species are accelerated is called the dark or sheath space. However, the self-bias voltage is much greater for the powered electrode than for the earthed electrode. This is because electrons are much more mobile than positively ionised species, so under the rf electric field they tend to accumulate close to the powered electrode which causes it to develop a large negative self-bias [106]. This is known as the Debye effect. The bias between both electrodes is measured using a voltmeter between the plates, and a circuit to filter out the rf signal. Figure 4.1 shows the deposition system.

One particular feature of the DP800 system was that both electrodes are water-cooled and that the earthed electrode could be heated up to 250 °C, if required. These depositions were carried out at ambient temperature, a pressure of 200 mTorr and at varying $rf$ powers, and hence varying dc self-bias voltages. The effect of pressure was to vary the mean free path of ions in the plasma, such that a low pressure would increase the ion flux onto the substrate table and hence would be likely to increase the self-bias voltage. The precursor gases were methane and helium in the ratios of 30:75 standard cubic centimetres per minute (sccm). This ratio was chosen as a smaller helium con-
4.3 Post deposition processing

There were two methods used for the processing of films after deposition. The first was thermal annealing and initially two annealing processes were investigated. The first used an 8 kVA optical rapid thermal annealer with a flowing nitrogen atmosphere. The ramp-up times were generally in the order of 20 K s$^{-1}$, and cooling to room temperature took approximately 5 minutes. The second used a graphite strip in the presence of a vacuum better than $10^{-5}$ mbar. It was found that the graphitisation threshold was
approximately 100 °C higher for this system than the other, which may be explained if one assumes that ambient oxygen would catalyse the graphitisation process by favouring the combustion products CO₂ and H₂O. Therefore the vacuum annealing process was the chosen method, though the cool-down time was considerably longer.

The second technique employed was ion-implantation. This was carried out in-house using a Danfysik system, which had the capability to reach voltages of around 200 kV (which results in an ion energy of 200 keV for singly charged species) and beam currents in the order of mA if required. However, these implants were carried out below 50 keV, using a low beam current of 20 μA in order to minimise heating during implantation. Normally, the ions were generated either through sputtering or glow decomposition of precursors. Generally the aim was to implant a uniform profile throughout the film, and this was achieved by carrying out two implants at different energies in order to create a double-hump characteristic. The energies were simulated using TRIM92 and SUSPRE v1.4. The dopant species investigated were boron and nitrogen. Carbon was also implanted as a control in order to ascertain the effects of ion-beam damage.

Top contacts were deposited onto the α-C:H film using an Edwards E306A multi-crucible evaporator, or an in-house-designed evaporator. Schottky contacts have been previously reported in diamond but not in α-C:H. The pressure during evaporation was

![Figure 4.2 Impurity profile for boron implantation of PAC at a dose of 10^{14} \text{ cm}^{-2} \text{ per implant, as simulated using SUSPRE 1.4}](image)
approximately $1 \times 10^{-6}$ Torr. The contacts were laid down by a dot grating, allowing devices of a diameter between 0.25 mm and 2 mm to be fabricated onto one sample. Generally, gold was used as the top contact material, though aluminium, chromium, nickel and titanium were also investigated. It was found that the $I/V$ characteristics were not dependent on the choice of contact material. The metal thicknesses were measured using a crystal thickness monitor, and generally were in the range of 150-300 nm.

Most of the previous work in the literature has been performed in the low electric field ($\sim 10^3$ V cm$^{-1}$) regime, as measured using planar (gap-cell) contacts. This type of measurement may be compromised should there exist any form of conductive surface on the film, as in the case of ta-C where it has been established that the surface is $sp^2$-rich. This may result in conduction across the surface rather than the bulk of the film. The measurements presented in this study are performed using metal-carbon-metal sandwich structures which result in a measurement through, rather than across, the bulk of the film. Furthermore, this allows the measurement of electrical conduction in the high electric field ($\sim 10^5 - 10^6$ V cm$^{-1}$) regime at which different electronic processes occur, in addition to low electric field measurements. These processes can reveal additional valuable information pertaining to the electronic structure and properties of the material.

4.4 Measurement procedures

4.4.1 $I/V$ measurements

The system used was a custom-designed measurement system with one probe sitting on the bottom electrode and one on the top electrode. Gold needles were used to probe the contacts in order to measure the $I/V$ characteristics. A Keithley 487 source was used as the voltage generator and picoammeter. The picoammeter / voltage source was computer-controlled which allowed the measurement of varying voltages, with varying intervals between measurement, both in terms of voltage and dwell time. Also, current versus time measurements were possible, which allowed such factors such as trapping time constants to be measured.

$I/V$ versus temperature ($I/V/T$) measurements were performed using MSM sandwich
structures, and gold top contacts and a CrN back contact. Before the measurements were performed, the samples were annealed at 300 °C for 5 minutes in a vacuum better than $10^{-5}$ mbar. The reason for this was to ensure temperature stability, as it had been found that measuring the $J$ versus $E$ characteristics at high temperatures without previously annealing had the effect of reducing the conductivity of the device at room temperature. The measurements were performed using the Keithley 487 picoammeter / voltage source and probe station onto which a chuck was mounted allowing measurements to be performed between room temperature and 180 °C. A 5 minute wait time at every measurement temperature ensured that good temperature stability was obtained for each measurement. Resistivity values were derived from the slope of the $J$ versus $E$ characteristic at electric fields of $< 2 \times 10^5 \, \text{V} \, \text{cm}^{-1}$.

4.4.2 Ellipsometry

Measurements were carried out on the a-C:H on Si samples to ascertain film thickness and refractive index using a Transitarics manual rotating polariser / analyser ellipsometer. A helium-neon laser of power 1mW and wavelength 632.8 nm was used at an angle of 70° from the normal to the substrate. Thickness readings were verified using a Sloan Dektak IIA profilometer.

![Figure 4.3 Schematic of a rotating polariser / analyser ellipsometer](image)
4.4. Measurement procedures

A narrow beam of laser light was directed onto the sample, and the reflected light was collected by the analyser, which was mounted onto a photodiode and photomultiplier in order to measure the received light intensity. The act of measurement consisted of applying polarised monochromatic light at a pre-defined angle of incidence to the film and analysing the reflected ray with respect to the two polarization angles usually defined as $\delta$ and $\phi$. The incident ray was polarised by the polariser and the angle of polarisation was set by a compensator. After reflection, the light passed through another polariser, the analyser, and the angle of polarisation was calculated by rotating both the polariser and analyser until the light output was extinguished. As long as the material was homogenous and isotropic, simple electromagnetic theory allowed one to obtain a set of unique solutions for the refractive index of the film. This will be to within the error of the Vernier scale with which the polarisation angles were measured, which was 0.1°. Further details may be found elsewhere [107]. Dedicated software was used to calculate refractive index and thickness. The program also gave information as to the period $P$ of the measurement, as the correct thickness was the measured thickness $+nP$, where $n$ is an integer. $n$ was commonly found to be zero by verifying ellipsometric measurements with profilometric analysis. In order to check that the thickness was similar for films grown on silicon as compared to glass or metal substrates, Rutherford backscattering measurements were performed on all three types of sample and the resultant thickness values were found to verify to within 10%.

4.4.3 Optical absorption spectroscopy

This technique was used to obtain a measure of optical transitions between the valence band and the conduction band, which can be used to define a nominal band gap for amorphous materials. The $a$-C:H-on glass samples were placed in a Camspec M330 spectrophotometer for optical absorption analysis. Transmittance was measured for the range 190-900 nm. The spectrometer used a deuterium uv-bulb for wavelengths below 350 nm and an incandescent bulb above 350 nm. The photon wavelength was varied using a variable diffraction grating. The output light was detected using a photodiode. Values of absorption coefficient were calculated for every measurement taken through the energy range, using the data provided, and the following equation:
4.4. Measurement procedures

\[ I = I_0 \exp(-\alpha d) \]  \hspace{1cm} (4.1)

\( I \) was the intensity at a particular wavelength and \( d \) was the film thickness. A control measurement was performed using a bare Corning 7059 substrate which provided values of \( I_0 \) at each measurement wavelength. \( \alpha \) defined the absorption coefficient of the material at a particular incident light energy. The reflection coefficient was assumed to be the same for the glass substrate and the substrate plus the film and therefore was neglected.

These absorptions occur due to a dipole interaction causing energy transitions of electrons in the material. There will be transitions between any two states in the DOS, resulting in a corresponding absorption at the transition energy, and localised - localised transitions are highly unlikely as this would mean a transition from one site in physical space to another just above it being available and empty. As the material is amorphous there is no requirement for the conservation of \( k \), so indirect transitions are also allowed, as long as the energy of the incident photon is equal to the transition of the electron, according to the law of conservation of energy. The resulting absorption coefficient versus energy plot lacks sharp features corresponding to the band edges, both due to the amorphous disorder and the loss of \( k \) conservation.

There is no precise method for quantifying the band gap in amorphous materials due to the existence of band tails, but there are two commonly used methods in obtaining optical band gap parameters from absorption data. The first involves simply defining the edges of the optical band gap as the energies at which the optical absorption coefficient falls below a certain fixed value, which is most commonly \( 10^4 \text{ cm}^{-1} \) [4]. This is known as the \( E_{04} \) optical band gap. The second model derived by Tauc [108] assumes that the density of states \( N(E) \) increases as a power law of energy from an extrapolated conduction or valence band edge. Therefore, if it is assumed that the density of states is parabolic in shape, it is possible to extrapolate a band gap value. This is known as the Tauc optical band gap and is the most commonly used optical notation for amorphous materials. The equation of the relationship is:

\[ \alpha \nu = B [\hbar \nu E_{opt}]^2 \]  \hspace{1cm} (4.2)
where $\alpha$ is the absorption coefficient, $h$ is Planck's constant, $\nu$ is the frequency of the absorbed photon, $E_{\text{opt}}$ is the optical band gap, and $B$ is the Tauc parameter, which gives information as to the sharpness of the band tail. In the case of amorphous silicon, a high $B$ parameter indicates a sharp band tail and hence a low tail state density [4].

As well as the optical band gap, it is also possible to explore $N(E)$ from the optical spectrum to a certain extent. For example, it has often been observed that the optical absorption has an exponential dependence near the band gap energy. An equation describing this is:

$$\alpha = \alpha_0 \exp(\beta \nu)$$  \hspace{1cm} (4.3)

where $\alpha_0$ and $\beta$ are constants. This is known as the Urbach equation [4], and the $\beta$ parameter can provide information about the shape of the band tails. An increase in $\beta$ often coincides with a decrease in disorder, resulting in the introduction of states into the band gap [4].

### 4.4.4 Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy is used to quantify the density of paramagnetic electron spins, which are a consequence of positive $U$ dangling bond defects [4]. When a quantum state is occupied by a single electron, it is normally degenerate, but is split on the application of a magnetic field, and it is the transition between these energy levels that gives rise to the EPR signal. The transition generally occurs at microwave frequencies. The signal is commonly a first derivative and must be integrated twice to ascertain the total paramagnetic density within the sample. This may be in terms of an areal density or volume density [105].

Also the spectrum gives information about the local bonding structure. In particular, the $g$ value may shift due to spin-orbit coupling between other electron states; this gives detailed information about the local bonding structure of the defect. It is common to expect a $g$-value of around 2.0055-2.0060 to correspond to a silicon dangling bond and a $g$-value of 2.0028 to correspond to a carbon paramagnetic spin [109].

Furthermore, interactions may occur between the electron when it is close to a nucleus (most commonly H), resulting in further splitting of the energy levels. This is known as
the hyperfine interaction and can give information about the localisation of the defect [105]. More often, in α-C:H the hyperfine is unresolved and leads to a broadening of the signal [110]. Linewidth broadening can also be a result of a dipole interaction between like spins.

EPR measurements were made in the University of Dublin under the supervision of Dr R. C. Barklie. They were carried out on the samples grown on high resistivity Si at room temperature, using a $TM_{011}$ cavity at a microwave frequency of 9.9 GHz, at a field modulation of 100 kHz. The required EPR parameters of the sample was obtained by comparing with standard markers, which were standard pitch in KCl, for spin populations, and F$^+$ centres in MgO, for $g$-values.

4.4.5 Rutherford backscattering

Rutherford backscattering spectroscopy (RBS) relies on the Coulombic repulsion of nuclei resulting in the scattering of incident (for example He) high energy ions. The energy spectra of the backscattered ions is collected, and further sample information is derived from this. Energy loss of the incident ion occurs due to two main factors: the energy lost to the nucleus and the energy lost to the electronic lattice before hitting the nucleus. The first is due to the conservation of momentum and mass-energy as these collisions are elastic. Hence, a light target nucleus will result in a greater energy loss than a heavier one. This allows the user to ascertain the atomic mass within the sample. The second is due to how deep inside the sample the target nucleus is. The incident particle will undergo electronic stopping as it passes through the material and therefore the energy of the backscattered ion will be reduced if it collides with a nucleus further inside the sample, as compared to one on the sample surface. This allows depth resolution of the atomic species within the sample. There are many other important factors to take into account, such as channelling, which occurs if the incident ions are allowed to penetrate far into the sample due to its lined-up lattice channels as a consequence of its crystallinity; however this is not important in our case. RBS is a valuable tool but only with atoms of atomic mass typically greater than 14, as lower atomic masses will not be able to backscatter the incident ions.

This measurement was performed by Drs C. Jeynes and N. P. Barradas in the University of Surrey. A 2 MV Van der Graff generator was used to create a beam of $^4$He$^+$ that
impinged on the sample. Backscattered ions at an angle of 165° were analysed in order to obtain a depth profile using the Datafurnace program NDF v6.3 [111].

4.4.6 Elastic recoil detection and nuclear reaction analysis

Elastic recoil detection analysis (ERDA) is a complimentary technique to RBS which also relies on the principle of elastic collisions. However, this time a heavy incident ion (typically $^{14}$N or $^{35}$Cl) is used, and the energy spectrum of recoiled ions are measured. This is of use when ascertaining the species within the sample, if they are of low mass. In particular, hydrogen is the lightest element and as such will be recoiled; hence this method is often used to ascertain the hydrogen content of thin films. In our case, ERDA was carried out in the Forschungszentrum Rossendorf under the supervision of Drs U. Kreissig and N. P. Barradas. A beam of 35 MeV $^{35}$Cl$^{7+}$ ions was used and two detectors were employed; a Si surface barrier at 38° and a Bragg chamber at 30°. The data was once again analysed using the DataFurnace program NDF v6.3.

Another method used to obtain the H content is nuclear reaction analysis (NRA). Materials are bombarded by ions and the elements are identified and measured from their characteristic nuclear reaction products. The energy and yield of these products gives information towards the isotope present. Also, elemental depth profiles can be determined by the energy loss of the incident ions, as in RBS. This technique was used to determine the H content of our $a-C:H$ films, using the 5 MV Tandem accelerator of the Forschungszentrum Rossendorf. The nuclear reaction of interest was:

$$^{15}N + ^{1}H \rightarrow ^{12}C + ^{4}He + \gamma$$  \hspace{1cm} (4.4)

The $^{15}N^+$ ions required a characteristic energy of 6.385 MeV to undergo the nuclear reaction, plus any extra energy required in order to compensate for the energy loss as a result of stopping, in order for the H content to be taken at a specific depth. Our samples were measured at a depth of 40 nm by Dr D. Grambole in the Forschungszentrum Rossendorf. The $\gamma$ rays as a consequence of the nuclear reaction had an energy of 4.43 MeV. This reaction is known as the $^1H(^{15}N, \alpha\gamma)^{12}C$ reaction.
4.5 Experimental considerations

The following summarise the experimental problems that were overcome in order to produce reproducible and consistent optical and electronic data from the a−C:H films.

4.5.1 Thickness inconsistencies

Firstly, it was observed that films grown on the earthed electrode possessed a large thickness variation. This was approximately ±5 % over a 2 cm sample. This led to inaccuracies in optical band gap and $J/E$ data of a similar order of magnitude. The solution for this was to place the samples approximately three quarters of the radius of the platen, where the thickness variation was at a minimum. Also, samples larger than 2 cm$^2$ were avoided. If the length of the sample was greater than this, the sample was placed with the width radially, to reduce the thickness inconsistency.

As a result, there was therefore a very large (over 100 %) thickness variation over the whole of the platen. Films grown in the centre of the platen were very thin and possessed anomalous optical properties. This further emphasised the need to always place the samples on the same part of the platen, and measure and keep the distance between the sample and the centre of the platen constant between depositions, which was performed by measuring the distance prior to deposition.

4.5.2 Contamination

During deposition, it was necessary to ensure that the a−C:H films grown were as free of contaminants. This was achieved by utilising the following procedures. Firstly, the gases used were of electronic-grade purity: all precursors had a purity of 99.99 % or higher. Secondly, it was necessary to pump the gas lines in order to ensure a reduced contamination risk. This was carried out by activating the gas line and closing the source at the gas bottle, in order to pump the entire volume of the line and also to minimise damage to the gas regulator, which cannot sustain the pressure differential between a pumped line and gas bottle pressure, which is typically 10s or 100s of bar.

Thirdly, leak checks were frequently carried out, over both the chamber and the gas lines. This was achieved by closing the gate valve, and monitoring the rate of increase in base pressure, as measured from the capacitance manometer. This was carried out
both with only the chamber, and also with the chamber and any pumped lines, in order
to check whether the gas lines possessed any leaks. A value of approximately 3 mTorr
min$^{-1}$ was the lowest that was normally recorded. Should there be any leak, this was
detected by filling the chamber up to overpressure with helium and using a helium leak
detector externally. Also, the base pressure was carefully monitored and was recorded
to be $2 - 3 \times 10^{-4}$ Torr, as measured from the chamber exhaust using a Penning gauge.
Any deviation from this could be evidence of a vacuum leak.

Fourthly, during depositions, one had to ensure that the chamber was properly degassed
before a deposition was carried out. Both water vapour from the atmosphere and any
cleaning material (for example isopropanol) were sources of contamination and both had
to be expelled before deposition could be performed. This was performed by waiting
typically 30 mins, between pump-down and deposition. The leak rate, as has been
described above, was the best evidence as to whether the chamber had fully degassed.

Other precautions included regular cleaning of the chamber between depositions using
isopropanol, and also using an oxygen plasma between deposition batches. The chamber
O-ring seal also had to be cleaned and checked periodically. Obviously, care had to be
taken when handling the samples, which were always manipulated using tweezers.

4.5.3 Adhesion and delamination

It was noted that DAC films grown on the upper electrode were intrinsically highly
stressed, which led to film delamination. This has already been attributed to high
internal stresses [112]. Hence, films deposited at the optimum self-bias for diamond-
like growth were the most likely to delaminate. However, the films were much more
prone to delamination at higher film thicknesses. It was found that the adhesion of DAC
films was best on Si substrates, and worst on metal-on-glass substrates. For example,
at a power of 200 W, the maximum film growth was approximately 100 nm on a Si
substrate but only 70 nm on a glass substrate and 50 nm on a CrN-on-glass substrate.
Hence, the deposition times, and therefore thicknesses, were reduced, generally to the
range of 40-60 nm.

The reason for this variation was that C was forming covalent bonds with the Si surface,
preventing delamination. It is also possible that the poor thermal conductivity of glass
and metal-on-glass substrates would also contribute to delamination, as the surface of
the substrate could thermally expand due to heating during ion bombardment, and this would be therefore greater for these substrates than for Si. As the expansion coefficient for C is close to Si, [113], the mismatch during growth would be smaller and hence the films would be less likely to cracking.

Another significant observation was that the films grown on the earthed electrode were very soft, and could easily be scratched with tweezers. This could lead to misleading ellipsometric results and a low device yield. There was also a large concentration of particulates and "dust" following deposition in these films. This could have been due to the cracking of the film buildup on the powered electrode, which then fell onto the earthed electrode during deposition, as well as other factors [114]. Efficient cleaning using isopropanol and also an oxygen plasma reduced this to a minimum. However, the particulate content would still reduce the device yield, such that only the smaller devices (0.5 mm diameter or less) were likely to function.
Chapter 5

Electrical properties of as-deposited \( a-C:H \)

5.1 Introduction

The opto-electronic properties of \( a-C:H \) have been documented by several researchers. However, there is still much debate as there is a large variation in the film properties which have been reported by different groups, as outlined in Chapter 3. It is necessary in these studies to fully characterise the film and outline the important film parameters before studies into processes such as nitrogen doping and ion implantation are performed. This is because different groups grow different types of \( a-C:H \) film which, with a decreasing Tauc band gap ranging from 3 to 0.5 eV, ranges from polymer-like (PAC) to diamond-like (DAC) and graphite-like (GAC). Even within these subdivisions, there is large scope for variations in properties such as \( sp^2 \) and hydrogen content.

Furthermore, in the field of \( a-C:H \) other researchers in the past have only investigated the electrical properties of “diamond-like” carbon films which possess a high defect density of \( \sim 10^{20} \) spins cm\(^{-3} \) [33], which is likely to result in conduction through some type of defect band and not through an extended state. Polymeric films possess a much lower defect density in the order of \( 10^{17} \) spins cm\(^{-3} \) [109] and therefore are less likely to conduct through midgap defects. Also, there will be a higher probability of doping with these films, as the Fermi level is less likely to be pinned at midgap.

In this section we will ascertain the low- and high-field transport properties of PAC and DAC films, and the effect of varying the DC self-bias. This would have the effect
of changing the film structure from one form to another [37]. At high DC biases (above 300 V) the films are likely to become graphitic, according to Amaratunga [112].

The following Table is a characterisation of the as-deposited $a$–C:H films grown using the Plasma Technology DP800 system at the University of Surrey. Section 4.2 reports that there is a large DC self-bias developed on the powered electrode and a smaller bias on the earthed electrode (the plasma potential - typically 20-30 V). This causes the films grown on the earthed electrode to be polymer-like in nature (PAC), the evidence for which is the presence of a large amount of hydrogen in the films, determined using ERDA, whilst those grown on the powered electrode are diamond-like (DAC) and possess higher hardness and stress.

<table>
<thead>
<tr>
<th></th>
<th>PAC</th>
<th>DAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H content (at. %)</td>
<td>55-60</td>
<td>40-45</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>$10^{14} - 10^{15}$</td>
<td>$10^{11} - 10^{13}$</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.5-1.7</td>
<td>1.9-2.2</td>
</tr>
<tr>
<td>Tauc gap (eV)</td>
<td>2.5-2.7</td>
<td>0.7-1.2</td>
</tr>
<tr>
<td>$E_{\text{g}}$ gap (eV)</td>
<td>3.0-3.8</td>
<td>1.0-1.5</td>
</tr>
<tr>
<td>Spin density (cm$^{-3}$)</td>
<td>$10^{17-18}$</td>
<td>$10^{19-10^{20}}$</td>
</tr>
<tr>
<td>Hardness (GPa) [37]</td>
<td>2-4</td>
<td>6-8</td>
</tr>
<tr>
<td>Stress (GPa) [112]</td>
<td>0.1 - 1</td>
<td>2-5</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$) [37]</td>
<td>1.4-1.6</td>
<td>1.6-2.0</td>
</tr>
</tbody>
</table>

Table 5.1 Generalised properties of PAC and DAC films.

As shown in this table, PAC films show a lower density of paramagnetic defects and wider optical band gap than the more commonly grown DAC films. However, PAC films possess lower hardness than DAC films and possess a lower temperature stability, due to the presence of additional H which would become mobile at higher temperatures in a similar manner to $a$–Si:H [4]. The temperature stability of these two types of film will be reported in Chapter 6, with respect to the optical and electrical properties.
5.2 Optical properties

The following films were grown at a pressure of 200 mTorr and an rf power of 200 W, which equated to a DC self-bias voltage of -175 V on the powered electrode and \sim -20 V on the earthed electrode, onto Corning 7059 substrates. Lower wavelengths were unobtainable as the glass absorbed heavily in the ultraviolet region in the range of 190-300 nm. In order to determine the absorption coefficient $\alpha$ the thickness of the film was required and this was determined by also growing films onto silicon substrates which were measured using ellipsometry using an incident light wavelength of 632.8 nm. The method for obtaining the absorption coefficient and Tauc values is outlined in Section 4.4.3. The following Figures (5.1-5.2) were obtained by firstly calculating the absorption coefficient $\alpha$ from the transmittance data, and then either plotting

![Image](image-url)

**Figure 5.1** Optical absorption plots for films grown on the earthed electrode: (a) $E_{04}$ plot, (b) Tauc plot.
5.2. Optical properties

It may be observed that for the films grown on the earthed electrode, the $E_{04}$ plot yields an optical band gap value of 3.5 eV and the Tauc plot gives a value of 2.5 eV. It is commonly reported that the Tauc value for optical band gap is smaller than the $E_{04}$ value [37]. Also it is observed that in the high energy region a straight fit to the Tauc plot is good but at lower energies the measured line deviates from the straight line. For films grown on the powered electrode, the $E_{04}$ plot yields an optical band gap value of less than 1.4 eV, which is the limit for measurement using our optical absorption spectrometer which has a maximum wavelength of 900 nm. The Tauc plot yields a straight line which intercepts the x-axis at a value of 0.7 eV. The fit to the Tauc plot is better in the low energy region than for the films grown on the earthed electrode.

Figure 5.2 Optical absorption plots for films grown on the powered electrode: (a) $E_{04}$ plot, (b) Tauc plot.

This logarithmically against energy, or calculating values using the Tauc method [108], respectively.
5.3 Electrical properties

The Tauc plot will be the chosen method in which to measure optical band gap, as the band gap is interpolated assuming parabolic band edges, which is likely to yield a better indication of electronic band gap than the $E_{04}$ value which more arbitrarily defines the optical band gap as the absorption limit below a certain value.

5.3 Electrical properties

In order to determine the low and high field electrical properties of the powered and earthed electrode grown a-C:H films they were deposited onto metallic substrates. Chromium sputtered onto glass in a nitrogen atmosphere was chosen due to its superior properties in terms of high conductivity and mechanical strength. Other substrates too were investigated, namely evaporated Al and Ti, and the characteristics were not found to deviate significantly. Therefore it appeared that the characteristics were not back-contact dependent. Metal-semiconductor-metal sandwich structures were fabricated by evaporating metallic top contacts onto the films. Once again a range of materials were employed (Au, Ti, Al, Cr) and it was observed that there was no dependence on the top metal contact. For the studies conducted here Au was chosen as a top contact material as the evaporation temperature was lower ($\sim 100 \, ^\circ C$) than with the other materials, which was established by placing temperature strips in the evaporation chamber. Therefore, there was a lower risk of in-situ annealing during evaporation than with the other contacting materials. The current versus voltage characteristics were measured using a probe station and Keithley 487 picoammeter / voltage source. Current density ($J$) values were calculated from the current by dividing by the contact area and it was found that they were the same within measurement error, for the range of contact sizes. Therefore, there was no appreciable edge effects contributing to the total current. Values of electric field were determined from the voltage by dividing by the film thickness.
5.3. Electrical properties

5.3.1 Earthed electrode grown films

5.3.1.1 J/E Characteristics

The current density (\(J\)) versus electric field (\(E\)) in linear and log plots, and \(\ln(\text{current density})\) versus field\(^{1/2}\) of a typical 100 nm thick film grown on the earthed electrode is shown in Figure 5.3. It can seen from (a) that up to an electric field of \(4 \times 10^5\) V cm\(^{-1}\) the current density scales approximately linearly with electric field which allows low-field values of resistivity to be calculated. For this film the calculated value is \(2 \times 10^{15}\) \(\Omega\) cm. A linear \(J/E\) characteristic at these electric fields suggests that electronic transport is occurring either by hopping within a defect band close to the Fermi level, conduction in the band tails or conduction through extended states \([1, 4]\), rather than any of the mechanisms that apply in the high field, such as space-charge-limited current \([9]\), Poole-Frenkel \([11]\) conduction or the Schottky effect \([115]\). At higher fields the current increases with applied voltage in a parabolic fashion, this is indicative of conduction mechanisms such as space-charge-limited current (SCLC).

It is shown in Figure 5.3(b) that there is a large degree of hysteresis in the \(J/E\) characteristic, as when the voltage is reduced from the maximum value, the measured current is lower than the current which was measured on the ramp-up. This is most likely to be an effect of the capacitance of the device, and the long time constant which is a result of the high resistivity of the film. This will be examined in Section 5.5.2.

Figure 5.3(c) plots \(\ln J\) versus \(E^{1/2}\), which is the conventional graph \([13]\) for the purpose of fitting to Poole-Frenkel or Schottky Effect conduction. The analysis performed in later studies will examine Poole-Frenkel conduction in terms of a \(\ln J/E\) versus \(E^{1/2}\) relationship, which is in accordance to the equation shown in Section 2.4.2. However, from the plot shown here the slope of the graph will not be significantly different from the case of the \(\ln J/E\) versus \(E^{1/2}\) plot. This figure shows that an approximately straight-line region is obtained in the field\(^{1/2}\) range from 400 to 700 V\(^{1/2}\) cm\(^{-1/2}\). Therefore, it is possible that either of these two mechanisms is applicable. The analysis of the slope will be performed in Section 5.5.2.

Figure 5.4 shows the characteristics of films grown to different thicknesses on the earthed electrode in order to check whether conduction is contact or bulk limited. Should conduction be contact limited, \(J\) will be the same irrespective of film thickness when
Figure 5.3 Current versus voltage characteristics for films grown on the earthed electrode: (a) linear $J$ versus $E$ plot, (b) log $J$ versus $E$ plot, (c) ln $J$ versus $E^{1/2}$ plot.
Figure 5.4 Current versus voltage characteristics for films of differing thicknesses grown on the earthed electrode: (a) $J$ versus $V$ plot, (b) $J$ versus $E$ plot, (c) $\frac{J}{d}$ versus $\frac{V}{d^2}$ plot.
plotted against $V$, according to Simmons [14]. It can be seen in Figure 5.4(a) that the $J$ versus $V$ characteristics do not coincide for the three film thicknesses, which excludes a contact-limited conduction process. If the conduction was bulk-limited, then the current would be determined by the electric field over the device, so the $J$ versus $E$ characteristic would be the same for all film thicknesses. This is plotted in Figure 5.4(b). It can be seen that once again the $J$ versus $E$ curves do not coincide for the three film thicknesses.

A common high-field conduction mechanism in MSM structures is space-charge-limited current (SCLC) where the dependence follows a parabolic relationship which varies according to the density and distribution of states within the band gap. Figure 5.4(c) shows the variation of $J/d$ against $V/d^2$ on log-log axes for the three film thicknesses to investigate if SCLC is governing high-field conduction according to the equations outlined in Section 2.4.1. It may be observed that although the curves for the three different film thicknesses do not coincide at low voltages, they approach a similar line at higher voltages. A slope may be calculated from this line and is found to be 2.0. This suggests a power law dependence of current against voltage, i.e. $J \propto V^{2.0}$, and indicates trap-free SCLC.

5.3.1.2 $J/E/T$ measurements

As shown by Mott and Davis [1] and outlined in the Chapter 2, conduction may occur via carriers excited into the extended states, into localised states in the band tail, or hopping at the Fermi level (either thermally activated or VRH). The dominant mechanism will be determined by the temperature and therefore it is necessary to perform $J$ versus $E$ measurements as a function of temperature.

Figure 5.5 shows the variation of $\ln(\text{conductivity})$ against $-q/kT$ for a PAC film. It may be observed that at $-q/kT$ values of less than 33, corresponding to a measurement temperature of less than 100 °C, there is no variation of conductivity with temperature, and therefore the activation energy in this range is zero within measurement error. At higher temperatures (> 110 °C) a straight-line dependence is observed for $\ln J$ versus $-q/kT$ plot which indicates a thermally activated process which fits the Arrhenius law. From the slope of the graph an activation energy may be determined and the value derived is 0.68 eV ± 0.05 eV.
5.3. Electrical properties

5.3.2 Powered electrode grown films

5.3.2.1 $J/E$ characteristics

The current density ($J$) versus electric field ($E$) in linear and log plots, and ln(current density) versus (electric field)$^{1/2}$ of a 50 nm thick film grown on the powered electrode is shown in Figure 5.6. Higher film thicknesses resulted in delamination and were therefore unobtainable. This films was grown at an rf power of 200 W which equated to a DC bias voltage of -175 V. It was observed that at low electric fields ($< 2 \times 10^5$ V cm$^{-1}$) the current density scales linearly with the electric field yielding a resistivity value of $1.2 \times 10^{13}$ Ω cm. This indicates that low field conduction is also dominated by the carrier transport mechanisms described in Section 2.3, namely either extended state conduction, band-tail conduction or hopping at or near the Fermi level.

It can be observed in Figure 5.6(b) that the $J$ versus $E$ characteristic is symmetrical with respect to polarity of field, and possesses a much greater turn-on slope than that shown for films grown on the earthed electrode, as shown in Figure 5.3. Also the degree of hysteresis is smaller. This is because the resistivity of the film is two orders of
Figure 5.6 Current versus voltage characteristics for films grown on the powered electrode: (a) linear $J$ versus $E$ plot, (b) log $J$ versus $E$ plot, (c) In $J$ versus $E^{1/2}$ plot.
magnitude smaller than that for films grown on the earthed electrodes, and therefore the capacitive time constant $RC$ is two orders of magnitude smaller.

A mechanism which applies to films possessing a high defect density is the Poole-Frenkel effect, although the Schottky effect is also applicable for many semiconducting films. Figure 5.6(c) shows that a straight line is obtained if $\ln J$ versus $E^{1/2}$ is plotted. This indicates that either of these two mechanisms may be appropriate. A detailed analysis of the slope of this curve in order to distinguish between these two mechanisms will be performed in Section 5.5.2.

### 5.3.2.2 $J/E/T$ measurements

Figure 5.7 shows the variation of $\ln(\text{conductivity})$ against $-q/kT$ for this film. In this case, at lower temperatures (20-80 °C), the temperature dependence fits an Arrhenius law which yields an activation energy of 0.28 eV ± 0.04 eV. At higher temperatures (100-160 °C) the slope of the characteristic increases slightly and for this region the derived value of activation energy is 0.31 eV ± 0.03 eV.
5.4 Effect of DC bias voltage

As has been reported in the literature, for films that are deposited on the powered electrode of a rf–PECVD reactor the DC bias of deposition is an important factor in determining the opto-electronic properties of the a–C:H film. Several authors have shown that the effect of increasing DC bias is to narrow the optical band gap [29, 28] and increase the conductivity [31]. However the effect on the high-field conduction mechanism has not been ascertained as yet. Furthermore, the films grown under a low DC bias would be similar in opto-electronic properties to films grown on the earthed electrode, which possess a DC bias equivalent to the plasma potential - typically 20-30 V. It has been shown in Section 5.3.2 that films which are deposited under a DC bias of -175 V are likely to exhibit Poole-Frenkel conduction at high fields and films deposited on the earthed electrode show space-charge-limited current. Therefore it is instructive to demonstrate a bias voltage where the conduction process changes from one type to another.

It was necessary to measure the DC bias voltage and its variation with rf power, in order to vary the material properties of films grown on the powered electrode. This was performed by introducing a choke into the rf power supply at the powered electrode as shown in Figure 4.1. The variation in bias voltage with increasing rf power is shown

![Graph showing the effect of varying rf power on DC self-bias voltage for CH₄ and CH₄/He plasmas.](https://example.com/graph.png)

**Figure 5.8** Effect of varying rf power on DC self-bias voltage for CH₄ and CH₄/He plasmas.
5.4. Effect of DC bias voltage

in Figure 5.8 for a 30 sccm CH\textsubscript{4} plasma, and a mixture containing 30 sccm CH\textsubscript{4} and 75 sccm He. It can be seen that as the rf power was increased the DC bias increased. Furthermore it is observed that the DC bias is greater when the plasma contains a mix of CH\textsubscript{4}/He rather than only CH\textsubscript{4}. The reason is that He has a higher ionisation energy threshold than CH\textsubscript{4} which moves the plasma energy to higher values. Therefore the plasma temperature is increased and the greater density of ionic and electronic species results in a greater DC bias being recorded.

5.4.1 Optical Properties

The films were grown under standard conditions onto Si and Corning 7059 substrates for refractive index and optical absorption analysis, respectively. The variation of refractive index and Tauc band gap with DC bias voltage is shown in Figure 5.9. It

![Figure 5.9 Variation of refractive index and Tauc band gap with increasing DC bias.](image-url)
can be seen that as the bias voltage is increased there is an increase in refractive index from 1.60 to 2.25, which is accompanied by a decrease in Tauc band gap from 2.4 eV to 0.5 eV. The film grown under a DC bias of -50 V shows an optical band gap of 2.3 eV and a refractive index of 1.6, which compares to an optical band gap value of 2.5 eV and refractive index value also of 1.6 for films grown on the earthed electrode. This suggests that this film too is polymeric in nature.

5.4.2 Electrical Properties

In order to ascertain the variation in $J$ versus $E$ characteristic with increasing DC bias voltage during deposition, films were grown onto sputtered CrN-on-glass substrates and top contacts were evaporated onto the films. The variation in electrical properties with increasing DC bias voltage is shown in Figure 5.10. At the lowest DC bias voltage, the magnitude of current is close to the noise threshold for the measurement apparatus. Increasing the DC bias to -110 V has the effect of increasing the current density by 3 orders of magnitude. When the DC bias voltage is -165 V the characteristic changes in nature and shows a sharper turn-on slope which is an indication of the onset of Poole-Frenkel conduction. This remains for films grown at higher DC bias voltages though the magnitude of current density increases with bias voltage over 2 orders of magnitude. At a bias of -260 V there is little further increase in the current density.

![Figure 5.10 Variation of $J$ versus $E$ characteristic with increasing DC self bias.](image)
5.4.3 EPR Properties

In order to determine the variation of paramagnetic spin density and linewidth as a function of DC bias voltage, films were grown onto highly insulating (100 Ω cm) Si substrates and were analysed using EPR spectrometry. Figure 5.11 shows the variation of the EPR properties with increasing DC bias voltage. It may be observed that up to a bias voltage of -120 V, the paramagnetic spin density shows an increase from $3 \times 10^{17}$ cm$^{-3}$ to $1 \times 10^{20}$ cm$^{-3}$ and the linewidth shows a concomitant increase from 0.8 mT to 1.4 mT. At higher DC bias voltages the spin density stabilises at $1.8 \times 10^{20}$ cm$^{-3}$ and the linewidth shows a sharp decrease to 0.6-0.7 mT. The lineshape was found to change from Gaussian to Lorentzian at a DC self-bias voltage of -125 V and above.

![Figure 5.11 Effect of DC self-bias voltage on paramagnetic defect density and linewidth, as measured using EPR.](image)
5.5 Discussion

5.5.1 Optical properties

The optical data as shown in Figures 5.1-5.2 show that both the Tauc and $E_{04}$ band gap are considerably wider for films grown on the earthed electrode as compared to films grown on the powered electrode. According to Robertson [116] in $a$–$C$ the optical band gap is predominately governed by the size and density of the $sp^2$ clusters within the material. A small cluster size relates to a wide band gap, according to the equation

$$E_g \approx \frac{6}{N^{1/2}}$$  \hspace{1cm} (5.1)

where $N$ is the number of 6-fold rings within a cluster. Therefore, for a film possessing a Tauc band gap of 2.5 eV $N \approx 6$, and for a film possessing a Tauc gap of 0.7 eV $N \approx 73$. Robertson states in a later paper [23] that the Tauc gap may be narrowed as a consequence of the distortion of planar rings due to film stress. The film grown on the powered electrode is likely to be highly stressed as it is comparable in its properties with DAC films, and therefore the additional stress may cause a lowering of the band gap. It is still likely, however, that films grown on the powered electrode contain a smaller $sp^2$ cluster size than films grown on the powered electrode and therefore the $sp^2$ content is lower.

In the case of the films grown on the earthed electrode, the deviation from the fit to the Tauc model at energies lower than the band gap suggests that tail states extend into the band gap away from the parabolic band tails that define the Tauc gap of the material. The fact that the fit is much closer to the experimental data from films which are grown on the powered electrode shows that the band tail more closely resembles a parabola in this case, and also there are fewer tail states below the Tauc-defined band gap limit.
5.5. Discussion

5.5.2 Electrical properties

5.5.2.1 Earthed electrode grown films

It can be seen in Figure 5.3(a) that the current rise with applied voltage is linear at low fields and in (b) that the characteristics show a large degree of hysteresis which suggests either a large contribution of device capacitance or trapping. It has been observed in a separate experiment that as the time interval between measurements is increased between 0.5 s per 0.1 V measurement step to 2 s per measurement step, the degree of hysteresis is seen to decrease. This means that there is a transient increase in current as the voltage is increased which decays as the measurement time is increased, which is indicative of a capacitive effect. Now assuming $C = \varepsilon_0 \varepsilon_r / d$ and $R = \rho / A$, the time constant $RC = \rho \varepsilon_0 \varepsilon_r$. If $\varepsilon_r = 2.6$, i.e. the square of the refractive index, and $\rho = 2 \times 10^{15} \, \Omega \, \text{cm}$, then the calculated time constant is approximately 460 s. Therefore, over the time of measurement performed here, a considerable residual voltage caused by the capacitance of the device ($V_C$) exists over the device due to stepping up to the maximum voltage value even as the measurement voltage ($V_M$) is then stepped back down to zero. Therefore the overall voltage across the film is lower than the applied voltage due to the capacitance contribution, as $V_{TOT} = V_M - V_C$, and hence causes the observed hysteresis.

In order to ascertain whether high-field conduction may be governed by Poole-Frenkel or Schottky conduction, it is necessary to investigate Figure 5.3(c). By applying the Poole-Frenkel equations shown in Section 2.4.2 and the slope $\beta = 1/kT[\varepsilon^3 / \pi \varepsilon_0 \varepsilon_r]^{1/2}$, and ignoring the $E$ prefactor which would only effect the $y$–axis values in the low field, the derived value of permittivity is 110, which is higher than the value derived from the square of refractive index, which is approximately 2.6. Therefore, the Poole-Frenkel effect does not govern the conduction process within these films. The Schottky effect also does not control conduction as in this case a slope of $\beta / 2$ would yield a dielectric constant value of approximately 28, which is also higher than the derived value.

SCLC has been used in order to fit to the $J/E$ characteristics to ascertain the density of states within the band gap [18, 19]. However in the case of this material the trap density is not as high as in the case of previously observed $a-$C:H films and therefore an analysis assuming either a trap-free material or a material with a density of shallow traps is applicable. Applying the equation $J = 9 \mu \varepsilon_0 \varepsilon_r E^2 / 8d$ [9] from Section 2.4.1, it
can be seen that for different thicknesses \( J/d \) will be proportional to \( V/d^2 \) with a slope of 2 when plotted on log-log axes. This is shown in Figure 5.4(c) where it can be seen that the curves appear to coincide in the high-field region. The slope of this section is 2.0 which is close to the theoretical value. The low-field conduction follows a linear dependence with voltage and this would account for the deviation from the fit to SCLC at lower electric fields.

Assuming a value of \( \epsilon_r \) to be 2.6 (the square of the refractive index), by extracting the slope from a \( J \) versus \( E^2 \) plot, a mobility value of \( 1.2 \times 10^{-10} \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) is derived, which is low when compared to other semiconducting films, for example \( a-\text{Si:H} \) which possesses a room temperature mobility of the order of \( 1 \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) [4]. The mobility of \( ta-\text{C} \) has been derived by Clough et al. [99] from measurements of a field-effect transistor to be in the order of \( \sim 10^{-6} \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \). However, the resistivity of \( ta-\text{C} \) is commonly in the order of \( 10^7 \) \( \Omega \text{cm}^{-1} \) [62] which is lower than the measured value for PAC films in this study, \( \sim 10^{15} \) \( \Omega \text{cm}^{-1} \). Therefore, the low mobility of carriers in PAC films contributes significantly to the high resistivity values which are observed.

**Activation energy** The value of \( E_{\text{act}} \) for the earthed electrode grown films below a measurement temperature of 100 °C, which is zero within measurement error, as shown in Figure 5.5, suggests that any strongly thermally activated mechanism such as extended state or band tail conduction is ruled out for PAC films at room temperature, and therefore conduction at low electric fields is dominated by hopping. Simmons [14] suggested that the absence of an activation energy the majority of carriers would be condensed in traps or donor sites. If the centres are closely spaced, the carriers may tunnel between nearest neighbour sites, which is known as tunnel or nearest-neighbour hopping, as shown in Section 2.3. Due to the lack of any clear temperature dependence, and also the fact that due to the high resistivity of the films any variation is within 10 % of each other, and therefore within the experimental error of the measurement apparatus, it is not possible in our case to ascertain whether this type of hopping dominates or another mechanism, for example VRH.

At temperatures above 100 °C, the value of \( E_{\text{act}} \) has been shown from Figure 5.5 to be approximately 0.7 eV. The most likely mechanism is the transport of carriers excited to localised states at the band edges, as one would expect a change from hopping to band-tail conduction as the temperature was increased, rather than a transition directly
5.5. Discussion

to transport in the extended states. The value of band gap obtained from the Tauc method is approximately 2.5 eV. Therefore, assuming that the Tauc method describes the energy gap between the band edges, assuming that they are parabolic, the Fermi level is not at midgap but at 0.7 eV from one of the band edges. Previous studies have shown that intrinsically grown $a$-$C$ is $p$-type [78] and an explanation for this is that the dangling bond defect in carbon has a lowered energy leading to $p$-type conductivity. In this case it is therefore more likely that the 0.7 eV activation energy represents the energy difference between the Fermi level and the valence band rather than the conduction band edge.

5.5.2.2 Powered electrode grown films

From Figure 5.6(a) it has been observed that the resistivity value for films grown on the powered electrode is two orders of magnitude smaller than those grown on the earthed electrode. This has been reported in the literature, by for example Stenzel et al. [31], who showed that the resistivity increases as a function of optical band gap for $a$-$C$:$H$ films. This increase could be related to either an increase in the energy gap between the Fermi level and the extended states, or an increase in the density and distribution of hopping sites which contribute to the conductivity of the material.

It has been observed that for films of differing thicknesses the current density versus applied electric field appear to coincide, which suggests that conduction in the high field is bulk-limited. As shown in Table 5.1, these films possess a high defect density of the order of $10^{19} - 10^{20}$ paramagnetic spins cm$^{-3}$, as determined using EPR. A large density of paramagnetic defects implies a large density of trap states and hopping centres which would dominate the conduction process.

In order to ascertain from Figure 5.6(c) whether either Poole-Frenkel or Schottky conduction govern high-field conduction in these films it is necessary to calculate the theoretical permittivity value using the equations described in Sections 2.4.2 and 2.4.3. Using the P-F equations the derived value of permittivity is $4.1 \pm 0.5\%$, which is very close to the permittivity value derived from the square of the refractive index, which is approximately 4.5. Using the Schottky method the derived permittivity value is 1.0, which is lower than the value derived from the square of the refractive index. Therefore, the Poole-Frenkel effect is the most likely high-field conduction mechanism for this type
of film. This would account for the fact that that conduction appears to be bulk-limited rather than contact limited, according to the current scaling with film thickness.

**Activation energy** From Figure 5.7 the low-temperature $E_{act}$ value of 0.28 eV and the high-temperature $E_{act}$ value of 0.31 eV may either correspond to a transition between hopping transport to band tail conduction, or a transition between band tail and extended states conduction. The dependence in the lower temperature region is not a straight line, so it is possible that another mechanism is governing conduction at the band tail (for example VRH) and the 0.31 eV activation energy describes transport in the band-tail. However, a lower temperature activation energy of 0.28 eV is likely to be too high for hopping at the Fermi level where the density of states is likely to be narrower. Therefore, we will assume extended-states conduction in the higher temperature region, when a 0.31 eV activation energy is compared to the Tauc band gap of 0.7 eV, it is found that the Fermi level would be placed close to midgap. It is likely that undoped DAC is slightly $p-$type [23]. A similar characteristic was reported by Chan et al. who derived a high-temperature activation energy of 0.34 eV, close to the value obtained here, which was attributed to extended states conduction. This value was close to that reported for highly resistive diamond films which suggested the presence of deep acceptor trap states which resulted in the intrinsic $p-$type conduction of diamond. Similar values of activation energy have also been derived in the case of GAC [117] and ta-C [59] and in those cases were attributed to the energy difference between the Fermi level and the valence band edge.

5.5.3 Variation with DC bias

The variation in optical properties as a function of DC bias has been reported previously in the literature [37, 32] and has been attributed to an increase in $sp^2$ content of the material. This is due to a higher impinging energy of ionic species which are generated in the plasma onto the film. Although intermediate energies favour $sp^3$ formation according to the subplantation model proposed by Lifshitz [118], higher energies would favour $sp^2$ bonding. Therefore, an increase in ion energy may cause an in-situ re-ordering process as the film is grown. An increase in the $sp^2$ content of the material would suggest either an increase in the density of small clusters, or an increase in the cluster size. The band gap variation shows that the cluster size is increasing according
to models proposed by Robertson [5], but an increase the density of distorted clusters will also result in a narrowing of the band gap [23].

An increase in the EPR spin density indicates an increase in the concentration of either odd-membered rings or odd-membered clusters. At lower biases (< -125 V) the density of paramagnetic spins increases greatly as does the linewidth, and the optical band gap collapses. A mechanism for the increase in linewidth value for a Lorentzian lineshape is the dipolar broadening due to the increase in the density of adjacent spins and therefore an increase in interaction between them, according to our analysis which can be found elsewhere [119]. This indicates an increase in the density of $sp^2$ clusters but not in the cluster size. The collapse of the Tauc band gap may be attributed to the increase in the cluster density coupled with an increase in film stress as has been recorded in the literature [37, 32], and could also result in a narrowing of the band gap [23].

At higher biases the decrease in linewidth has been attributed to a motional averaging of the local magnetic field, which is likely to be due to the exchange interaction. This has been shown [110] to be as a consequence of an increase in delocalisation which will occur because of an increase in cluster size. Over this range the spin density increases more slowly which indicates that the concentration of individual $sp^2$ clusters is increasing to a small degree. This is also reflected in the band gap data and indicates that, at higher biases, the $sp^2$ cluster size is increasing rather than the cluster density.

In order to analyse the variation in electrical properties, as shown in Figure 5.10, it is necessary to ascertain which mechanism applies over each range of DC bias voltage. Up to a bias voltage of -110 V the high-field current characteristic remains parabolic in nature which, when compared to films which are grown on the earthed electrode, indicates that SCLC dominates. However the low-field resistivity decreases from $\sim 10^{15}$ to $\sim 10^{12}$ $\Omega$ cm. The mechanism of room temperature conductivity in samples that are grown on the earthed electrode has been shown to be via hopping owing to the extremely low value of activation energy. These films are similar in terms of electrical properties and therefore the increase in current magnitude for these samples may be explained by an increase in the concentration of centres which contribute to the hopping current.

Above a bias voltage of -110 V conduction may be dominated by the Poole-Frenkel effect. In order to verify this it is necessary to fit to the Poole-Frenkel equation as shown in the Section 2.4.2, and calculate values of dielectric permittivity from the
5.5. Discussion

The slope of the ln $J/E$ versus $E^{1/2}$ plot. These may be compared with the values of the square of refractive index. This data is shown in Table 5.2 for the three samples which may be exhibiting Poole-Frenkel conduction.

<table>
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<th>$\varepsilon_r$ ($n^2$)</th>
</tr>
</thead>
<tbody>
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<td>175</td>
<td>5.3 ± 0.5</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>215</td>
<td>5.0 ± 0.5</td>
<td>4.7 ± 0.1</td>
</tr>
<tr>
<td>260</td>
<td>8.7 ± 0.5</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5.2 Comparison of $\varepsilon_r$ derived from Poole-Frenkel slope and that derived from $n^2$ for films with increasing DC bias voltage.

The dielectric constant values are close to those derived from the square of the refractive index which indicates that the three films are conducting via the Poole-Frenkel effect. Also it may be observed that in these cases the value of $\varepsilon_r$ exceeds that derived from the square of the refractive index and for the film grown at the highest DC bias voltage, the deviation is at its greatest. Explanations for the variation of the Poole-Frenkel factor with increasing defect density has been outlined by Simmons [10] and Hill [12]. Simmons suggested that if the highly defective films contained donor centres which are below the Fermi level as well as shallow neutral traps, the value of the $\beta$ factor will be reduced. Hill [12] suggested that if the Coulombic centres were to overlap, then Poole conduction will dominate and a ln $J$ versus $E$ relationship will occur, which is not observed in the case of this study. However a more recent study by Lau et al. [120] suggested that the P-F coefficient changed in a gradual manner from $\beta_{PF}$ to $\frac{1}{2}\beta_{PF}$ in the case of $a$–SiN$_x$:H films as the concentration of defects increased. It was suggested that as the defect concentration increased, the density of charged (both donor-like and acceptor-like) defect states increased, resulting in many more charged defect states than neutral states. A similar result to that obtained by Lau et al. has been found, which suggests that, as in their case, conduction is dominated by the Poole-Frenkel effect over this range of bias voltages.

It is instructive to apply the Poole-Frenkel equation in Section 2.4.2 in order to determine the trap density $N_C$ for these films, by plotting ln $J/E$ against $E^{1/2}$ and using the relationship $J_0 = e\mu N_c \exp(E_g/2kT)$. Table 5.3 shows the variation in $N_C$ as compared to the values of paramagnetic defect density, which were derived using EPR.

It is observed that there is a large degree of uncertainty when deriving the $N_C$ values
5.5. Discussion

<table>
<thead>
<tr>
<th>DC bias (-V)</th>
<th>$N_C$(PF) (cm$^{-3}$) $\pm$50%</th>
<th>$N_V$ (EPR)(cm$^{-3}$) $\pm$10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>$2 \times 10^{18}$</td>
<td>$1.4 \times 10^{20}$</td>
</tr>
<tr>
<td>215</td>
<td>$6 \times 10^{18}$</td>
<td>$1.6 \times 10^{20}$</td>
</tr>
<tr>
<td>260</td>
<td>$7 \times 10^{17}$</td>
<td>$1.6 \times 10^{20}$</td>
</tr>
</tbody>
</table>

Table 5.3 Comparison of trap density ($N_C$) derived from Poole-Frenkel intercept and paramagnetic defect density ($N_V$) derived using EPR for films with increasing DC bias voltage.

which are to a large extent dependent on the values of band gap. Also it is observed that there is no variation in trap density with increasing DC bias which corroborates with the EPR data, which also shows no variation over this bias range within error. The $N_C$ values are between 1 and 3 orders of magnitude lower than the EPR-obtained $N_V$ values which means that the density of Poole-Frenkel active sites is lower than the density of paramagnetic defect sites. Therefore it can be stated that the dependence of current magnitude extrapolated to zero voltage ($J_0$), which shows an increase over the DC bias range, can be attributed to the narrowing of the band gap and hence the reduced excitation energy to the extended states, rather than an increase in the density of trapping centres.

It must be noted, however, that EPR measures the concentration of paramagnetic defects whilst the Poole-Frenkel analysis performed here [12] gives an indication of the concentration of defect sites which are charged when unoccupied. The Poole-Frenkel active centres are the sites which control the high-field electronic transport in the material, and therefore their concentration may not relate to the concentration of unpaired spins within the material.
5.6 Summary

The opto-electronic properties of films grown on both electrodes of an \( rf \)-PECVD system have been categorised. It is observed that films grown on the earthed electrode show the optical and electrical properties such that these films may be referred to as PAC, in terms of their wide Tauc band gap and high resistivity. These films have been shown to exhibit low-field room-temperature conduction most closely resembling hopping conduction with a very low activation energy. At temperatures above 100 °C the variation of conductivity with temperature suggests that the Fermi level is 0.7 eV from the valence band edge. Conduction at higher electric fields is governed by SCLC as derived for a trap-free insulator. This is expected due to the wide band gap and low defect density of the material.

DAC films have been grown on the powered electrode at a DC bias of -175 V. These films have been shown to be exhibiting conduction in the band tail at room temperature and conduction in the extended states at higher temperatures. The activation energy value is 0.3 eV above a measurement temperature of 100 °C. At higher electric fields, the carrier transport appears to be dominated by Poole-Frenkel conduction. The concentration of EPR-active centres appears to be three orders of magnitude greater than the concentration of P-F active trap states.

As the DC self-bias of deposition is increased it has been shown that the Tauc band gap narrows, the refractive index increases and the defect density increases concomitantly. This indicates an increase in the \( sp^2 \) content within the films. The optical and EPR variations have been attributed to an increase in the \( sp^2 \) cluster density at lower biases, and an increase in cluster size at higher bias. The electrical characteristics have shown a change from space-charge-limited current to Poole-Frenkel conduction above a DC bias of -110 V. The magnitude of the Poole-Frenkel conductivity has been shown to be as a consequence of the narrowing of the band gap of the material, rather than a further increase in the density of P-F active trap states.
Chapter 6

**In-situ** nitrogen modification of 
\(\alpha{-}C:H\)

## 6.1 Introduction

There have been many cases where the electronic doping of \(\alpha{-}C:H\) has been reported in the literature, although the issue is contentious. Section 3.5 reviews the previous reports of nitrogen addition into \(\alpha{-}C\) thin films. Some groups suggest that the role of N is as an electronic \(n\)-type dopant [76], and other groups describe effects which can be attributed to re-structuring of the film [27, 31] causing a narrowing of the band gap with a concomitant change in conductivity, as a consequence of \(sp^2\) re-ordering. Doping appears to be influenced, therefore, by several factors, including the exact configuration of the deposition system. Therefore, it is of importance to ascertain the role of N as a structural or electronic dopant. This will be carried out using optical as well as electrical measurements in order to ascertain factors such as refractive index and Tauc band gap.

The alloying of \(\alpha{-}C:H\) to form \(\alpha{-}C:H:N\) is of importance if the material has potential as a large area semiconductor. The driving force of \(\alpha{-}C:H\) in this role is its inexpensive nature of manufacture. In order to fabricate a large variety of devices, it is necessary that the material may be doped \(n\)-type so that junction diodes / bipolar transistors may be fabricated. Furthermore, doping using a gaseous precursor is more cost effective than using other techniques, such as ion implantation, and is more applicable to large
6.2. Atomic nitrogen content

Ion beam analysis (IBA) was carried out on films grown in the DP800 reactor using a 30:75 mix of methane and helium at a pressure of 200 mTorr and a power of 200 W (-175 V DC bias in the case of the powered electrode grown films). The deposition time was 5 minutes, which resulted in 100-120 nm thick films on the earthed electrode and 50-80 nm thick films on the powered electrode. Nitrogen was incorporated into the film by the addition of N\textsubscript{2} gas into the reactor at various flow rates. ERDA and RBS experiments were performed using an incident beam of 35 MeV Cl\textsuperscript{7+}. It was found that a beam fluence of 2.2 \mu C was sufficient to sputter the films away completely. However when the fluence was reduced to 0.11 \mu C, two measurements performed on the same spot gave the same values, indicating that sputtering and H out-diffusion was not occurring to such an extent as to significantly reduce the absolute values. The data was analysed using the DataFurnace program which used a simulated annealing algorithm in order to calculate the elemental depth profile from the multiple spectra.

Figures 6.1-6.3 show the variations of nitrogen, carbon and hydrogen content with increasing N\textsubscript{2} flow rate. In the case of the earthed electrode grown films, it can be seen that as the flow rate is increased, the N content increases, and the greater the flow rate, the less the increase in N content. This is accompanied by a corresponding decrease in the C concentration. The H concentration is shown to increase slightly from 55 at. % to 60 at. % as the flow rate increases up to a flow rate of 5 sccm, though this is within the experimental error of approximately 5 %.

For the DAC films grown on the powered electrode, the N content increases with flow rate in a similar manner to the earthed electrode grown films, and the C content, after an initial rise up to 58 % up to a flow rate of 5 sccm, shows a corresponding decrease. The H content in these films falls as the carbon content rises from 47 % to 35 %, and then remains approximately constant. It may also be noted that despite PAC and DAC films being markedly different in structure and their optical and electrical properties, the N uptake as a function of nitrogen flow rate is similar. This suggests that the concentration of ionised nitrogen within the plasma is determining the N content.
6.2. Atomic nitrogen content

Figure 6.1 Atomic nitrogen contents for films grown on the powered and earthed electrodes with increasing N\textsubscript{2} flow rate, as measured using RBS/ERDA.

Figure 6.2 Atomic carbon contents for films grown on the powered and earthed electrodes with increasing N\textsubscript{2} flow rate, as measured using RBS/ERDA.

Figure 6.3 Atomic hydrogen contents for films grown on the powered and earthed electrodes with increasing N\textsubscript{2} flow rate, as measured using RBS/ERDA.
6.3 Optical properties as a function of nitrogen content

The variation of optical band gap with increasing nitrogen content, as shown in the literature, have been discussed in Section 3.5. As can be seen in Figure 3.11, different groups have reported differing trends with some observing an increase in optical band gap with nitrogen content, some a decrease and some an increase followed by a decrease. Furthermore, these measurements have been performed on different types of films but the effect of nitrogenation on PAC films has not been established as yet. Therefore it is necessary to establish the effect of nitrogenation on these films, and clarify the observations on DAC films.

The following films were grown on both the powered and earthed electrodes of the DP800 reactor under standard conditions outlined in Section 4.2. The nitrogen flow rates were correlated to atomic N content values using the data shown in Figure 6.1. The variation of the refractive index and optical band gap are shown in Figure 6.4 for earthed electrode grown PAC films and in Figure 6.5 for powered electrode grown

![Figure 6.4 Variation in (a) refractive index and (b) Tauc optical band gap with increasing nitrogen content for PAC films grown on the earthed electrode](image-url)
DAC films. For PAC films the Tauc band gap shows an approximately linear reduction from 2.6 eV to 2.2 eV with increasing nitrogen content. This is an indication of $sp^2$-reordering within the film, or at least an increase in the mean $sp^2$ cluster size, if not the $sp^2$ content [5]. This type of observation is usually concomitant with a rise in the refractive index; however, this is not the case in our films as the refractive index appears to remain constant at a value of 1.6 irrespective of the nitrogen content. In the case of the DAC films, it can be seen that the Tauc band gap shows an increase from 0.7 eV for a film possessing 1.5 at. % N, to 1.0 eV for a film possessing 4.0 at. % N. The refractive index shows a corresponding decrease from 2.1 to 1.9, over the same N content range. For higher N contents both the optical band gap and refractive index remains constant.
6.4 Electrical properties as a function of nitrogen content

The electrical properties of a-C:H films have been previously studied as a function of nitrogen content. Section 3.5 also shows the variations in resistivity and activation energy reported in the literature in Figures 3.9-3.10. It can be seen that the conductivity has been shown to increase as the N content increases. This could be due to doping or graphitisation of the film. The activation energy measurement appears to be dependent on film type with DAC films showing an increase followed by a decrease which is consistent with doping, and GAC films showing only a decrease, more consistent with graphitisation. PAC films have not been discussed in the literature and one would expect these materials to be promising in terms of having the possibility of doping these materials, as they possess a low defect density which indicates that the Fermi level might not be pinned at midgap. Therefore, in this study the electrical properties of these materials will be categorised with respect to nitrogen content.

PAC films were prepared on the earthed electrode using the procedures described in Section 4.2. Films were also deposited onto silicon (n and p-type both with resistivities of 0.01-0.02 Ω cm) both of which possessed ohmic back contacts of gold antimony and aluminium, respectively. Metal-semiconductor-silicon (MSS) structures were thereby fabricated and the characteristics were found to be very similar to those derived from the MSM structures.

6.4.1 Earthed electrode grown films

6.4.1.1 J/E characteristics

The current density versus applied electric field for PAC films grown on the earthed electrode onto CrN substrates, as a function of nitrogen content, is shown in Figure 6.6. It has observed in Section 5.3.1 that the conduction appears to be linear at low fields. This indicates that low-field conduction is occurring through hopping. It can also be seen that all of the characteristics are symmetrical, and therefore there is little evidence of a Schottky barrier. Analysis of the characteristics shows that the resistivity decreases as a function of the nitrogen flow rate used during film deposition, from a value of ~10^{15} Ω cm for a film containing 0.4 % N (nominally zero nitrogen) to a value of ~10^{12} Ω cm for a film containing 6.6 at. % N.
6.4. Electrical properties as a function of nitrogen content

Figure 6.6: Current versus voltage characteristics for films grown onto CrN substrates with differing nitrogen contents, grown on the earthed electrode.

6.4.1.2 $J/E/T$ measurements

$J/E/T$ measurements were performed as a function of N content using a MSM sandwich structure, using gold top contacts and a CrN back contact as described previously. Prior to measurement the sample was annealed at 300 °C for 5 minutes at a pressure less than $10^{-5}$ mbar. As well as assuring temperature stability, another consequence of the post-deposition anneal would be to activate the in-situ dopant atoms and hence electronically dope the material. $J/E$ measurements were performed between room temperature and 180 °C and resistivity values were derived from the slope of the $J$ versus $E$ characteristic at electric fields below $2 \times 10^5$ V cm$^{-1}$. It was once again observed that for all of these samples there was no change in resistivity up to a measurement temperature of ~ 110 °C. Above this temperature ln $\sigma$ was plotted against $-q/kT$ and from the resultant slope, values of activation energy $E_{act}$ were obtained.

Figure 6.7 shows the variation of activation energy as a function of N content for PAC films grown on the earthed electrode. It can be seen that up to a N content of 2 at. %, the activation energy increases from approximately 0.7 to 0.9 eV. As the N content is further increased to 7 at. % the activation energy decreases to 0.8 eV. The decrease of activation energy over this range is concomitant with a decrease in Tauc band gap from 2.5 eV to 2.1 eV. However, the initial increase in activation energy is not observed in the Tauc band gap variation for films possessing a N content of ~ 2 at. %. Furthermore,
6.4. Electrical properties as a function of nitrogen content

the resistivity has been shown to decrease monotonically from \( \sim 10^{15} \, \Omega \, \text{cm} \) to \( \sim 10^{12} \, \Omega \, \text{cm} \) over the whole of the N content range. This is not mirrored in the activation energy variation. The resistivity, band gap and activation energy measurements will be discussed in Section 6.6.

6.4.1.3 EPR measurements

In order to supplement the electrical data the films were measured using electron paramagnetic resonance (EPR) spectroscopy using the procedure described in Section 4.4.4. The variation of EPR spin density and linewidth for the earthed electrode grown films are shown in Figure 6.8. It can be seen in the case of the PAC films, the spin density remains approximately constant within measurement error at \( 2 - 5 \times 10^{17} \, \text{cm}^{-3} \) as the N content is increased. The linewidth falls from 1.2 mT to 0.8 mT at approximately 3 at.% N. It has been found [111] that as the N content is increased, more of the hydrogen within the film is bonded onto N than C. This would cause a decrease in the broadening of the EPR signal due to unresolved hyperfine interaction, which has been established as the broadening mechanism for this type of film [110].
6.4. Electrical properties as a function of nitrogen content

Figure 6.8 EPR spin density and linewidth as a function of nitrogen content for PAC films grown on the earthed electrode.

6.4.2 Powered electrode grown films

Here the electrical properties of powered electrode grown $a-$C:H films are studied as a function of nitrogen content. These films are more similar to those reported in the literature according to their high hardness, low band gap (less than 1.5 eV) and high defect density ($10^{19} - 10^{20}$ cm$^{-3}$). The high defect density makes these films less promising candidates for electronic doping as the Fermi level is more likely to be pinned by the defect states than in the case of the PAC films. DAC films were therefore prepared on the powered electrode using the procedure outlined in Section 4.2 and $J/E$ characteristics were performed on the MSM structures using the procedures shown in Section 4.4.
6.4. Electrical properties as a function of nitrogen content

6.4.2.1 \( J/E \) characteristics

Figure 6.9 shows the variation of \( J \) versus \( E \) characteristics for the DAC films which were grown with different N contents on the powered electrode. It is observed that the \( J/E \) characteristics differ significantly compared to the polymer-like films, in that the current magnitude is much greater, and the shape of the characteristic is not parabolic. The shape of the characteristic appears to be similar to the undoped case for all nitrogen levels, which suggests that the Poole-Frenkel effect governs high-field conduction for all of these films. There is an initial small increase in Poole-Frenkel conductivity for a film containing 4.1 % N, followed by a steady decrease for higher N levels. Therefore, the effect of N addition appears to be the opposite compared to the effect of N addition into the PAC film.

\[
\begin{align*}
\text{Figure 6.9 Current versus voltage characteristics for DAC films with differing nitrogen contents grown on the powered electrode.}
\end{align*}
\]

6.4.2.2 \( J/E/T \) measurements

\( J/E/T \) measurements were performed as a function of N content using a MSM sandwiching structure containing powered electrode grown films, using gold top contacts and a CrN back contact as described previously. Before measurement the sample was annealed at 300 °C for 5 minutes in a vacuum better than \( 10^{-5} \) mbar, for similar reasons to those outlined previously. \( J/E \) measurements were performed between room
temperature and 180 °C and resistivity values were derived from the slope of the $J$ versus $E$ characteristic at electric fields below $2 \times 10^5$ V cm$^{-1}$. In order to be consistent with previously outlined studies, only measurements above a temperature of 100 °C were investigated, corresponding to extended-state conduction as outlined in the previous Chapter. In $\sigma$ was plotted against $-q/kT$ and from the resultant slope, values of activation energy $E_{\text{act}}$ were obtained.

![Graph showing activation energy as a function of N content for films grown on the powered electrode.](image.png)

**Figure 6.10** Activation energy as a function of N content for films grown on the powered electrode.

Figure 6.10 shows the variation of activation energy as a function of N content for DAC films grown on the powered electrode. It may be observed that up to a N content of $\sim 4$ at. % the activation energy increases from approximately 0.3 to 0.5 eV which appears to stabilise in the region of 0.5-0.6 eV for higher N contents. This variation is concomitant with an increase in Tauc band gap from 0.7 eV to 1.0 eV.

### 6.4.2.3 EPR measurements

Electron paramagnetic resonance (EPR) spectroscopy was performed in a manner described in Section 4.4.4. The variation of EPR spin density and linewidth for the films grown on the powered electrode are shown in Figures 6.11. In the case of these films, on the small addition of N (3.5 at.%) decreases the spin concentration from $1.8 \times 10^{20}$ cm$^{-3}$ to $5 \times 10^{19}$ cm$^{-3}$ as the N content is increased from 1.5 at.% to 3.0 at.%, and the linewidth increases from 0.8 to 1.4 mT. At higher N concentrations the spin density
remains approximately constant and the linewidth decreases, eventually to 1.1 mT. Therefore, nitrogenation of DAC films up to 3 at.\% has been shown to reduce the EPR spin density by one order of magnitude and increase the linewidth. Using the relationship $\Delta B_{pp} = 8.12 \times 10^{-21} N_s$ (assuming $g=2.0025$) for dipolar broadening [110] yields an expected linewidth value of 1.6 mT for the film with the highest spin density. The low linewidth value for this film is likely to be due to motional effects arising from the exchange interaction. For films which were grown with higher N contents the linewidth contribution from dipolar broadening is only in the range of 0.2-0.4 mT which suggests that another mechanism is increasing the linewidth.
6.5 Annealing of nitrogenated $a-C$ films

Annealing is an important industrial process in the case of hydrogenated amorphous silicon, because the defect density of dangling bond defects is reduced leading to a better electronic material [4]. Previous studies of annealing on the opto-electronic properties of $a-C$ have been shown in Section 3.3. It has been mentioned that Burden et al. [35] showed that the optical band gap of PAC films could be increased by annealing, which suggested that the optical absorption edge was sharpened as a result of defect passivation. This was also found in the case of $ta-C:H$ by Conway et al. [48] who showed that it corresponded to a minimum in the conductivity and EPR spin density. Therefore it was inferred that the defect density of $ta-C$ could be reduced by annealing. However, the effects of nitrogenation followed by annealing have not been reported. It has been shown that N addition may increase the optical gap of DAC [78, 117] which may be as a consequence of a sharpening of the band tail. Therefore, the annealing of nitrogenated films may show whether activated N within the film acts as a defect passivator or electronic dopant. However, Burden et al. [35] showed that the graphitisation threshold for PAC films existed around an annealing temperature ($T_A$) of 400 °C. Therefore, the influence of nitrogen on this threshold may also indicate whether or not nitrogen is initiating a graphitisation of the $a-C$ film.

6.5.1 Optical measurements

Films were grown using the standard DP800 process on both electrodes of the PECVD reactor. The investigation entailed the effect of annealing on non-nitrogenated samples and samples grown with a $N_2$ flow rate of 10 sccm, which corresponded to a N content of 5.2 at.% for the PAC films and 5.6 at.% for the DAC films. The measured N contents for films grown without nitrogen added during the process were 0.4 % for the PAC films and 1.4% for the DAC films and these films are nominally non-nitrogenated. Following deposition, gold top contacts were evaporated onto the samples grown on metallic substrates in a manner described in Section 4. The samples were then annealed under a flowing nitrogen ambient using a 8 kVA optical rapid thermal annealer. All anneals were performed for 5 minutes. The ramp up to the annealing temperature was in the range or 5-10 seconds and the ramp down was between 30 seconds and 2 minutes.

The variation of Tauc band gap, film thickness and refractive index for non-nitrogenated
and nitrogenated PAC films as a function of annealing temperature is shown in Figure 6.12 and for DAC films is shown in Figure 6.13. For non-nitrogenated PAC films, the optical band gap remains high (above 2.5 eV) and approximately constant until \( T_A = 300 \) °C. At higher temperatures the optical gap decreases, eventually to less than 1 eV at the highest annealing temperature. The same occurs for nitrogenated PAC films with a correspondingly lower initial and final optical gap. The film thickness shows a decrease for both non-nitrogenated and nitrogenated PAC films such that at the highest temperature the final thickness is less than 20% that of the initial thickness, with the greatest changes once again occurring above \( T_A = 300 \) °C. Finally, for both types of film, the refractive index remains constant at approximately 1.6 until temperatures greater than 300 °C are attained, at which the refractive index rises. The change is greater in the case of the nitrogenated film (up to 2.2) than in the non-nitrogenated film (1.8-1.9).
6.5. Annealing of nitrogenated $a-C$ films

The variation of the Tauc band gap, film thickness and refractive index for non-nitrogenated and nitrogenated DAC films is shown in Figure 6.13. The Tauc band gap of unnitrogenated DAC remains close to 0.7 eV, the refractive index varies only from 2.0 to 2.1 and the film thickness does not deviate significantly as the annealing temperature is increased. Therefore, these films are shown to be thermally stable up to $T_A=500$ °C. In the case of nitrogenated DAC films, however, above an annealing temperature of 300 °C the optical gap falls from 0.9 to 0.2 eV, the thickness falls to about 80% of its initial value and the refractive index rises from 1.95 to 2.15. Therefore, these films are more comparable to PAC films in terms of their thermal stability.
6.5.2 Electrical measurements

The following measurements were carried out on the MSM structures. Figure 6.14 shows the variation of $J$ versus $E$ characteristic for non-nitrogenated and nitrogenated PAC films as a function of annealing temperature $T_A$. It may be observed that for the non-nitrogenated case, there is very little variation in current magnitude until the annealing temperature is raised to $T_A = 250 \, ^\circ\text{C}$. At this point the film increases in conductivity by approximately half an order of magnitude. The shape of the characteristic remains parabolic, however. At the higher temperature $T_A = 400 \, ^\circ\text{C}$, the conductivity of the film has increased by at least 2 orders of magnitude and also a change in conduction mechanism is observed in that the turn-on of the characteristic becomes sharper. This is consistent with the optical data which shows large changes in properties at $T_A > 300 \, ^\circ\text{C}$.

In contrast with the nitrogenated films grown on the earthed electrode, at the lowest temperature of $T_A = 150 \, ^\circ\text{C}$ a small decrease in conductivity of approximately half an order of magnitude is observed. This remains up to $T_A = 250 \, ^\circ\text{C}$ and at higher temperatures, there exists a large increase in conductivity of approximately 2-3 orders of magnitude, in a similar manner to the non-nitrogenated case, although the conductivity is significantly higher.

This can be contrasted to the case of non-nitrogenated and nitrogenated DAC films, as shown in Figure 6.15. Here it can be seen that in the non-nitrogenated case there is a decrease in conductivity as $T_A$ is raised to 250 °C. It is important to note however that these films have already been shown to exhibit Poole-Frenkel type conduction and this appears not to change as the annealing temperature is raised. Annealing at higher temperatures resulted in film delamination and therefore could not be measured. In the case of the nitrogenated films, a decrease in conductivity of approximately 1 order of magnitude is noted for $T_A=150 \, ^\circ\text{C}$, followed by an increase at $T_A = 250 \, ^\circ\text{C}$. The characteristics appear to remain similar in shape, however, indicating that Poole-Frenkel conduction still applies even at this annealing temperature. For $T_A = 400 \, ^\circ\text{C}$, the current density increases significantly in a manner resembling the PAC films, which is concomitant with a comparison between the optical properties.
Figure 6.14 \(J/E\) characteristic as a function of annealing temperature for (a) non-nitrogenated and (b) nitrogenated PAC films.

Figure 6.15 \(J/E\) characteristic as a function of annealing temperature for (a) non-nitrogenated and (b) nitrogenated DAC films.
6.5.3 EPR measurements

EPR measurements were made on the earthed electrode grown samples as a function of annealing temperature, and the spin density and linewidth data are presented in Figure 6.16. It is observed that as $T_A$ increases the spin density increases from $3 \times 10^{17}$ cm$^{-3}$ at room temperature to $7 \times 10^{18}$ cm$^{-3}$ at $T_A = 500$ °C. Above this temperature the spin density falls to $3 \times 10^{18}$ cm$^{-3}$. The linewidth increases from 0.6 to 1.7 mT up to $T_A = 100$ °C, and then falls to a value of 0.3 mT at $T_A = 600$ °C. Over the temperature range the lineshape changes from Gaussian to Lorentzian above $T_A = 400$ °C. A change to a Lorentzian lineshape may indicate effects such as exchange [105].

![Figure 6.16](image-url) (a) EPR spin density and (b) linewidth as a function of annealing temperature for non-nitrogenated films grown on the earthed electrode.
6.6 Discussion

6.6.1 Films grown on the earthed electrode

6.6.1.1 Microstructural properties

The data shown in Figures 6.1-6.3 for films grown on the earthed electrode have been reported elsewhere [111]. The C content shows a sharp decrease up to a nitrogen flow rate of 5 sccm, and a smaller decrease at higher flow levels. This is concomitant with the H content variation which shows an increase over the same flow rate and then remains approximately constant at higher flow rates. When correlated to the FT-IR study for PAC films, as performed by Anguita et al. [121], it may be observed that the predominant C-H stretch corresponds to sp\(^3\)-hybridised carbon. The C-H stretch intensity decreases with increasing N\(_2\) flow rate and the N-H intensity increases. This information together with these results suggests that as the N content increases the H is preferentially bonded to N rather than C, so that N is effectively replacing C in the polymeric matrix. The C content decreases as a result.

The fact that the C content always remains above 30 at. % suggests that there is always a significant concentration of C-H bonds even for films with the highest N content. A high intensity of C≡N bonds also exists which suggests that a significant proportion of the N is bonded either into olefinic chains or aromatic rings. There is also a low intensity and hence concentration of C≡N bonds which suggests that only a small proportion of these bonds exist within the nitrogenated film.

For the films grown on the earthed electrode it can be seen from Figure 6.4 that the Tauc optical band gap has reduced as the N content has increased. It is known that there are three main factors that dictate the optical band gap in a-C; namely the proportion of sp\(^2\) /sp\(^3\) bonding, the distribution and density of the defect states and the possibility of C forming CN alloys. Therefore, the variation in band gap could be due to sp\(^2\) bond formation leading to cluster formation. According to a simplified model [5] where \(E_g = 6/N^{1/2}\) as quoted previously, a decrease in the gap from 2.6 to 2.1 eV would correspond to the number of benzene rings within a cluster increasing from 5 to 8. On the other hand, the effect of C alloying with N and forming a C-N mixed band could also give rise to this variation in optical band gap, due to optical absorption in this band.
However, if the variation is due to $sp^2$ bond formation, this would generally coincide with a corresponding increase in refractive index, but only a small increase is observed, as shown by Figure 6.4. The Penn model [122] suggests that the refractive index is dependent on the band gap $E_g$ and the plasmon energy $E_p$ according to the following relationship:

$$n^2 - 1 = \left(\frac{E_p}{E_g}\right)^2$$  \hspace{1cm} (6.1)

Therefore, a large decrease in the band gap with only a small change in the refractive index of a material may indicate a decrease in the plasmon energy which can be explained by a decrease in the density of the material. If a C-N alloy is formed, not only would the density decrease but also the band gap as well. It is also likely, however, that a small increase in the mean size of the $sp^2$ clusters using the analysis performed previously may explain the decrease in optical gap from 2.6 to 2.1 eV.

Over the N content range, it has also been found that the Tauc $B$ parameter which characterises the sharpness of the band tail has been observed to increase from approximately $2.5 \times 10^3$ eV cm$^{-1}$ at 0.4 at.% N to $4.7 \times 10^3$ eV cm$^{-1}$ at 6.6 at.% N. For most amorphous materials, one would most normally expect the $B$ parameter to decrease as a result of the broadening of the band-tail, as the optical band gap decreases. Therefore, because the band gap has been shown to decrease over this N content range, this indicates that the strength of the absorption in the high-energy (3-4 eV) region has increased. If the concentration of $sp^2$ clusters contributing to transitions in this energy range was to increase, then the absorption would increase as a consequence. This appears to be the case in these films and indicates also an increase in the $sp^2$ content.

### 6.6.1.2 Electrical properties

The $J$ versus $E$ plots of the PAC films as shown in Figure 6.6 are symmetrical, and only show a small current density increase with applied electrical field. The magnitude of the current is also low, suggesting that these films are highly insulating, which may indicate that they lack mobile carriers. Also it is observed that the conduction appears to be linear at low fields, as observed previously in the undoped films.
The high-field conduction mechanism of these films may be examined using the analysis performed in Section 5.5.2. Conduction is more likely to be bulk limited rather than contact limited as the characteristics are highly symmetric. Although not shown for brevity, there was also no dependence on the back contact, whether it was n-type Si, p-type Si or CrN. One possible form of bulk conduction is Poole-Frenkel conduction [12], as shown in Figure 2.5. It has been shown in Section 5.5.2 that the value of dielectric constant yielded is not realistic for undoped films if Poole-Frenkel type conduction is assumed. Therefore, it is likely that the Poole-Frenkel effect is not governing electronic conduction through these films irrespective of the N content. This is to be expected, as the defect density of this material remains low ($\sim 10^{17}$ cm$^{-3}$), so that there are unlikely to be sufficient trapping centres to allow this type of conduction.

Therefore, it is likely that SCLC remains the governing conduction mechanism for these films. It has been found that the high-field $J$ versus $E$ dependence remains parabolic irrespective of N content, i.e. $J \propto V^2$, which further corroborates this assumption. Using the standard SCLC equation for a trap-free insulator [9] and assuming a value of $\varepsilon_r$ to be 2.6 it is found that the value for carrier mobility varies from $1.2 \times 10^{-10}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the case of the undoped film to $0.9 \times 10^{-10}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the case of a film containing 6.6 at. % N. Within experimental error the variation is negligible and suggests that the addition of N does not alter the carrier mobility within the film. Therefore, any decrease in resistivity must be attributed to an increase in low-field conductivity.

In the low-field regime it has been shown that the room-temperature resistivity decreases by over two orders of magnitude over the N content range, and the Tauc band gap shows a concomitant decrease from 2.6 to 2.1 eV. The change in resistivity may be attributed to the band gap variation but an examination of the temperature dependence of the conductivity shows that this is unlikely to be the case. It has been mentioned that below a measurement temperature of $\sim 110$ °C there is no measurable increase in conductivity with increasing temperature. This suggests that conductivity in this regime is not thermally activated and therefore is likely to be governed by a hopping process where the energy distribution of the density of states contributing to the hopping current is narrow. Therefore, any increase in conductivity over the N content range must be attributed to an increase in the density and distribution of hopping sites or an increase in the number of carriers at the Fermi level. An investigation of
the equations used for VRH and nearest-neighbour hopping (see Section 2.3) shows that both mechanisms are band-gap independent and depend on such factors as the density of states at the Fermi level and the localisation factor. Due to the fact that the temperature dependence of conductivity is not measurable in this case, it is not possible to evaluate which of these two mechanisms is likely to dominate in the case of these films.

The high-temperature (i.e. $> 110 \, ^\circ\mathrm{C}$) activation energy has been shown to increase from 0.7 to 0.9 eV, and then decrease to 0.8 eV as the concentration of nitrogen is further increased. Conduction in the band tail is likely to be the dominant transport process, as higher temperatures are likely to be required in order to promote carriers into the conduction or valence band with a material of a band gap in excess of 2 eV. It has been previously stated that the 0.7 eV activation energy is likely to be associated with activation to the valence band. Previous work has shown that the addition of nitrogen may move the Fermi level from the valence band edge to the conduction band edge in the case of $a$–C:H [76, 78] and $ta$–C [80, 70]. This is said to occur through a compensated state where the activation energy shows a maximum value due to the passivation of C defects which causes the intrinsic $p$–type conductivity of the material.

As discussed by Robertson [87] for films with a significant $sp^2$ content, such as PAC films, the presence of N in an aromatic cluster may result in the formation of a $N_{3\pi}$

Figure 6.17 Possible bonding configuration allowing weak N-doping in $sp^2$ hybridised clusters within polymeric films: (a) graphitic site, and (b) $N_{3\pi}$ site.
site which will weakly dope the material. This is because the extra valence electron of N can donate electrons by entering a $\pi^*$ state. Three of the valence electrons would form three $\sigma$ bonds with adjacent C atoms, one electron would fill the C $\pi$ state and the fifth electron would enter a $\pi^*$ state, resulting in a weak doping effect. A schematic of the model is shown in Figure 6.17. As can be seen in (a) the bonding of a C atom in the graphite structure will be made up by 3 $\sigma$ electrons and 1 $\pi$ electron which will pair up with the $\pi$ electron of an adjacent C atom to form a $\pi$ bond. In the case of (b), the bonding in this type of $sp^2$-hybridised N site will comprise 3 $\sigma$ electrons, 1 $\pi$ electron and 1 $N\pi^*$ electron which will move the Fermi level upwards. This $N\pi^*$ electron will be paramagnetically active but the EPR variation shown in this study has found that the paramagnetic defect density does not vary within measurement error. Therefore, should this model be applicable, the density of these sites is likely to be very low, which is to be expected as the structure is not thermodynamically favoured due to its instability, due to the loss in enthalpy of formation according to the difference in bonding and antibonding energies.

The model postulated above is reinforced by FT-IR data as reported by Anguita et al. [121], who reported that the addition of nitrogen into the film had the effect of increasing the C=N concentration by a factor of at least 5. It is therefore likely that much of the N within the film exists in aromatic clusters, and there is a significant probability that some of the N would enter into a $N_3\pi^*$ site. Further evidence for this postulation exists in the variation of activation energy with N content. In the undoped case the value of 0.7 eV would describe the energy gap between the Fermi level and the valence band, which is consistent with the intrinsic $p$-type conductivity reported in amorphous carbon. A small addition of N ($\sim 2\%$) would move the Fermi level to the $N\pi^*$ site, and the 0.9 eV activation energy value would describe the energy gap between the new position of the Fermi level and the conduction band-tail edge.

The variation in room temperature conductivity is also consistent with this model as it is dependent on the density of states at the Fermi level and the hopping probability from one site to another. In undoped films, carriers hop at the Fermi level and Dasgupta et al. [8] showed that this hopping process occurs between $sp^2$ clusters. A small addition of nitrogen will move the Fermi level upwards and if the concentration and distribution of the $sp^2$ clusters does not change then the conductivity will not change. This is because the number of carriers at the Fermi level will remain the same, although in the
case of the addition of N the carrier now exists in a Nπ* site rather than a Cπ site.

It has been observed that over the whole N content range the Tauc band gap shows a narrowing from 2.6 to 2.1 eV. A decrease in optical gap is consistent with an increase in cluster size. This will result in the introduction of both states in the band tails (even membered clusters) and states at the Fermi level (odd-membered clusters) [5]. Any increase in cluster size would reduce the mean distance between all adjacent sp² clusters and hence increase the hopping probability between the odd-membered clusters. This would result in an increase in room temperature conductivity. Therefore, the conductivity variation of the material is consistent with an increase in both the odd and even-membered cluster size which manifests itself as a reduction in optical band gap.

![Figure 6.18](image)

**Figure 6.18** Hypothetical position of the conduction band, valence band and Fermi level due to the addition of N into PAC films.

For films possessing a higher N content (2-6 at.%), the fall in activation energy from 0.9 to 0.8 eV is consistent with the fall in Tauc band gap from 2.5 to 2.1 eV. This suggests that the reduction in activation energy is a result of the narrowing of the band gap, as carriers are excited from the Nπ* orbital to the π* band tail over an energy gap which has been reduced. There is no evidence in this case of a further shift in the Fermi level towards the conduction band, as the activation energy remains high (~ 0.8 eV) and does not appear to further reduce with the introduction of additional nitrogen. The reduction of both the band gap and $E_{\text{act}}$ at higher N contents suggests that both the
valence band and the conduction band are broadening with an increase in N content and therefore the Fermi level is remaining pinned 0.8 to 0.9 eV from the conduction band edge. The hypothetical position of the Fermi level as compared to the conduction and valence band edge is shown in Figure 6.18. It is shown that the addition of N has the likely effect of moving the Fermi level by 1 eV towards the conduction band edge at low N levels, at which it remains approximately pinned.

The band structure of amorphous carbon was reported upon by Robertson and O’Reilly [116]. A tight-binding Hamiltonian was used for modelling the electrons, and was fitted to experimental photoemission and optical measurements. It was stated that the defect states in DAC have been experimentally shown to form a continuous distribution across the pseudogap which allow conduction by hopping. In this case, though, the lack of any clear temperature dependence of room-temperature conductivity suggests that the defect band in which hopping conduction occurs is narrow. Due to the high hydrogen content of these films, the cluster size is likely to be reduced which increases the defect creation energy, hence reducing their thermodynamic probability [116]. This explains the low EPR spin density and activation energy for undoped PAC films.

Robertson suggested that the addition of N was likely to increase the density of gap states due to compensation. This would limit the doping efficiency such that for DAC films the Fermi level would only move upwards by 0.2 to 0.5 eV. When compared to

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**Figure 6.19** Schematic of the movement of the Fermi level and change in the density of states due to the addition of nitrogen into PAC films.
this study the Fermi level has been shown to move by as much as 1 eV. The fact that the room-temperature activation energy of N-doped PAC films is also negligible, as shown in this study, indicates that the defect band causing hopping at the new Fermi level position is narrow, as in the undoped case. This fact coupled with the low midgap DOS which is suggested from the EPR measurements suggests a smaller degree of autocompensation for PAC films than DAC films. Therefore a movement in the Fermi level of 1 eV is plausible with these polymeric films. However, it is likely that a degree of compensation has still reduced the doping efficiency such that the band-tail activation energy always remains as high as 0.8 eV. A schematic DOS of the processes outlined here is shown in Figure 6.19.

6.6.1.3 Variation with annealing

The variation of the band gap and refractive index as a function of annealing temperature for PAC, as shown in Figure 6.12, shows that for the nitrogenated and the non-nitrogenated film, the refractive index increases and the optical band gap shows a corresponding decrease particularly above an $T_A = 400 \, ^\circ\text{C}$. This is due to the formation of larger $sp^2$ clusters within the film, which has also been documented by others [35, 36, 121]. However, it should be noted that graphite has a refractive index of 1.8, and therefore the increase to above this value may be explained by the formation of $sp^2$ clusters which will be isotropic and non-planar, so the value of refractive index for graphite is not applicable. Nitrogenated films seem to be more sensitive to annealing than non-nitrogenated films which means that the presence of nitrogen in the film appears to promote this process. This is expected as nitrogen bonds in a threefold-coordinated site than a fourfold-coordinated site, and an increase in temperature leading to an increase in free energy may activate this process. However in both cases the threshold temperature for the onset of $sp^2$ re-ordering is in the range of $T_A = 300 - 400 \, ^\circ\text{C}$. This is reinforced by the electrical data (Figure 6.14) which show very little change in the non-nitrogenated film up to the graphitisation threshold.

Bounouh et al. [36] measured the H content and FT-IR spectra of PAC and DAC films as a function of annealing. They suggested that the effect of annealing on polymeric films was to sharply decrease the $sp^3$ C-H fraction, which was measurable at $T_A = 300 \, ^\circ\text{C}$ and concomitant with a decrease in the H fraction. Above this temperature very little of the $sp^2$ C-H band was visible and the C=C band increased greatly in strength.
This suggests that in our case the sharp increase in conductivity and refractive index and decrease in thickness and Tauc band gap above $T_A = 400 \, ^{\circ}C$ may be ascribed to the evolution of H within the film which results in a $sp^2$ rich matrix comprising C=C bonds, which are likely to exist within aromatic clusters.

The nitrogenated film annealed at $T_A = 100 \, ^{\circ}C$ shows an initial decrease in conductivity followed by an increase at higher temperatures. It may be stated that conduction in this material, is likely to be occurring via hopping at the Fermi level between $sp^2$ clusters in a manner postulated by Dasgupta et al. [8]. Therefore, any decrease in conductivity must be attributed to a decrease in hopping site density and/or a decrease in the hopping probability between sites. The addition of nitrogen may result in the formation of $N_3$ sites between which room-temperature conduction is occurring, which cause a movement of the Fermi level and hence an increase in activation energy. According to this model, room-temperature conduction will now occur between these sites as they lie at the Fermi level. This structure is unstable, and the concentration of these sites is likely to be low as the presence of an electron in a $N\pi^*$ site will reduce the enthalpy of formation of the site. Other structures are more stable due to their negative enthalpy of formation, such as benzene (-83 kJ mol$^{-1}$), pyridine (-140 kJ mol$^{-1}$) or pyrrole (-108 kJ mol$^{-1}$). Therefore, it is likely that the effect of annealing would be to reduce the density of the $N_3$ sites which would lead to the restructuring of these sites into pyridine- or pyrrole-like structures. The pyridine structure is likely to be favoured on account of its higher enthalpy of formation. The decrease in conductivity with annealing at low temperatures ($T_A = 100 \, ^{\circ}C$) is therefore consistent with the model postulated above.

The variation in EPR properties suggests that there is little change in paramagnetic defect density up to $T_A = 300 \, ^{\circ}C$ but the linewidth increases sharply at $T_A = 100 \, ^{\circ}C$. This type of trend has been analysed by Barklie et al. [123] who surmised that annealing up to $T_A = 300 \, ^{\circ}C$ will not significantly restructure the film and hence the spin density will remain the same. Above $T_A = 300 \, ^{\circ}C$ the introduction of $sp^2$ islands will increase the spin density as because the unpaired electrons produced by the rupture of C-H bonds are stabilised by the resonance with the $\pi$ states of the rings, and also because 5 and 7-membered rings are formed. As the annealing temperature is raised above $T_A = 500 \, ^{\circ}C$, the formation of larger graphitic sheets will result in a decrease in the concentration of $sp^2$ sites and therefore a corresponding decrease in the paramagnetic density. Annealing above $T_A = 350 \, ^{\circ}C$ would reduce the linewidth due to increases in
the exchange interaction bought about by greater delocalisation of electronic charge, which is associated with an increase in the $sp^2$ cluster size.

6.6.2 Films grown on the powered electrode

6.6.2.1 Microstructural properties

According to the data shown in Figures 6.1-6.3, the N content increases as a function of nitrogen flow rate. Up to a flow rate of 5 sccm the C content increases with a corresponding decrease in the H content. This may be compared to the optical data as shown in Figure 6.5, which shows a decrease in refractive index from 2.1 to 1.9 at low N contents with a concomitant increase in the Tauc band gap from 0.7 to 1.0 eV. The increase in optical band gap is also concomitant with a decrease in EPR spin density from $\sim 10^{20}$ cm$^{-3}$ to $\sim 10^{19}$ cm$^{-3}$, as shown in Figure 6.8.

An increase in the C content at the expense of the H content is consistent with an increase in the $sp^2$ content of the films as unsaturated bonds will contain less H than saturated bonds. The increase in $sp^2$ content due to the addition of nitrogen is similar to the PAC case as discussed previously, and has also been shown by Franceschini et al. [124] and Bhattacharyya et al. [125]. Silva et al. [78] also observed a decrease in the H content due to the addition of N and this was also interpreted as an increase in the $sp^2$ content. This increase has been shown by FT-IR studies to manifest itself as an increase in the relative C=N bond fraction.

However, over this range the optical band gap has been shown to increase rather than decrease and the paramagnetic spin density has been shown to decrease by one order of magnitude. An increase in the optical band gap indicates either an decrease in the $sp^2$ cluster size [5] or a decrease in the stress within the film [23]. It could also indicate a reduction in the density of carbon defects which will result in a decrease in the density of paramagnetic defects and also a reduction in the density of states in the band tail. Robertson [87] proposed that a possible effect of the introduction of N into the film will be to passivate existing carbon defects through the formation of a compensated state which was represented atomically as $C^+_4N^-_3$. The formation of such a state is consistent with the EPR variation, implying a decrease in the C defect density, and the increase in the optical band gap due to the passivation of states within the band tail.
It was reported by Schwan et al. [117] that the effect of nitrogen addition was a decrease in film stress to below the 10-12 GPa benchmark in their films. Furthermore, a decrease in the paramagnetic spin density will indicate that the concentration of odd-membered clusters or rings is decreasing with an increase in N content. Therefore, it is reasonable from this data to surmise that on the addition of a small amount of nitrogen, there is an increase in the $sp^2$ content which results in an increase in the cluster size, and is offset by a concomitant decrease in film stress. The net result is that there is a decrease in the paramagnetic spin density due to the formation of larger (rather than a greater density) clusters, and that the decrease in stress causes the increase in the optical band gap.

Above this flow rate there is a small decrease in C content which is concomitant with a small increase in the H content. It may be noted that in the case of PAC, an increase in the N content of the film coincides with an increase in the N-H fraction at the expense of the C-H fraction. It is likely that at high N levels, a similar process is happening in this case. Therefore, the results presented here suggest that at high levels, the additional N is bonding with H at the expense of C, resulting in an increase in the N-H fraction.

6.6.2.2 Electrical properties

The $J$ versus $E$ characteristics of the DAC films are shown in Figure 6.9. These contrast with those derived from the PAC films in that they possess an appreciable turn-on slope. This may be analysed using the Poole-Frenkel equation [12]. The undoped DAC film has already been shown to follow Poole-Frenkel conduction. It is more likely that these films will exhibit Poole-Frenkel conduction rather than SCLC or Schottky emission, as the defect density is sufficiently high that conduction is more likely to be defect controlled, rather than be limited by the space charges, or by a barrier. Furthermore, the existence of a barrier is likely to have little effect on the resulting $J/E$ characteristics, as conduction is more likely to occur through a defect band, rather than in the conduction or valence bands. Therefore, by applying the Poole-Frenkel equations as outlined in Section 2.4.2 and plotting $\ln(J/E)$ versus $E^{1/2}$, straight line relationships have been found and from the $\beta$ slope values of dielectric constant $\varepsilon_r$ have been calculated. These have been compared with those derived from the square of the refractive index as shown in the Table 6.1.
6.6. Discussion

<table>
<thead>
<tr>
<th>N content (at.%)</th>
<th>$\varepsilon_r$ (PF)</th>
<th>$\varepsilon_r$ ($n^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>4.4 ± 0.5</td>
<td>4.5 ± 0.1</td>
</tr>
<tr>
<td>4.1</td>
<td>5.5 ± 0.5</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>4.7</td>
<td>6.3 ± 0.5</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>5.2</td>
<td>5.5 ± 0.5</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>5.6</td>
<td>8.3 ± 0.5</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>6.4</td>
<td>7.6 ± 0.5</td>
<td>3.6 ± 0.1</td>
</tr>
</tbody>
</table>

Table 6.1 Comparison of $\varepsilon_r$ derived from Poole-Frenkel slope and that derived from $n^2$ for films with increasing N content.

These values calculated from the slope of the Poole-Frenkel curve are close to those derived from the square of the refractive index and these films are likely to be exhibiting Poole-Frenkel conduction. In all cases the value of $\varepsilon_r$ exceeds that derived from the square of the refractive index and for the film grown with the highest N content, the deviation is at its greatest. This may be explained by the fact that the PF-measured dielectric constant is a static measurement whilst the refractive index-measured dielectric constant is a dynamic measurement (at the frequency of excitation due to the He/Ne laser). Furthermore, the dielectric constant is dependent on the polarisability of the film which is a function of the bonding within the film. It is possible according to the Penn model [122] that an increase in the net bond polarisations due to the incorporation of C-N or N-H bonding may influence the dielectric constant of the material and lead to deviations between the optically and electrically measured values.

Also, as the flow rate of nitrogen is increased, the conductivity shows a small increase followed by a steady decrease beyond a certain N content. It is already known that the Poole Frenkel prefactor $J_0$ depends on the trap density $N_C$ of the material as well as the band gap. The band gap has been shown to increase from 0.7 to 1.0 eV. Therefore, we can ascertain $N_C$ for these films from the $\ln J_0$ values in a manner described in Section 5.5.2. Table 6.2 shows the variation in $N_C$ as compared to the values of paramagnetic defect density, as derived using EPR.

Once again taking into account the large degree of uncertainty when deriving the $N_C$ values which are to a large extent dependent on the values of band gap, the trap densities obtained are reasonable and in the region of $10^{15} - 10^{18}$ cm$^{-3}$. Furthermore, the small increase in conductivity with N content of 4.2 at.% as shown in Figure 6.9 may be
6.6. Discussion

<table>
<thead>
<tr>
<th>N content (at. %)</th>
<th>$N_C$(PF) ±50% (cm$^{-3}$)</th>
<th>$N_V$ ±10% (EPR)(cm$^{-3}$)</th>
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</thead>
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</tr>
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<td>4.7</td>
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<td>$2 \times 10^{17}$</td>
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</tr>
<tr>
<td>6.2</td>
<td>$5 \times 10^{17}$</td>
<td>$4 \times 10^{19}$</td>
</tr>
</tbody>
</table>

Table 6.2 Comparison of trap density ($N_C$) derived from Poole-Frenkel intercept and paramagnetic defect density ($N_V$) derived using EPR for films with increasing N content.

explained by an increase in the trap density ($N_C$) of 2 orders of magnitude. At higher N levels the trap density decreases slightly but the band gap increases significantly and it is likely that both contribute to the decrease in P-F conductivity which is observed. Looking at the equation shown in Section 2.4.2, a small change in band gap would result in a large change in the P-F conductivity ($J_0$) as it is an exponential term. Therefore, the increase in band gap is consistent with a decrease in $J_0$ which is observed.

At low levels N introduces a number of trapping centres which increase the P-F conductivity of the film. The variation of P-F conductivity at higher N levels may be associated with a small decrease in trap density and the increase in optical band gap. The band gap variation coincides with a decrease in paramagnetic defect density by one order of magnitude. The increase in the optical band gap of the material modifies the Poole-Frenkel conductivity ($J_0$) by increasing the height of the Coulombic potential well and hence reducing $J_0$.

Finally, the variation of activation energy from 0.3 to 0.5 eV as shown in Figure 6.10 is concomitant with the variation of optical band gap from 0.7-1.0 eV. This suggests that the Fermi level remains close to the centre of the band gap irrespective of N content. This is to be expected with a material of a paramagnetic density $> 10^{19}$ cm$^{-3}$, as the defects will tend to pin the Fermi level resulting in no n-type doping of the material with increasing N content. Other authors have either observed the weak n-type doping of DAC films or the passivation of defects [31, 117, 78].
6.6. Discussion

6.6.2.3 Variation with annealing

It is observed that, within experimental error, over the annealing temperature range the Tauc band gap and refractive index of the non-nitrogenated films do not change. This suggests that these films are stable up to \( T_A = 500 \, ^\circ C \). A reason for this is that these films contain a smaller hydrogen content (45 % as opposed to 55 % ) than the films grown on the earthed electrode. This may be compared with work performed by Bounouh et al. who found similarly that the optical band gap reduced for polymeric films at \( T_A = 300 \, ^\circ C \) but for diamond-like films the threshold was \( T_A = 500 \, ^\circ C \).

According to the IR data, below \( T_A = 300 \, ^\circ C \) an increase in the aromatic \( sp^2 \) C-H fraction was measured. Little change in the C=C fraction was observed which indicates that the size of the clusters was not increasing, and for this reason the band gap had not narrowed. There was no variation in H content over the temperature range which was concordant with little change in the film thickness.

When compared to the data presented here it appears that the results are similar and point towards little change in the thickness, refractive index or Tauc band gap of the non-nitrogenated film, which suggests little evolution of H and no increase in the cluster size. In terms of the electrical properties it has been observed that the P-F current density \( J_0 \) decreases by approximately 2 orders of magnitude. With no change in optical band gap the change in \( J_0 \) must be attributed to a decrease in the trap density (\( N_C \)) of approximately 1 order of magnitude, by applying the P-F equations and calculating \( N_C \) from the \( y \)-intercept of the \( \ln J/E \) versus \( E^{1/2} \) plot. Therefore, as a consequence of thermal annealing to \( T_A = 150 \, ^\circ C \) the optical properties have remained constant, but the P-F trap density has reduced.

This can be compared to the nitrogenated case where, at \( T_A = 150 \, ^\circ C \), a two orders of magnitude reduction of P-F conductivity is observed without any change in band gap. By applying the Poole-Frenkel equations it is found that \( N_C \) has also reduced by one order of magnitude at this annealing temperature. Therefore it appears that there is no difference in the nitrogenated or non-nitrogenated case in terms of the variation of trap density with moderate annealing, and therefore, nitrogen does not appear to play a part in decreasing the density of P-F active sites following annealing. It is possible that a small degree of restructuring from olefinic \( sp^2 \) clusters to aromatic \( sp^2 \) clusters is occurring, in the manner described by Bounouh et al.. In order to produce one aromatic
site, three olefinic sites would have to be joined, which will cause a net reduction in the concentration of individual $sp^2$-hybridised sites. This will therefore decrease the total member of trap (olefinic and aromatic) states and therefore decrease the trap density. An alternative hypothesis is if there was unbound H which could passivate trap states and hence reduce their net concentration, as suggested by Conway et al. [48].

At higher temperatures ($T_A > 250 \, ^\circ{}C$) the optical data suggests that the nitrogenated diamond-like film has re-ordered into a $sp^2$-rich state whilst the non-nitrogenated film has not. This is likely to be a consequence of nitrogen preferring three-fold sites rather than four, and therefore may catalyse the graphitisation process. The closure of the optical band gap is indicative of an increase in the $sp^2$ cluster size and the decrease in film thickness is concordant with the evolution of H from the film, which is also likely to be due to the formation of larger clusters.
6.7 Summary

It has been shown that the effect of the in-situ addition of nitrogen to the plasma is significantly different for PAC and DAC a-C:H thin films. In the case of PAC, the band gap has been shown to narrow which is likely to be a consequence of a small increase in the \( sp^2 \) cluster size. The \( J/E \) characteristics show that the high-field current conduction remains space-charge-limited, and the variation with N content indicates little increase in carrier mobility. The conductivity variation with temperature shows weak doping, as the activation energy increases from 0.7 eV to 0.9 eV due to a small addition of nitrogen. This represents a movement of the Fermi level from 0.7 eV from the valence band edge to close to midgap. A model based on the formation of \( sp^2 \)-hybridised N doping clusters has been postulated. It is likely that these clusters exist in small concentrations owing to their intrinsic instability, which explains the low doping efficiency. The conductivity of the nitrogenated PAC films has been shown to decrease when the films are annealed up to 250 °C, which supports the hypothesis that the doping centres are thermally unstable.

In the case of DAC films, the addition of nitrogen appears to increase the band gap of the material and decrease the EPR spin density, which indicates a decrease in the density of both localised band-tail states and states around the Fermi level. This is concomitant with a small increase followed by a decrease in Poole-Frenkel conductivity, which has been attributed to an increase in the density of trapping centres, coupled with the increase in band gap, and hence an increase in the excitation energy required for trapped carriers to surmount the Coulombic potential well. However, the Fermi level appears to be pinned irrespective of nitrogen content which is expected due to the high defect density of the material. The variation of the electronic properties with increasing annealing temperature suggests that the concentration of trap states is reduced in both the nitrogenated and non-nitrogenated case. The ellipsometric and band gap data shows that nitrogenated films re-order into an \( sp^2 \) rich state at a lower transition temperature than non-nitrogenated films.
Chapter 7

Ion implantation of \( a-C:H \)

7.1 Introduction

Ion implantation is a commonly used tool in semiconductor processing to dope and modify materials. Advantages of ion implantation include the ability to add a known quantity and depth distribution of impurities into the material, without alloying the material. However, the disadvantages include the requirement of a sophisticated high vacuum system which increases the cost of such a technique, and most importantly the physical damage incurred on the material, particularly if the ion dose is high. Techniques such as thermal annealing have been employed after implantation in order to remove much of the ion-beam-induced damage.

Section 3.6 outlines the previously reported studies of ion implantation as a method of introducing dopant species into \( a-C \). These include detailed studies by Prawer et al. and McCulloch et al. [92, 97, 98] who investigated \( \text{Xe}^+ \) and \( \text{C}^+ \) implantation into DAC and \( ta-C \) respectively. Both suggested that the material restructured into a \( sp^2 \) rich film, however the differences between the resulting properties of these films have not been discussed previously in any detail. Other studies, for example by Watanabe et al. [126], Ingram et al. [94], Doll et al. [95] and Grigull et al. [127, 128], have shown changes in film properties as a function of ion dose, for example a decrease in the hydrogen content. However, to the knowledge of this author, no studies investigating the ion implantation of polymeric films have thus far been carried out. These films are promising in terms of modification through this route as their as-deposited defect density is low, of the order of \( 10^{17} \text{ cm}^{-3} \) [109] so the effects of ion beam damage on
the opto-electronic properties will not be masked by the intrinsic defect density of the material. The two parameters of ion species and ion dose have the most significant effect on the resulting opto-electronic properties of the film and these have been investigated in this study.

7.2 Simulations

Before any implant was carried out it was necessary to perform simulations in order to ascertain a suitable energy window in order to obtain a doping profile through the film. The simulation package chosen was SUSPRE v1.4. The advantage over the standard package, TRIM, is that it is possible to calculate a sputtering rate which is dependent on ion dose, resulting in a dose-dependent calculation. It was found that two implants would be required per sample in order for a uniform doping profile to be obtained, as shown in Figure 4.2. The simulation parameters are shown below and Table 7.1 shows the range, straggle and erosion rate parameters as derived using SUSPRE.

- H content - 55% (measured using RBS/ERDA)
- C content - 45% (measured using RBS/ERDA)
- Density - 1.718 g cm$^{-3}$ (measured using EELS)
- Beam current - 20 μA cm$^{-2}$

<table>
<thead>
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<th>Energy (keV)</th>
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<th>Impl.2</th>
<th>Impl.1</th>
<th>Impl.2</th>
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<th>Energy (keV)</th>
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</thead>
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<td>0.0021</td>
<td>0.0030</td>
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</tr>
<tr>
<td>carbon</td>
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</tr>
<tr>
<td>nitrogen</td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 7.1 Calculated implant ranges, stragglers and erosion rates for boron, carbon and nitrogen implantation into PAC films.
7.3 Implant series 1: Implantation in a wide dose range

These films were grown on the earthed electrode of the rf–PECVD reactor. Depositions were carried out at the standard conditions outlined in Section 4.2 and the resulting film was approximately 100 nm thick. Films were then implanted with boron, carbon or nitrogen ions at the energies displayed in Table 7.1. The dose range was between $2 \times 10^{12}$ ions cm$^{-2}$ (2 implantation energies, each at $10^{12}$ ions cm$^{-2}$) and $2 \times 10^{16}$ ions cm$^{-2}$ (each energy at $10^{16}$ ions cm$^{-2}$). In order to ensure that energy was not a factor between implants, it was chosen not to vary the incident ion energy for different doses, so sputtering was not taken into consideration at this stage. Films were analysed using the techniques outlined in Section 4.4.

7.3.1 Optical / compositional measurements

Preliminary RBS data has shown that up to an ion dose of $2 \times 10^{15}$ cm$^{-2}$, the atomic percentage of implanted boron and nitrogen is below the measurement threshold. At the dose of $2 \times 10^{16}$ cm$^{-2}$, the boron concentration was 4.7 atomic %.

7.3.1.1 Thickness and refractive index

The variation of thickness and refractive index with implant dose for the three ions can be seen in Figures 7.1-7.2. It is observed that, for the different ions, there appeared to be little change in refractive index or thickness for doses less than $2 \times 10^{15}$ cm$^{-2}$. At $2 \times 10^{15}$ cm$^{-2}$, the refractive index increased and a decrease in thickness was observed. At an ion dose of $2 \times 10^{16}$ cm$^{-2}$, the film had thinned to approximately 45% of its as deposited thickness and the refractive index had increased to 2.1. This may be compared to Section 6.5, which reports that at annealing temperatures of 400°C, PAC films had thinned to approximately 40% of its initial thickness and the refractive index had increased to 1.8. Both of these factors were interpreted as evidence for the evolution of hydrogen from the sample, and a re-ordering into a $sp^2$-rich state [35]. Also the nitrogen-implanted samples appear to show the largest increase in refractive index and decrease in thickness. Nitrogen is a heavier ion than carbon or boron, so it is likely that a greater degree of ion-beam damage and sputtering has occurred in comparison with the other two species.
Figure 7.1 Film thickness as a function of ion energy, for the three different implant ions.

Figure 7.2 Refractive index as a function of ion energy, for the three different implant ions.
7.3. Implant series 1: Implantation in a wide dose range

7.3.1.2 Tauc band gap and resistivity

The variation of Tauc optical band gap with implant dose is shown in Figure 7.3. The optical band gap remains approximately constant until an ion dose of \(2 \times 10^{15} \text{ cm}^{-2}\) is employed. At this dose the band gap decreases to 1.3 eV, and eventually to 0.2 eV for the boron ion dose of \(2 \times 10^{16} \text{ cm}^{-2}\). This decrease can be explained by \(sp^2\) re-ordering, or the introduction of localised defect states as documented for sputtered amorphous silicon by Street [4]. Furthermore, it can be seen that the band gap reduction is also species dependent, in that the nitrogen-implanted samples have the greatest reductions, compared to the carbon and the boron ions. This trend is the same as for the refractive index and thickness data, which suggests that the ion-beam damage, or the possible \(sp^2\) re-ordering, is greatest with nitrogen at the largest doses.

The variations of resistivity with implant dose, for the three implant species, are shown in Figure 7.4. It can be seen that the primary effect of an increase in ion dose is to decrease the resistivity. For example, the effect of increasing the ion dose from \(2 \times 10^{12} \text{ cm}^{-2}\) to \(2 \times 10^{16} \text{ cm}^{-2}\) is to decrease the resistivity from approximately \(10^{14} \Omega \text{ cm}\) to approximately \(10^8 \Omega \text{ cm}\), for each of the ion species. However, there is a difference between the three implant ion species, in that the reduction in resistivity is the greatest with the nitrogen ion and the smallest with the boron ion. This effect coincides with the optical and compositional data. Also, there is an initial increase in resistivity with an ion dose of \(2 \times 10^{12} \text{ cm}^{-2}\) of less than half an order of magnitude. Although small, this is greater than the error of measurement, which is approximately 10 %, and indicates a decrease in the density of hopping sites which contribute to low-field conductivity. A similar result has been reported for ion-implanted DAC films by Wang et al. [96].
7.3. Implant series 1: Implantation in a wide dose range

Figure 7.3 Tauc optical gap as a function of ion energy, for the three different implant ions.

Figure 7.4 Through-the-film resistivity as a function of ion energy, for the three different implant ions.
7.3. **Implant series 1: Implantation in a wide dose range**

### 7.3.1.3 Hydrogen content

Figure 7.5 shows the variation of hydrogen and carbon content as a function of implant dose. The carbon content was derived as 100 % minus the hydrogen content, and therefore allows one to deduce the carbon content from the data. There is a decrease in the hydrogen content of the films, as the ion dose is increased from $2 \times 10^{13}$ cm$^{-2}$ to $2 \times 10^{15}$ cm$^{-2}$. This is consistent with the decrease in film thickness due to increasing ion dose. Hydrogen loss from a-C:H films has been described elsewhere [36, 35], and has been shown to be concomitant with film thinning.

It is observed that in the case of B-implanted films, a significant decrease in H content is observed when an ion dose of $> 2 \times 10^{15}$ ions cm$^{-2}$ is attained. In the case of C-implanted films, reductions at a dose of $2 \times 10^{15}$ ions cm$^{-2}$ are observed and for the N-implanted films, there is weaker evidence for a H reduction at $> 2 \times 10^{13}$ ions cm$^{-2}$. This is concomitant with the optical and microstructural data. Finally it is seen that the H contents are much larger in the case of films measured using RBS/ERDA (B-and N-implanted series) than those measured using NRA (55 at.% in unimplanted case as compared to 45 at.% as measured using NRA). It is suggested that in the case of NRA, where the energy loss through the film must be taken into account in order to ascertain the H signal within a certain depth from the film surface. The stopping powers which are required to do this are calculated from a matrix of carbon and hydrogen and as such will not be able to accurately model an amorphous polymer such as our film. The measurements performed using ERDA are absolute and therefore less sensitive on the stopping powers, and so are likely to be more accurate.

Figure 7.6 shows the NRA of C-implanted films in more detail. The rate of change of H signal with incident of $^{15}$N$^{2+}$ measurement ions is shown for the various C implant doses. It is observed that up to a C ion dose of $2 \times 10^{14}$ ions cm$^{-2}$ the out diffusion for the samples is so high that even with a bombardment of approximately $10^{12} \ 15$N$^{2+}$ ions at least a 2 % drop in H content is observed. The gradual reduction of H in our films upon ionic bombardment is consistent with partial loss of mainly unbounded H. At the highest ion dose of $2 \times 10^{15}$ ions cm$^{-2}$ the slope of the graph is considerably shallower indicating that the out diffusion is much weaker. This indicates that by this dose, much of the unbound H within the film has out-diffused and hence the unbound percentage of H within the film is less.
7.3. Implant series 1: Implantation in a wide dose range

Figure 7.5 Hydrogen and carbon content as a function of ion energy for the three different implant ions, as measured using ERDA for B and N and NRA for C.
7.3. Implant series 1: Implantation in a wide dose range

7.3.2 Electrical measurements

7.3.2.1 $J/E$ measurements

The $J$ versus $E$ characteristics as a function of implant dose, for the three implant ions, are shown in Figures 7.7-7.9. The predominant effect of the ion beam, as previously shown in Figure 7.4, is to increase the conductivity of the device. Therefore, it can be said that the ion beam significantly modifies the electronic properties of the film. However, in all cases at the lowest dose of $2 \times 10^{12}$ ions cm$^{-2}$ there is a small decrease in conductivity when compared to the unimplanted samples.

Secondly, it can be seen that the increase in conductivity is greater in the case of the nitrogen-implanted samples than the boron- or carbon-implanted samples. This can be explained by two competing factors; namely, variations associated by varying degrees of ion beam damage, or electronic doping of the material in the case of the nitrogen implanted sample. Nitrogen is a heavier ion and possesses a greater cross section than boron or carbon, and hence is expected to cause a greater degree of implantation damage than the other two species.

It is observed that there is a clear change in conduction mechanism, as judged qualita-
7.3. Implant series 1: Implantation in a wide dose range

Figure 7.7 $J$ versus $E$ characteristics for boron-implanted PAC films as a function of ion dose.

Figure 7.8 $J$ versus $E$ characteristics for carbon-implanted PAC films as a function of ion dose.

Figure 7.9 $J$ versus $E$ characteristics for nitrogen-implanted PAC films as a function of ion dose.
7.3. Implant series 1: Implantation in a wide dose range

tively from the shape of the \( J \) versus \( E \) characteristic, as the ion dose is increased. At a dose of \( 2 \times 10^{13} \text{ cm}^{-2} \) and below, for all three implant ions, the conduction mechanism appears to be the same as that for the unimplanted samples, as the curve is parabolic and obeys a power law dependence with electric field. For the highest dose the mechanism is different and more closely resembles Poole-Frenkel type conduction. This is because when \( \ln J/E \) is plotted against \( E^{1/2} \), as outlined in Section 2.4.2, a straight line is observed. For the intermediate doses, neither mechanism appears to dominate. In the case of the boron-implanted sample at a dose of \( 2 \times 10^{15} \text{ cm}^{-2} \), a clear turn-on in current occurs for the film above an electric field of \( 4 \times 10^5 \text{ V cm}^{-1} \). This sample is investigated in more detail in a later part of this chapter. Finally, the threshold ion dose at which the optical properties change, as shown in Figure 7.3, which is a dose of \( 2 \times 10^{14} \text{ cm}^{-2} \), appears to be lower in the case of the electronic properties. This suggests that there is a regime in which the conduction properties of the material may be altered without modifying the optical and microstructural properties of the material significantly.

7.3.2.2 \( J/E/T \) measurements

In order to ascertain the low-field conduction mechanism as a function of temperature, electrical measurements were performed over a range of temperatures up to 180 °C. In a manner described previously, the samples were annealed prior to deposition at 300 °C in a pressure lower than \( 10^{-5} \text{ mbar} \) for 5 minutes. Only samples in the dose range of \( 2 \times 10^{14} - 2 \times 10^{15} \text{ cm}^{-2} \) were investigated; this was because there appeared to be little significant difference in optical and electrical properties for samples which were implanted at a lower dose, and higher doses resulted in an almost complete closure of the band gap. It was found that when \( \ln \sigma \) was plotted against \( -q/kT \), straight-line regions were obtained above a measurement temperature of 110 °C, and the measured activation energy was the slope of this graph. Table 7.2 shows the variation of activation energy for samples of different implantation dose and species.

It is observed that the effect of the implantation is in all cases to reduce the activation energy. It is instructive to investigate the films which have been implanted at the lower dose \( (2 \times 10^{14} \text{ cm}^{-2}) \), as at the higher dose the activation energy would be further reduced as a consequence of the narrowing of the band gap of the material. When compared with the unimplanted sample, the C-implanted film possesses an \( E_{\text{act}} \) value
Table 7.2 Activation energy in the range of 110-180 °C as a function of ion dose and species.

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Dose (cm(^{-2}))</th>
<th>(E_{act}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimplanted</td>
<td>-</td>
<td>0.68 ± 0.07</td>
</tr>
<tr>
<td>B</td>
<td>(2 \times 10^{14})</td>
<td>0.41 ± 0.09</td>
</tr>
<tr>
<td>B</td>
<td>(2 \times 10^{15})</td>
<td>0.32 ± 0.03</td>
</tr>
<tr>
<td>C</td>
<td>(2 \times 10^{14})</td>
<td>0.56 ± 0.04</td>
</tr>
<tr>
<td>C</td>
<td>(2 \times 10^{15})</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>N</td>
<td>(2 \times 10^{14})</td>
<td>0.65 ± 0.07</td>
</tr>
<tr>
<td>N</td>
<td>(2 \times 10^{15})</td>
<td>0.42 ± 0.01</td>
</tr>
</tbody>
</table>

which has been reduced by 0.1 eV. In the case of the B-implanted film \(E_{act}\) has reduced by 0.3 eV and in the case of the N-implanted film there is no change in \(E_{act}\), within measurement error. For the films implanted at the higher dose (\(2 \times 10^{15}\) cm\(^{-2}\)), in the case of the B- and C- implant there is a decrease in activation energy of approximately 0.4 eV and for the N-implant there is only a decrease of 0.3 eV.

7.4 Implant series 2: B implantation in a narrow dose range

It was found from the previous study that the implantation dose range where the greatest changes occurred was between \(2 \times 10^{14}\) and \(2 \times 10^{15}\) cm\(^{-2}\), as most of the changes in the optical, electrical and microstructural properties occurred over this range. Therefore a second implant series was performed in this range. Also, the boron implant at \(2 \times 10^{15}\) cm\(^{-2}\) needed to be reproduced, as the film possessed a characteristic turn-on in current above a threshold electric field. As will be seen in Figure 7.12, this was indicative of hysteresis in the \(J/E\) characteristic. In particular, it was of interest whether this turn-on and hysteresis was dominated by one type of carrier or another, and whether it could be made asymmetrical by reducing the supply of carriers from one of the contacts. This was investigated by implanting two films of different thicknesses and therefore either implanting through the whole of the film or only a part of it.

Films were grown on Si and Corning 7059 substrates on the water-cooled earthed electrode of the \(rf-PECVD\) system. Films were implanted with B ions at energies of
7.4. Implant series 2: B implantation in a narrow dose range

20 and 26 keV in the dose range of $2 \times 10^{14}$ cm$^{-2}$ to $6 \times 10^{15}$ cm$^{-2}$ using the original simulation parameters shown in Table 7.1. Electrical measurements were made on Au/a–C:H/Cr devices. The variation in optical band gap and resistivity of the PAC films is shown in Figure 7.10, including the data from the lower and higher implantation doses performed in the previous study.

It is observed that on increasing the dose to $2 \times 10^{14}$ cm$^{-2}$, the Tauc gap remains approximately constant within experimental error but there is a one order of magnitude decrease in resistivity. By contrast for doses greater than $2 \times 10^{14}$ cm$^{-2}$, the optical gap falls and eventually reaches 0.2 eV at the highest ion dose, with the film resistivity decreasing from $6 \times 10^{12}$ $\Omega$ cm to $6 \times 10^8$ $\Omega$ cm - a decrease by 4 orders of magnitude.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.10}
\caption{Tauc optical band gap and resistivity as a function of boron ion dose.}
\end{figure}
7.4. Implant series 2: B implantation in a narrow dose range

7.4.1 EPR measurements

Room temperature electron paramagnetic resonance measurements were made using the procedure outlined in Section 4.4.4. Relaxation times were measured using the power saturation method discussed elsewhere [105]. These measurements were made on all implanted films; however signals from C related centres with $g \sim 2.0028$ were only observed for films implanted with doses higher than $2 \times 10^{15} \text{ cm}^{-2}$. At lower doses the EPR signal is dominated by signals with $g \sim 2.0055 - 2.0061$, associated with Si related defects [109]. Figure 7.11 shows that the spin concentration increases with dose from $3 \times 10^{17} \text{ cm}^{-3}$ in the unimplanted sample up to $2.7 \times 10^{20} \text{ cm}^{-3}$ at the highest dose of $2 \times 10^{16} \text{ cm}^{-2}$. In this dose range the EPR signal has a Lorentzian lineshape, and the peak-to-peak linewidth $\Delta B_{pp}$ reduces from 0.83 mT to 0.13 mT, as shown in Figure 7.11(b).

It is instructive to calculate the relaxation times corresponding to the spin-lattice interaction ($T_1$) and the spin-spin interaction ($T_2$), in order to ascertain whether the source of the observed linewidth value is the coupling of the paramagnetic spin to the lattice of the exchange / hopping of paramagnetic spins. The variation in the spin-lattice, $T_1$, and the spin-spin, $T_2$, relaxation time with dose are shown in Figure 7.11(c). As the implantation dose is increased, $T_1$ shortens from $1.1 \times 10^{-5} \text{ s}$ to $6 \times 10^{-8} \text{ s}$ while $T_2$ is observe to lengthen from $1.4 \times 10^{-8} \text{ s}$ to $5.1 \times 10^{-8} \text{ s}$. This indicates an increased contribution due to the exchange / hopping of paramagnetic spins with implantation dose.

Using the method employed by Barklie et al. [110], the dipolar ($\omega_p$) and exchange ($\omega_c$) frequencies may be calculated from the available values of $T_1$ and $T_2$. These correspond to the degree of dipolar broadening and exchange narrowing which account for the observed linewidth. The ratio of $\omega_c/\omega_p$ is found to be 1.9 for the unimplanted sample, which increases to 4.8 for the film implanted to $2 \times 10^{15} \text{ cm}^{-2}$, and then rises to 16.7 and 50 for the two highest doses. The ratio of $\omega_c/\omega_p$ indicates the efficiency in which the rapidly fluctuating magnetic field is able to average out the static dipolar broadening. Values over 10 indicate efficient motional narrowing, in this case as a result of extensive $sp^2$ re-ordering [110]. This occurs only in the two highest doses. In the case of the $2 \times 10^{15} \text{ cm}^{-2}$ film, extensive $sp^2$ re-ordering has not occurred, but motional narrowing has increased the ratio as compared to its unimplanted value.
Figure 7.11 EPR spin density, linewidth and relaxation time as a function of boron ion dose.
7.4.2 Electrical measurements

The $J$ versus $E$ characteristic of the $a$-C:H diodes over the range of boron ion doses are shown in Figure 7.12. Apart from the curve at $2 \times 10^{15} \text{ cm}^{-2}$, the characteristics are symmetrical with the magnitude of the current increasing by many orders of magnitude as the dose increases. It is interesting to note that when compared to Figure 7.7, a similar range in conductivity may be achieved over a much narrower dose range, indicating that the predominant re-ordering and increase in conductivity occurs over this range. Furthermore, in the film implanted at $2 \times 10^{15} \text{ cm}^{-2}$, this sample shows asymmetry which manifests itself as increased hysteresis in the negative sweep. This is investigated in more detail below.

7.4.3 Hysteresis effects

Figure 7.13 shows the $J$ versus $E$ characteristics for two films implanted at a dose of $2 \times 10^{15} \text{ cm}^{-2}$ with as-deposited thicknesses of 120 and 190 nm, respectively. Following implantation the thicknesses had reduced to 80 and 104 nm, respectively. Upon applying a positive voltage to the top contact the current increases and there is a pronounced hysteresis with a larger current on the return sweep to zero voltage. Also, it can be seen that in the positive sweep the 80 nm thick film is one order of magnitude higher in conductivity than the 104 nm thick film; however, the characteristics are similar with hysteresis resulting in a current enhancement. The negative sweep shows an even larger degree of hysteresis in the 80 nm thick film and no hysteresis in the 104 nm thick film. Therefore, the 104 nm thick film shows hysteresis in the positive sweep only and not the negative sweep, which results in the rectification stated above.

It was thought that the behaviour of trapped carriers might be influencing the current density of these films, as this type of hysteresis might be expected if carriers are trapped and decay with a long time constant, so current versus time measurements were performed at varying voltages for the sample implanted with boron ions at $2 \times 10^{15} \text{ cm}^{-2}$ (Implant series 1). The resulting characteristics are shown in Figure 7.14. It can be seen that up to an applied voltage of 3 V, the current decays with time in a manner which is expected if the device is considered as a parallel-plate capacitor. However, above the voltage of 3V (which coincides the electric field at which the current rises, in other words, the turn-on voltage) the current shows an increase with time. This is
7.4. Implant series 2: B implantation in a narrow dose range

Figure 7.12 $J$ versus $E$ characteristic for boron-implanted PAC films as a function of ion dose in the range $2 \times 10^{14} - 6 \times 10^{15} \text{ cm}^{-2}$.

Figure 7.13 $J$ versus $E$ characteristic for $2 \times 10^{15} \text{ cm}^{-2} \text{ B}^+$ implanted polymeric films (implant series 2) of 80 and 104 nm thickness, respectively, showing hysteresis.
not commonly observed in most dielectric materials.

In order to supplement the electrical data, measurements were performed as a function of temperature up to 160°C, which is shown in Figure 7.15. It may be observed that between measurement temperatures of 23 to 80°C, the current density of the characteristic decreases by approximately one order of magnitude, in other words the film possesses a negative activation energy of \(0.51 \pm 0.02\) eV. A negative activation energy has not been reported in the literature for thin-film materials, to the author’s knowledge. At higher temperatures the activation energy becomes positive with the value quoted in Section 7.3.2.2, i.e. \(0.32 \pm 0.03\) eV. This coincides with a reduction in hysteresis up to the measurement temperature of 80 °C, which is not shown in the plot for the purposes of clarity. Above 80 °C there is no longer any hysteresis in the \(J/E\) characteristic.
Figure 7.14 Current density versus time characteristic for $2 \times 10^{15} \text{ cm}^{-2}$ B⁺ implanted PAC film at varying voltages (implant series 1).

Figure 7.15 Variation in positive voltage sweep of $J/E$ characteristic as a function of measurement temperature.
7.5 Discussion

7.5.1 Carbon self-implantation: A comparison

The most complete self-implantation study into DAC films to the author’s knowledge was reported by Prawer et al. [92], who performed in-situ measurements of resistivity as a function of carbon ion dose at an energy of 50 keV, together with optical band gap, Rutherford backscattering spectroscopy (RBS) and Raman measurements. This was later supplemented with electron paramagnetic resonance (EPR) measurements, as reported by Adel et al. [93]. McCulloch et al. [97] implanted 50 keV carbon ions and 200 keV xenon ions into ta−C, and also performed in-situ resistance measurements which were compared to those of diamond, and also measurements of the optical band gap. These studies will be compared to the work performed here.

Figure 7.16 shows the variation of room temperature resistivity with carbon implant dose, as shown by the various authors [92, 97, 129]. Firstly, it may be observed that the unimplanted resistivity differs markedly for each type of film; the PAC film is the most resistive with $\rho \sim 10^{14} \, \Omega \, \text{cm}$ and the DAC film has the smallest resistivity of

![Graph showing variation of resistivity vs. dose](image)

**Figure 7.16** Variation in room temperature resistivity of DAC [92], PAC [this work], ta−C [97] and diamond [97] films as a function of carbon implant ion dose.
7.5. Discussion

~ 10^6 Ω cm. Such a wide range of resistivities is common in a–C and highlights the range of film properties that films of the same conventional name (a–C:H in this case) possess. Also, it must be noted that the resistivity of the DAC, ta–C and diamond films were all measured using a gap-cell arrangement whilst the PAC films were measured using a sandwich structure (i.e. through the film). Therefore, the presence of a surface \(sp^2\) layer on the film may have contributed to the lower resistivity associated with all the films apart from PAC. Secondly, in the case of ta–C, DAC and diamond films a dose threshold resulting in a sharp decrease in resistivity is observed at ion doses of \(10^{15} - 10^{16}\) ions cm\(^{-2}\), which appears not to be the case for PAC films which show a much more gradual decrease in resistivity. Thirdly, the DAC, ta–C and diamond films possess the same values of resistivity at the highest ion doses (\(\sim 10^2\) Ω cm at an ion dose of \(3 \times 10^{16}\) ions cm\(^{-2}\)) which suggests that they may be restructuring into a similar type of film microstructure. PAC films, however, still show a resistivity 6 orders of magnitude higher. Finally, a closer inspection of the graph shows that both PAC and DAC films display a small increase in resistivity before the following decrease, at a dose of \(2 \times 10^{12}\) ions cm\(^{-2}\) for PAC films and \(3 \times 10^{14}\) ions cm\(^{-2}\) for DAC films.

Figure 7.17 Variation in Tauc optical band gap of DAC [92], PAC [this work] and ta–C [97] films as a function of carbon implant ion dose.
7.5. Discussion

This can be compared to the variation of optical band gap as determined using the Tauc method for DAC, PAC and ta–C films, as shown in Figure 7.17. In the case of the ta–C data, this data corresponds to Xe+ implantation at 200 keV, but it is possible to convert this into a carbon ion dose if one recognizes that the resistivity variations are the same for the two ions with a dose offset of approximately one order of magnitude [97], which has been performed in this case. It can be seen that both the PAC and ta–C films show a decrease in band gap at a similar ion dose of $10^{14} - 10^{15}$ ions cm$^{-2}$, from 2.5 eV (ta–C) and 2.7 eV (PAC) down to below 0.7 eV in both cases. Before this threshold ion dose neither of these films show any significant change in band gap. By contrast, no decrease is observed for DAC films, whose optical band gap decreases from 1.5 eV to 1.0 eV above a dose of $10^{15}$ ions cm$^{-2}$. The resistivity variation follows that of ta–C at these high doses, so one would expect a similar optical band gap trend.

The DAC and PAC films deposited by rf–PECVD contain as-deposited hydrogen, and the variation of hydrogen content with ion dose is shown in Figure 7.18. It is observed that both types of film contain a large as-deposited hydrogen content, ~ 35 at. % in the case of DAC and 48 at. % in the case of PAC. It must be noted though that the

![Figure 7.18](image)

**Figure 7.18** Variation in hydrogen content of DAC [92] and PAC [this work] films as a function of carbon implant ion dose.
H content in PAC films was measured using NRA and the DAC films were measured using RBS which may lead to some uncertainty as to the magnitude of the absolute hydrogen contribution. In particular, PAC films have been shown to possess 55 % H according to elastic recoil detection analysis [111]. However, the trends remain clear; above a dose of $10^{14}$ ions cm$^{-2}$ both types of film show significant hydrogen loss, which has also been shown by other groups [94]. It appears also that above the critical dose the H content loss for the two types of film coincide and appear to be approximately linear (on this graph) once the critical ion dose is reached. This suggests a process where the number of incident ions results in a corresponding out-diffusion of hydrogen. It is also shown in Section 7.3.1.3 that much of the H contained within a–C:H films is unbonded, and it is likely that this is out-diffused at the lowest doses, leaving only bound H at the higher doses. This could explain the H loss between $10^{13}$ and $10^{14}$ ions cm$^{-2}$ for the PAC films.

Figure 7.19 shows the variation of paramagnetic spin density and linewidth for DAC and PAC films, as measured using EPR. Firstly, it may be observed that the unimplanted defect density is much larger in the case of the DAC film ($2 \times 10^{20}$ cm$^{-3}$) than the PAC film ($3 \times 10^{17}$ cm$^{-3}$). It is evident that the DC self bias of the DAC films during growth was much greater than that of the PAC films, which were deposited on the earthed electrode of a rf–PECVD reactor and hence grew under a self bias developed purely by the plasma potential (tens of V). Secondly, it can be seen that both films show an increase in paramagnetic spin density with implantation dose as would be expected. However, the magnitude of increase is almost two orders of magnitude in the case of PAC films as compared to less than one order of magnitude for DAC films. Thirdly, the linewidth data shows that at a dose of $2 \times 10^{13}$ cm$^{-2}$, the PAC films possess a linewidth more than twice as large as DAC films. In both cases the linewidth decreases with implantation dose, particularly at $2 \times 10^{15}$ ions cm$^{-2}$, however in this case the change is much greater for DAC films (0.4–0.12 mT), though the dose range for the PAC films is much smaller and therefore the full variation may not be registered. For the highest doses the linewidth of the DAC films appear to remain constant over one order of magnitude in ion dose.

The differences in unimplanted resistivity between the different types of film will now be explained. This may be due to the fact that PAC films possess a low sp$^2$ content (10-30 %) as determined by electron energy loss spectroscopy suggesting a large fraction of
7.5. Discussion

Figure 7.19 Variation in (a) EPR spin density and (b) EPR linewidth of DAC [92] and PAC [this work] films as a function of carbon implant ion dose.

$sp^3$ C-H bonding [121], and a low density of paramagnetic defects ($\sim 10^{17}$ spins cm$^{-3}$) [109] which results in a low density of hopping centres. On the other hand the defect density for unimplanted ta-C and DAC is around $10^{20}$ spins cm$^{-3}$ [93, 130] which leads to a greater density of hopping centres and hence a more conductive film. Hopping conduction is the most likely mechanism as at room temperature the conductivity in
these types of film does not follow a \( \ln J \) versus \( 1/T \) dependence [131]. The DAC films grown by Prawer et al. may also contain a larger fraction of \( sp^2 \) bonding which manifests itself in the narrower band gap, causing the size and density of the hopping sites to be larger than those of \( ta-C \) and PAC, which would result in a lower resistivity assuming a hopping process between neighbouring \( sp^2 \) islands in a manner similar to that proposed by Dasgupta et al. [8]. However, this does not explain the 8 orders of magnitude difference in conductivity between PAC and DAC films, particularly as the band gap for unimplanted DAC is still appreciable (1.5 eV as opposed to 2.6 eV for PAC). Films possessing a band gap of 1.5 eV have been shown to possess a resistivity as high as \( \sim 10^9 \) \( \Omega \) cm.

Now the dose variation of resistivity with that of the optical band gap will be compared. In the case of diamond, the resistivity threshold has been explained by the formation of damage cascades that eventually overlap at higher doses, resulting in a highly conductive \( sp^2 \) re-ordered film [91]. As a similar resistivity behaviour is observed at very high doses in the case of DAC and \( ta-C \) films, the same effects are likely to be occurring in these films. However, one would therefore expect the optical band gap of the DAC films to decrease to less than 0.5 eV once the films underwent macroscopic graphitisation. A possible explanation is that although there is a very large fraction of \( sp^2 \) sites, the cluster size remains small and therefore, according to Robertson [23], the band gap remains significant. This is contradictory to the case of the \( ta-C \) and PAC films, as their band gaps decreases to close to zero above a dose of \( 10^{16} \) cm\(^{-2} \), so these films undergo macroscopic graphitisation at very high ion doses as their cluster size increases. However, it still is unlikely to be coincidental that the DAC, \( ta-C \) and diamond films all possess the same resistivity at ion doses of above \( 3 \times 10^{16} \) cm\(^{-2} \). This suggests that although DAC films possess a small cluster size and \( ta-C \) and diamond films possess a larger cluster size, they all conduct in a similar manner. The fact that as grown DAC films possess hydrogen does not account for why the band gap of these films is greater than that of the other films at an implantation dose of \( 10^{17} \) cm\(^{-2} \), as at these doses very little hydrogen is present in these films (around 4 %).

In order to analyse the EPR data in Figure 7.19 it is first necessary to ascertain from which mechanism the linewidth \( \Delta B_{pp} \) arises. In the case of the PAC films a large fraction of the signal is due to the high silicon related centres from the substrate [109] or the film-substrate interface which results in a \( g \)-value much higher than that expected
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for $a-C$ (2.0055-2.0060 as opposed to 2.0028). In the case of the PAC films the $g$-value remains in the 2.0055-2.0061 region over the measured dose range. Therefore, it can be deduced from this data is that the effect of ion implantation in PAC is to increase the density of Si paramagnetic spins, which masks the carbon-related signal. When compared to the DAC films, it was noted from the original work [93] that all the EPR resonances possessed a Lorentzian lineshape. In $a-C$ it has been shown that there are three competing mechanisms contributing to the origin of lineshape and the magnitude of linewidth [110]. These are: the unresolved hyperfine interaction with hydrogen nuclei leading to a Gaussian lineshape for H-rich films, the dipolar interaction between like spins leading to a Lorentzian lineshape, and the motional averaging of the local magnetic field due to the exchange of spin within a cluster or hopping between clusters, which is prevalent in films with a very high ($> 10^{19}$ cm$^{-3}$) spin density, and leads to a narrowed linewidth also of Lorentzian lineshape. Adel et al. [93] measured Lorentzian lineshapes for all of their films, which suggests that either dipolar broadening or exchange is responsible for the lineshape. Using the relationship

$$\Delta B_{pp} = 8.12 \times 10^{-21} N_s$$

(assuming $g=2.0025$) for dipolar broadening [110], where $\Delta B_{pp}$ is in mT and $N_s$ is in cm$^{-3}$, we obtain linewidth values of 1.6 mT to 7.3 mT over the dose range for the DAC films. The observed linewidth is in the range of 0.4 - 0.1 mT over the dose range which would therefore be as a result of exchange narrowing for all films including the unimplanted case.

The hydrogen variation shown in Figure 7.18 suggests that both PAC and DAC films show a similar hydrogen loss above the critical ion dose and it has been suggested by Prawer et al. [92] that the removal of hydrogen results in a depassivation of dangling bonds and a rise in the number of inter-gap states at approximately $10^{15}$ ions cm$^{-2}$. Therefore, for DAC films the role of increasing the ion dose is the reduction of hydrogen within the film, and hence the increase in spin density. This may lead to the increase in exchange between spins due to the formation of larger clusters and hence an effective electron delocalisation which also increases as the ion dose increases. This would result in greater carrier mobility and hence a decrease in resistivity which could explain the resistivity trend as shown in Figure 7.16. For the $ta-C$ films the increased conductivity is a result of macroscopic graphitisation. However, in the case of DAC films this has not occurred at the expense of a low band gap but as a result of the ion implantation-induced damage. The higher conductivity of the unimplanted DAC films may also be
explained through similar means, because as exchange is evident within these films it is possible that the conductivity is enhanced by the delocalisation due to $sp^2$ re-ordering.

Finally, there is evidence for an initial increase in resistivity with implantation dose for the hydrogenated (DAC and PAC) films at low ion doses. This has also been observed by Wang et al. [96] who suggested that the C-H $sp^3$ concentration had increased resulting in a decrease in the density of hopping centres. This is unlikely as the conversion of $sp^2$ bonds to $sp^3$ bonds is energetically unfavourable, although a thermal spike model could possibly account for this type of change, this would neglect the role of hydrogen which is required as this behaviour is only observed for hydrogenated films. What must be noted, therefore, is that at the dose of $2 \times 10^{12}$ ions cm$^{-2}$ for PAC films and $3 \times 10^{14}$ ions cm$^{-2}$ for DAC films, at which the increases in resistivity occur, the hydrogen contents remain constant. Therefore, it is possible that there is an atomic redistribution of mobile hydrogen due to recoil from the incident ion flux, which re-passivates dangling bonds and hence increases the resistivity. This type of mechanism has already been suggested in the case of the thermal annealing of PAC [35] and $ta$-C:H [48].

7.5.2 Effect of ion species

The optical data suggests that above an ion dose of $10^{14}$ cm$^{-2}$ the greatest changes in Tauc band gap and refractive index are with the N ion and the smallest changes are with the B ion. The effect of ion beam damage has been observed to re-order the film into an $sp^2$-rich state which would narrow the band gap as the cluster size is increased. N is a heavier ion than B or C so the measurements are consistent with a greater degree of $sp^2$-reordering associated with the N ion than with the B or C ions. Although there is only a small difference in atomic mass between the implant ions (N=14, C=12, B=11) the implant energy was increased for the heavier ion as compared to the lighter ion, in order to obtain the same doping profile through the film. As the implantation energy is increased the deposited energy density will increase accordingly and the calculations performed by SUSPRE show that in the case of the low energy implant, the nuclear deposited energy in the case of N is 14.41 keV as compared for 9.71 keV in the case of B. This difference may account for the greater degree of $sp^2$-reordering in the case of the N ion as compared to the B or C ions. Also, the reduction in resistivity is greatest with the N ion and least with the B ion. This would indicate a greater hopping probability in films implanted with the heavier ion, which is consistent with a greater degree of $sp^2$-
reordering. This assumes that the room-temperature transport is governed by hopping between $sp^2$ clusters, as has been shown in the unimplanted case.

The activation energy variation shows that in the case of the three implant ions there is a reduction in $E_{act}$ at a dose of $2 \times 10^{14}$ cm$^{-2}$ even though there is no change in the Tauc band gap within experimental error. In the case of C-ion implantation it is unlikely that there has been any electronic doping effect. If the Fermi level has not moved this would suggest that the electronic band gap of the material has narrowed even though the optical band gap has not. At the higher dose of $2 \times 10^{15}$ cm$^{-2}$, the activation energy for all three ions has further reduced which is likely to be on account of a further narrowing of the electronic band gap of the material as a consequence of ion-beam damage.

The Tauc $B$ parameter, as discussed in Section 4.4.3, may be useful in explaining why, in the case of C implantation, the activation energy has decreased whilst the Tauc band gap has not at the ion dose of $2 \times 10^{14}$ cm$^{-2}$. In the unimplanted case the value for the Tauc $B$ parameter is $1.8 \times 10^3$ eV cm$^{-1}$ which increases to $4.4 \times 10^3$ eV cm$^{-1}$ at an ion dose of $2 \times 10^{14}$ cm$^{-2}$. As in the previous chapter, one would expect the $B$ parameter to decrease as a result of the broadening of the band-tail, if the optical band gap had remained constant but the electronic band gap had decreased. This may be explained using a similar argument as used previously. That is, that the strength of the absorption in the high photon energy (3-4 eV) region has increased as a result of ion-beam damage. If the net absorption over this energy range increases, the concentration of $sp^2$ clusters contributing to transitions in this energy range would have increased.

In the case of the N ion, though, the decrease in $E_{act}$ for this dose is less. In the case of N it was observed in the previous chapter that the effect of in-situ addition of a small amount of N in polymeric films was to increase $E_{act}$ from 0.7 to 0.9 eV. In this case, at the dose of $2 \times 10^{14}$ cm$^{-2}$ $E_{act}(N)$ is 0.1 eV greater than $E_{act}(C)$. It may be taken into account that the narrowing of electronic band gap is likely to be greater in the case of N than in the case of C on account of the greater degree of ion-beam damage. Therefore, it may be surmised that the doping effect in the case of N-implantation is analogous to the in-situ addition of N to the deposition plasma. The increase in $E_{act}$ when compared to the C-implantation case may be attributed to a small movement in the Fermi level towards midgap due to a weak doping effect. At the higher dose the decrease in activation energy is also least with the N ion, even though the band gap
has fallen to 0.7 eV when compared to 0.9 eV for the C ion and 1.3 eV for the B ion. 

\( E_{act}(N) \) for this film is 0.4 eV which suggests that the Fermi level is close to midgap.

In the case of the B ion at the implantation dose of \( 10^{14} \text{ cm}^{-2} \) the decrease in \( E_{act} \) for this dose is greater than for the C ion. It is likely that boron is a \( p- \)type dopant on account of its situation in Group III of the periodic table. If as-deposited PAC is intrinsically \( p- \)type, as suggested by several authors [77, 23], the B-doping of the material would further reduce \( E_{act} \), which has been observed in these films. The movement of the Fermi level at this dose would be the difference between the B-implant and C-implant \( E_{act} \) values, i.e. 0.15 eV. At the higher dose of \( 10^{15} \text{ cm}^{-2} \), however, there is little difference in \( E_{act} \) between the B-implant and C-implant case. This may be explained by the fact that the Tauc band gap is 0.4 eV wider in the case of the B-implanted sample than the C-implanted sample. Therefore, even if B-implantation has caused a further movement of the Fermi level towards the valence-band edge, this would not be observed in the \( E_{act} \) variation as the band gap has narrowed further in the case of the C-implant. As mentioned above this would be as a consequence of the greater degree of \( sp^2 \) re-ordering on account of the greater degree of ion-beam damage.

### 7.5.3 Effect of ion dose

#### 7.5.3.1 Band gap and resistivity variation

The results shown in Figure 7.10 and 7.11 indicate that there exist two regimes; one for doses up to and including \( 2 \times 10^{14} \text{ cm}^{-2} \) where the Tauc gap remains constant and the film resistivity falls by about 2 orders of magnitude, and another regime above this dose where, by the highest dose of \( 2 \times 10^{16} \text{ cm}^{-2} \), there is a near closure of the optical gap, a further reduction of the film resistivity by 4 orders of magnitude, and where exchange effects dominate the EPR linewidth and relaxation times. In order to analyse the resistivity variation, the equations for variable-range hopping (VRH) for electrons at the Fermi level, originally derived by Mott and Davis [1], have been applied to \( \alpha-C:H \) films [92]. Using a localisation factor, \( \alpha \), of \( 7.5 \times 10^6 \text{ cm}^{-1} \) as quoted by Orzeszko et al. [7], the required density of states at the Fermi level, \( N(E_F) \) would have to exceed \( 10^{29} \text{cm}^{-3} \text{eV}^{-1} \). From the measured spin density of \( 3 \times 10^{20} \text{ cm}^{-3} \) at the highest dose, an estimate of \( N(E_F) \) can be obtained assuming a maximum correlation energy of 2 eV [30]. This gives \( N(E_F) \sim 10^{20} \text{ cm}^{-3} \text{eV}^{-1} \), considerably
7.5. Discussion

less than that required for VRH. In the model of Dasgupta et al. [8], conduction at room temperature occurs via hopping between neighbouring $sp^2$ islands, and so is determined by the concentration of gap states and the separation between the $sp^2$ islands, as shown schematically in Figure 7.20. As the $sp^2$ content of the as-deposited films is low (30%), the hopping distance is large resulting in low conductivity. During ion implantation, localised heating results in the formation of highly localised $sp^2$ sites, which are small if the ion dose is below the graphitisation threshold, resulting in no change in optical band gap which is governed by the size of the largest clusters [116]. Above the graphitisation threshold, the ion tracks start to overlap as in the case of diamond [91]. The concentration of these introduced sites is proportional to the ion dose. Implantation at low doses therefore introduces nano-clustering smaller than the average cluster size, which maintains the wide band gap but increases the conductivity by decreasing the hopping distance. At higher doses, the film restructures over the bulk of the film, the band gap decreases accordingly, and the effects of exchange become prevalent.

**Figure 7.20** Proposed effect of ion implantation on hopping conductivity between adjacent clusters, below and above the dose of $6 \times 10^{14}$ cm$^{-2}$. 
7.5. Discussion

7.5.3.2 Variation in $J/E$ characteristic

The $J$ versus $E$ characteristics are shown in Figures 7.12. Apart from the curve at $2 \times 10^{15} \text{ cm}^{-2}$ the characteristics are symmetric and this indicates bulk-limited conduction. The $J/E$ at the lowest doses are consistent with space-charge limited currents in the bulk of the film [9], with the high field regime showing an approximately parabolic $J$ versus $E$ relationship, as shown in Section 5.5.2. The large increase in conductivity with increasing boron dose is attributed to restructuring and defect creation during ion bombardment. Ion damage has been shown to increase the paramagnetic defect density of amorphous silicon, with a concomitant increase in the and Urbach tail width and a reduction in the band gap [13]. A similar effect is expected in amorphous carbon but in addition any change in the proportion and distribution of $sp^2$ and $sp^3$ bonding during bond breaking and reformation will manifest itself in a change in the optical band gap. In Section 7.5.3.1 it has also been shown that there is an onset for $sp^2$ re-ordering which is in the range of $10^{14} - 10^{15} \text{ cm}^{-2}$.

For implantations at a dose of $6 \times 10^{14} \text{ cm}^{-2}$ and below, the $J/E$ characteristic remains parabolic which indicates SCLC, even though the conductivity has increased over three orders of magnitude. Applying the standard equation [9] yields a mobility value of approximately $2 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the film implanted at a dose of $6 \times 10^{14} \text{ cm}^{-2}$. This is an increase of over 1 order of magnitude when compared to the unimplanted case. Therefore, the increase in current magnitude up to a dose of $6 \times 10^{14} \text{ cm}^{-2}$ may be attributed to an increase in low field conductivity, coupled with an increase in the mobility of the SCLC at higher fields.

The results presented also show a very strong dose correlation of the band gap and spin density as determined using EPR, with the band gap falling from its initial value of 2.6 eV to 0.4 eV at the highest dose, and the spin density increasing from an initial value of $10^{17} \text{ cm}^{-3}$ to a final value of $10^{20} \text{ cm}^{-3}$ [133]. Therefore, as the ion dose increases, there is a narrowing of the band gap, an increase in defect density and an increase in the doping concentration. All these features promote the transport of carriers via the Poole-Frenkel effect. Indeed at the highest dose the $J/E$ characteristics are well described by the hopping of carriers between defect states in the bulk of the film, as a straight line log $J/E$ versus $E^{1/2}$ relationship is observed which is consistent with Poole-Frenkel conduction [10]. Since the film has the highest concentration of
impurities, it seems reasonable to assume that the current is due to transport between charged defect centres.

For the highest implantation dose log \( J/E \) versus \( E^{1/2} \) was plotted and the Poole-Frenkel parameters were derived using the equations outlined in Section 2.4.2. The \( \epsilon_0 \) values are tabulated in Table 7.3.

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<th>B</th>
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<td>( \epsilon_0 )</td>
<td>44</td>
<td>23</td>
<td>36</td>
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<tr>
<td>( N_C )</td>
<td>( 1.2 \times 10^{18} )</td>
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Table 7.3 Poole-Frenkel parameters as a function of ion species, for an ion dose of \( 2 \times 10^{16} \) cm\(^{-2} \).

In all three cases the P-F-derived \( \epsilon_0 \) values are almost one order of magnitude greater than the value derived from the square of the refractive index, which is approximately 4. The trap density has been shown to be similar for the three materials within experimental error. The spin density for the samples as measured using EPR is \( 3 - 6 \times 10^{20} \) cm\(^{-3} \) so the Poole-Frenkel trap density is approximately two orders of magnitude lower. The high current density value is attributed to the narrow band gap of these films - 0.1-0.2 eV, so the energy difference from the trapped state to the extended state is in this region.

In the case of \( a-\text{Si:H} \) and \( a-\text{SiN}_x: \text{H} \) several authors have noted a decrease in P-F-derived \( \beta \) value which equates to an increase in the \( \epsilon_0 \) value, as the defect density of the material increased [14, 13, 120]. Hill [12] suggested that for materials with a high defect density the Coulombic potential wells will overlap and the current characteristic follows a \( \ln J \propto E \) relationship akin to Poole conduction [134]. However, this has been shown not to occur in this study, as no linear \( \ln J \) versus \( E \) dependence is observed for films with the highest implantation dose. It was shown by Simmons [10] that if the insulator contains shallow neutral traps the \( \beta \) value decreases to half the value calculated from the square of the dielectric constant. This is possible in the material investigated here, where the band gap is narrow and therefore any trapped carriers have a low energy of excitation to the extended states.
7.5.4 Trapping and hysteresis

When examining the $J$ versus $E$ characteristics shown in Figure 7.12, it is shown that apart from the curve at $2 \times 10^{15}$ cm$^{-2}$, the characteristics are symmetrical with the magnitude of the current increasing by many orders of magnitude as the dose increases. Therefore, bulk controlled conductivity is assumed at the two extremes, each occurring for the unimplanted film and at the highest dose. For the unimplanted film, both the band gap and the metal barrier heights are high so the current will be controlled by defects concentrated at the Fermi level. At the highest dose, both the defect concentration and doping level are high and so again the current is controlled by bulk transport.

The $J/E$ characteristics for the films which were implanted at a dose of $2 \times 10^{15}$ cm$^{-2}$ with thicknesses of 80 and 104 nm are shown in Figure 7.13. Here, the Tauc optical gap is 1.3 eV and Poole-Frenkel conduction appears not to apply, as the calculation performed previously reveals a permittivity value far higher than that derived from the square of the refractive index. The presence of hysteresis at the intermediate dose indicates that we have a bipolar effect in which the presence of one type of carrier effects the transport of the other. During the first positive sweep, electrons are injected from the bottom contact and holes from the top contact and the trapping of holes may enhance the electron current [135]. If the holes are trapped, the number of trapped holes will depend on the magnitude of the positive voltage applied to the top current and how long the voltage is applied, as an increase in either parameter will increase the trapped space charge. This is the case in our films, where changing any one of these parameters was found to change the size of the loop, although this has not been shown for brevity. On reducing the positive voltage back to zero, holes remain trapped so the electron current is higher on the way down than on the way up leading to a loop in the characteristic. Similarly, for the 80 nm thick sample the negative characteristic shows a similar loop behaviour. This may be attributed to holes being injected and trapped, this time from the back contact, thus causing an increase in electron current.

Further evidence for a current enhancement due to a trapping process is shown in the current versus time measurement as shown in Figure 7.14. In this case it has been observed that for low applied voltages the measured current density decreases with time. This is consistent with a capacitive effect which, when the curve is fitted to
an exponential decay, yields a time constant value of approximately 1 s. Applying 
\[ C = A \varepsilon_0 \varepsilon_r / d \text{ and } R = \rho d / A , \]
the theoretical time constant for this device is \[ \rho \varepsilon_0 \varepsilon_r \]
which has been calculated to be 0.2 s. The discrepancy between these two values may 
be explained if another process is causing the increase in measured time constant. At 
higher measurement voltages the time constant increases until a voltage of 3 V where the 
current increases rather than decreases with time. This may be explained if the trapping 
of carriers causes an increase in current magnitude, which at low measurement voltages 
counteracts the capacitive decay of the current. At higher measurement voltages, as 
the voltage is applied, more carriers are trapped which causes a further enhancement 
in current over time.

Furthermore, as shown in Figure 7.15, below a measurement temperature of 80 °C, 
as the measurement temperature is increased the current magnitude decreases, but 
above this temperature it increases with increasing temperature. Should the current 
be enhanced by trapping, an increase in temperature will depopulate these traps via 
a thermionic emission mechanism. It has been shown that above a measurement tem­
perature of 80 °C the hysteresis is absent and the current at higher temperatures then 
increases with temperature. Above this temperature, therefore, the measurements are 
consistent with a model assuming that there are no longer any trapped carriers which 
cause the current enhancement.

The relationship between the trapping of carriers and the presence of hysteresis in 
the \( J / E \) characteristic is supported by the data shown above for the 104 nm thick 
film. In this case the boron ions were unable to penetrate to the bottom part of the 
film when implanted with the same energy and dose as used above. As shown in 
Figure 7.13, in this case in the negative voltage segment the current enhancement and 
hysteresis are missing, and therefore the device shows rectification of approximately 
an order of magnitude. This is interpreted as an absence of hole injection from the 
bottom contact into the unbombarded part of the \( \alpha\text{-C:H} \) film. The reverse current 
is therefore unmodified by the presence of holes. The fact that the hysteresis occurs 
for the positive but not the negative sweep indicates that holes are being trapped and 
the electron current is modified by the trapping process, rather than vice versa. This 
assumes that the ion damage creates trapping centres which are through the bulk of 
the film in the case of the 80 nm thick sample, and only through the top part of the film 
in the case of the 104 nm thick sample. Should electrons be trapped rather than holes,
and the hole current was modified, the hysteresis would only occur when electrons were injected and trapped, so the hysteresis would be in the negative and not the forward sweep for the 104 nm thick film.

There are two methods in which hole injection may modify and enhance the electron current within the film. The first assumes that conduction remains space-charge limited and is governed by the trapping of negative space charge which causes an impedance to electron flow. Therefore, hole injection may have the effect of reducing the magnitude of the negative trapped space charge by recombining with the trapped electronic charge, and thereby increasing the magnitude of the electron current. This will only happen if there was a sufficient electric field within the film in order for the trapping centres to trap holes. Such a model is shown figuratively in Figure 7.21(a). If there are no centres to trap holes, then the space charge will remain unperturbed and hence no current enhancement will be observed. This appears to be the case in the 104 nm thick film where the absence of current enhancement in the negative voltage sweep indicates no traps to allow hole injection and trapping from the bottom (Au) contact.

The second model applies if the electron current is contact-limited and the presence of positively charged space charge due to hole injection causes band bending which modifies the electron barrier height at the reverse-biased \( a-C:H:(B)/Cr \) barrier. For

![Figure 7.21](image-url) Figure 7.21 Band diagrams showing two possible models for hysteresis effect due to carrier trapping: (a) modification of space charge, (b) modification of barrier height.
MSM structures where contact-limited current applies the \( J/E \) characteristics are determined by the lowering of the barrier height with applied voltage, which is known as the Schottky effect [15]. By using the standard equations [115] and plotting \( \ln J \) versus \( E^{1/2} \), a straight line dependence below the switching voltage, which has not been shown for brevity. The value of dielectric permittivity may be calculated from this slope and the value obtained is approximately 2, which is close to the dielectric constant, as derived from the square of the refractive index, which yields a value of 5. Furthermore, an approximation of the barrier height can be derived using the standard equations, which has been calculated to be 0.8 eV, for both sides of the characteristic, i.e. both the \( a-C:H:(B)/Au \) contact and the \( a-C:H:(B)/Cr \) contact. The Tauc optical band-gap of the material has already been shown to be 1.3 eV in Section 7.4. Assuming that boron doping will enhance the movement of the Fermi level towards the valence rather than the conduction band, the 0.8 eV barrier is more likely to be an electron barrier. The proposed band diagram is shown in Figure 7.21(b). The presence of positive space charge, due to hole injection from the \( a-C:H:(B)/Au \) forward-biased contact, results in band bending which narrows the electrical thickness of the film, and hence increases the electric field at the reverse biased electron barrier. Again, should there be insufficient trapping centres for hole injection to occur then current enhancement would not occur, as is the case for the negative voltage sweep of the 104 nm thick film.

To conclude, bipolar effects have been observed which manifest themselves in the current enhancement with applied electric field and hysteresis in the \( J/E \) characteristic. \( J/E \) versus temperature and \( J \) versus time measurements have suggested that the trapping of carriers results in an enhancement of current magnitude which is both voltage and temperature dependent. The dependence on the back contact and film thickness suggest that holes rather than electrons are trapped which causes a modification of the electron current. Two models have been postulated. The first dictates that the trapped negative space charge density within the film will be reduced by recombination with positive space charge, which increases the free charge density and hence increases the electron current. The second model states that the presence of trapped holes at one of the contacts will modify the band bending in the film such that the electric field at the electron barrier is increased, thus increasing the current due to thermionic emission over this barrier. Therefore, the first model indicates the modification of a SCL process, whilst the second model indicates a modification of a Schottky barrier process.
7.6 Summary

The investigation of ion-implantation into PAC has shown that there is a threshold for $sp^2$ re-ordering in a manner similar to that of diamond [97]. This occurs at an ion dose of $10^{14} - 10^{15}$ ions cm$^{-2}$, which is also dependent on the atomic mass of the implanted species. As a result of $sp^2$ re-ordering the film thickness decreases due to H loss, and the EPR linewidth is reduced due to a motional averaging of the local magnetic field. This has been attributed to the exchange interaction which is a result of the greater delocalisation of the electronic charge. There may also be a weaker effect which results in an increase in conductivity at lower ion doses without any change in band gap. This has been attributed in part to an increase in the mobility within the films, although the high-field transport remains space-charge-limited up to a dose of $2 \times 10^{14}$ ions cm$^{-2}$.

The conductivity versus temperature variations have indicated that the activation energy is greater for N-implanted films and smaller with B-implanted films. This supports the hypothesis derived in the previous chapter, that intrinsically grown PAC is $p$-type and the addition of N results in a movement of the Fermi level towards midgap. Therefore, the data presented here is consistent with the N-doping model which has been suggested previously [87]. Similarly the activation energy has been shown to decrease with the addition of B which suggests an increase in the $p$-type doping of the material.

In the case of the B-implanted films a hysteresis effect has been observed and investigated which indicates that the conductivity may be enhanced by the trapping of carriers. The current versus time and conductivity versus temperature measurements, have indicated models based on carrier injection and trapping. This has been attributed to a depopulation of trapped carriers and hence a decrease in the current density with increasing temperature. Implanting through only the top part of the film and leaving the bottom contact unimplanted has shown that a diode-like characteristic may be achieved, by introducing trapping centres at only one of the contacts. According to the polarity of the diode a mechanism based upon the modulation of current due to the injection of holes at either contact has been postulated. This phenomenon has not been previously reported and is of significance for the fabrication of new $a$-C-based electronic devices.
Conclusions

The work presented here represents an in-depth study into the electrical characteristics of hydrogenated amorphous carbon thin films. Transport in both the low and high-field regimes have been investigated, and both have been shown to be informative as methods for describing the electrical properties of these films. This data has been correlated with optical absorption and electron paramagnetic data in order to fully understand the electrical properties of the material. Although polymer-like and diamond-like films are both referred to in the literature [131] as hydrogenated amorphous carbon, their opto-electronic properties differ greatly.

8.1 PAC films

The DC electronic properties of as-deposited PAC approach that of a dielectric insulating material. These films possess a very high resistivity of around $10^{15}$ $\Omega$ cm, low density of paramagnetic defects in the order of $10^{17}$ cm$^{-3}$ and a wide Tauc band gap of 2.6 eV. It has been shown that at room temperature, conduction at low fields is dominated by hopping and above a temperature of 110 °C, conduction in the band tails is dominant. At high fields, conduction follows a space-charge-limited current process as derived for a trap free insulator.

The in-situ addition of nitrogen into the plasma during deposition has been shown to weakly dope the film, with the activation energy first increasing from 0.7 eV to 0.9 eV and then decreasing to 0.8 eV at higher nitrogen levels. The Tauc band gap narrows over this range which suggests a small increase in the $sp^2$ content and/or alloying.
The conductivity increases monotonically with the N content which is attributed to an increase in the density of hopping centres. A model based on the introduction of \( N_{3\pi} \) doping sites has been postulated. The variation with annealing temperature suggests that these sites are thermally unstable and the conductivity of the nitrogenated film decreases with annealing as the density of the dopant sites is reduced. The high field conduction mechanism remains space-charge-limited over the nitrogen content range investigated in this work, which is from 0 to 8 at. %.

The boron, carbon and nitrogen ion-implantation into PAC has shown a threshold for \( sp^2 \) re-ordering at an ion dose of \( 10^{14} - 10^{15} \text{ cm}^{-2} \), above which the film thickness decreases, the refractive index increases, and the Tauc band gap decreases. At lower ion doses the resistivity is observed to increase without any change in band gap, which has been attributed in part to an increase in the space-charge-limited mobility. At an ion dose of \( 10^{14} \text{ cm}^{-2} \), the activation energy has been observed to be greater for nitrogen-implanted films and smaller with boron-implanted films than the carbon-implanted control. This is consistent with the literature [131] which cites that intrinsically grown PAC is \( p \)-type and the implantation of boron moves the Fermi level towards the valence band edge, whilst the implantation of nitrogen moves the Fermi level towards midgap. This is consistent with the nitrogen doping model presented previously [87], based on the introduction of \( N_{3\pi} \) sites.

Furthermore, a hysteresis effect has been observed which has been attributed to the trapping of carriers which cause an enhancement in current. Implanting through only the top part of the film and leaving the bottom contact unbombarded has resulted in rectification of over an order of magnitude, which has not previously been reported for this type of structure in \( a-C \). A mechanism based on the injection of holes causing the enhancement in electron current has been proposed.

### 8.2 DAC films

The DC electronic properties of DAC resemble that of a highly defective semiconducting material. The films possess a narrow band gap of 0.7 eV, high paramagnetic density of the order of \( 10^{20} \text{ cm}^{-3} \) and lower H content (45 at. %) than PAC films. It has been shown that room-temperature transport is governed by conduction in the band tail and at temperatures above \( 100 \text{ °C} \) by conduction in the extended states. High-field current
transport is dominated by the Poole-Frenkel mechanism.

The addition of nitrogen causes a decrease in paramagnetic density of one order of magnitude and an increase in band gap from 0.7 to 1.0 eV. The Poole-Frenkel conductivity is shown to increase by half an order of magnitude and then decrease by at least two orders of magnitude at higher nitrogen levels. This has been attributed to an increase in the density of Poole-Frenkel active trapping centres, coupled with a reduced probability of excitation into the extended states as a result of the increase in the band gap. The activation energy remains approximately half that of the Tauc band gap, between 0.3 and 0.5 eV, which suggests that the Fermi level is pinned at midgap. The effect of thermal annealing is a reduction in the density of trap states which cause a decrease in the Poole-Frenkel conductivity of the material.

8.3 Suggestions for further research

There are a number of studies that will supplement this study, including:

- Thermopower measurements. These would verify the type of carrier and would establish whether the hopping conduction in undoped PAC is due to holes, for example.

- Measurements of temperature down to 77 K. Although this would be problematic for PAC films as their high resistivity would result in currents below the sensitivity of a standard picoammeter source unless a highly sensitive ammeter was utilised, the dependence at lower temperatures would give valuable information as to the type of hopping mechanism which is occurring.

- Ion implantation of different dopant species. In the case of diamond, nitrogen has been shown to be a poor $n$-type dopant as it forms a deep donor level. The work presented here suggests that this is also the case in PAC. Phosphorus, for example, may be a more suitable candidate for $n$-type doping.

- Photoconductivity measurements. These have not been studied in this case, but due to the low paramagnetic density of PAC it is possible that it may be a photoconductive material. This would also give valuable information as to the carrier mobility.
Bibliography


