A STUDY OF

THE OPTICAL AND ELECTRONIC PROPERTIES

OF

AMORPHOUS SILICON NITRIDE

by

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ABSTRACT

Amorphous a-SiN$_x$(::H) films have been prepared by radio-frequency sputtering in an argon-nitrogen-hydrogen atmosphere. Both hydrogenated and non-hydrogenated films were studied along with films prepared by the glow-discharge decomposition of a gaseous mixture of silane and ammonia.

Photoemission experiments were performed on the sputtered samples. The position and strength of the core levels were determined, along with the plasma energies as a function of $x$.

A comprehensive study of the number and types of defects present within a-SiN(:H) was undertaken. Films sputtered at room temperature and at 200°C, both with and without hydrogen, were studied along with films prepared by the glow-discharge technique. The results obtained are discussed in the light of existing models.

Certain characteristic energies obtainable from optical data have been found for hydrogenated and non-hydrogenated films. These results are then related to other experimental results, in particular those from photoemission measurements.

Reflection measurements have been made in the range 0.5eV to 12eV on the sputtered and glow-discharge films. From the reflection measurements $\epsilon_2$ spectra were determined by Kramers-Kronig analysis. The dependence of the optical joint density of states with alloying was found from the $\epsilon_2$ data. It was found from these measurements that the top of the valence band gradually changes from Si3p states to N 2p$_z$ states.
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1.1 Amorphous Solids

The study of amorphous materials is a relatively new branch of solid state physics, much work having been carried out in the last decade. This interest has arisen not solely to gain a fundamental understanding of the amorphous state, but also because of the technological importance of these materials.

The current interest in hydrogenated amorphous silicon stems from the fact that it can be doped. Consequently in the thirteen years since doping was reported by Spear and Le Comber in 1975 there has been a rapid increase in our understanding of a-Si:H.

Among non-crystalline materials are liquid metals and semiconductors, glasses and amorphous films evaporated or deposited in other ways. Unlike the crystalline state, where the atoms are regularly arranged with respect to each other, the amorphous state is characterized by a lack of regularity, having no long-range order. However, there still remains some degree of local order; bond lengths and bond angles are essentially the same as those found in the crystalline counterpart. This is hardly surprising when it is remembered that the same chemical forces and chemical bonds hold both kinds of solid together.

This short-range order is directly responsible for observable semiconductor properties such as optical absorption edges and activated electrical conductivities. Of even more importance, at least in tetrahedrally coordinated materials, is the wide variation in the angle between second-nearest neighbours. This broad distribution of the so-called dihedral angle (see figure 1.1), appears to be the principal origin of the disorder in the atomic potential which in turn leads to tailing of the band edges and localization of the electron states.
Because many of the mathematical techniques used for describing crystals (Brillouin zones, Bloch states, group theory, selection rules, etc.) rely on a periodic structure, it has been necessary to use new approaches such as localization and percolation theory, which do not require any periodicity to describe the non-crystalline state.

Prior to the early 1900s solids were designated amorphous if they had a formless fracture surface (currently termed conchoidal fracture). With the advent of X-rays and their use in determining the structure of crystalline materials, it was found that those materials which were characterised as amorphous were also non-crystalline as evidenced by X-ray diffraction; that is, they do not exhibit the sharp rings associated with crystalline materials but instead exhibit a few broad haloes.

In addition to a structural classification we can also classify materials according to their mechanical (flow) behaviour. A distinctive class of amorphous solids are glasses, which are defined as amorphous solids which exhibit a glass transition.

Figure 1.1. Schematic illustration of the dihedral angle $\phi$ for the eclipsed and staggered bond configurations in a tetrahedrally bonded semiconductor.
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1.2 Glass Transition

The glass transition is the phenomenon whereby a liquid gradually becomes more viscous and shows more or less abrupt change in derivative thermodynamic properties (for example, heat capacity or thermal expansion) from liquid-like to crystal-like values with change of temperature. The definition of the term amorphous given above does not exclude liquids; therefore we must define what we mean by the term solid.

A solid is defined as a material whose sheer viscosity exceeds $10^{14.6}$ poise, while fluids (liquids and gases) have sheer viscosities of less than $10^{14.6}$ poise ($10^{13.6} \text{N s m}^{-2}$). This arbitrary division point corresponds to a relaxation time of one day. That is, a material is considered to be solid if there is negligible permanent change in its shape upon the application of a small force for one day.

Upon cooling a liquid below its melting point it will either crystallise or form a glass. During crystallisation the viscosity, entropy, volume and internal energy change discontinuously and the transformation is first order. In glass formation however, these properties change continuously, although the change may be rapid in the vicinity of the glass transition temperature ($T_g$).

Figure 1.2 depicts the temperature dependence of the volume of a material which may either crystallise or form a glass. The thermal expansion and heat capacity of the glass are generally observed to be close to that of the crystal. When the temperature is less than $T_m$ the liquid may become supercooled rather than crystallise. It will then gradually become more viscous with decreasing temperature. An abrupt change in volume at $T_m$ is observed for the crystallisation process whereas only a change in the slope is seen when glass formation occurs. The glass transition temperature $T_g$ is defined as the region over which the change of slope occurs. (Similar behaviour would also be exhibited by other extensive thermodynamic variables, entropy $S$ and enthalpy $H$).
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The glass transition even now is still only poorly understood due to its complexity.

1.3 Preparation of Amorphous Materials

It should be stressed at the outset that bulk properties of disordered materials are more sensitive to preparation techniques than is the case for single crystals, since imperfections such as voids, microcrystallites and phase separations are not easily controlled or characterised. For example, amorphous films are often composed of a disordered network of atoms interspersed with voids. The void content, at least in amorphous Ge or Si, is strongly dependent on preparation procedures and can range from about 15% in poorly prepared samples to near zero.

Figure 1.2. Schematic illustration of the change in volume as a supercooled liquid is cooled through the glass-transition temperature $T_g$. 
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1.3.1 Melt Quenching

One method used in the production of amorphous solids is melt quenching. The molten form of the material is rapidly cooled so as to prevent crystalline nucleation and growth. The solid is formed by the continuous hardening of the melt whereas crystallisation occurs as a discontinuous solidification with growth taking place at the liquid-solid interface. Not all amorphous materials can be prepared by this method.

1.3.2 Thermal Evaporation

This is one of the most frequently used techniques for producing amorphous films. If the source material has a low melting point it can be vapourized by heating in a resistive tungsten or molybdenum boat. Materials with higher melting points are evaporated by bombardment with high energy electrons from an electron gun. To reduce contamination the evaporation is performed in a good vacuum. The vapour condenses onto a cold substrate and thus the atoms are essentially frozen into the random positions at which they arrive.

A major problem with the technique is the variability in purity and composition of the resulting film. Multicomponent alloys are difficult to produce because the evaporation rates of individual components can differ dramatically.

1.3.3 Sputtering

Deposition by sputtering is more complicated than thermal evaporation but it does however offer greater flexibility and control over the deposition conditions. The process involves the bombardment of a polycrystalline target with ions from a low-pressure plasma. Target atoms are knocked from the target into the vacuum where they migrate under the influence of the plasma field to a substrate where they are collected and form the film. The samples used in the work described in this thesis were
prepared by sputtering and therefore a further detailed discussion of the sputtering technique is presented in Chapter Four.

1.3.4 Glow-Discharge Decomposition

This technique, like sputtering, relies on the production of a plasma by the application of a radio frequency (RF) field to a low-pressure gas, so as to produce the plasma. This leads to a chemical decomposition of the gas and the amorphous film grows on substrates placed in the plasma. Alloys can be prepared by admitting the necessary reactant gases into the chamber. The material most often produced by the glow-discharge technique is amorphous silicon (a-Si) using silane (SiH₄) as the reactant gas. For an informative review of the glow-discharge process see Brodsky (1978).

1.4 Amorphous Silicon Nitride

Amorphous silicon-nitrogen alloys have attracted much interest over the last few years due to their wide application in silicon device technology; as passivation layers, gate insulators in thin-film transistors, and as active components in MNOS FETS in which the charge storage property of their trapping states is utilised (see, e.g., Morosanu 1980 and Powell et al 1981; also see Chang 1977 and references therein).

Non-stoichiometric films offer the possibility of studying the development of the density of valence states as the nitrogen content is increased. The presence of hydrogen in samples of a-SiNx prepared by glow-discharge decomposition of SiH₄ and NH₃ may play an important role in the properties of the alloys. For a-Si films (x=0), it is well established that incorporation of hydrogen widens the optical gap and passivates dangling bonds, but its role in a-SiNx alloys has not been clarified to the same extent. For this reason films of silicon nitride with and without hydrogen have been studied.

Certain characteristic energies obtainable from optical measurements
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have been determined so as to help further an understanding of the electronic properties. To complement these, reflectivity measurements up to 12eV have also been carried out on films spanning the whole composition range so that the dependence of the electronic joint density of states with alloying could be found. Results from samples prepared by sputtering were compared with those prepared by the glow-discharge technique (kindly provided by the Dundee group) so as to see how preparation techniques affect the results.

Because of the many applications silicon nitride has in the electronics industry, a knowledge and understanding of the behaviour of the defect density with alloying and preparation conditions is of great value. A detailed study of the defect density by electron spin resonance (ESR) was therefore undertaken to see how nitrogen affects the density of defects present within the energy gap. Films prepared under a variety of conditions were studied in order to try and identify the defect centres and to understand fully any trends observed in the data as the nitrogen content of the films studied was gradually increased.
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THEORETICAL BACKGROUND

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2.1.2 Density of States

2.1.3 Defects

2.2 Optical Properties

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2.3.3 Variable-Range Hopping Conduction
2.1 Effects of Disorder on Electronic Properties

The wavefunction of each electron in a crystalline material is of the Bloch form

\[ \psi(k) = u(x,y,z)e^{ik \cdot r} \]  

where \( u(x,y,z) \) has the periodicity of the lattice and \( k \), the wavevector is a quantum number for the electron. Generally non-crystalline materials do not have wavefunctions of this form. However, the density of states \( N(E) \) is still a valid concept for non-crystalline materials because solutions to the Schrödinger equation with a random potential must still exist.

It is possible to calculate \( N(E) \) and the corresponding wavefunctions by assuming that the free-electron approximation is a good one and that electrons are not strongly scattered by lattice imperfections. In crystalline materials the interaction with the field of the lattice can lead to large deviations from the free-electron approximation; this is because the energy depends on the direction of \( k \) and also because of the formation of band gaps. Small deviations from a perfect lattice such as those due to phonons, impurities or defects lead to a finite mean free path \( L \), but, unless \( L \) is small \((kL-1)\), the changes in the density of states is not large. In non-crystalline materials, however, the disorder can lead to a very short mean free path and to large changes in the density of states. If the scattering by each atom is strong so that \( \Delta k/k-1 \) then \( k \) is no longer a good quantum number. Ioffe and Regel (1960) stated that the mean free path cannot be shorter than \(-1/k\) for strong scattering. For even stronger scattering the wavefunctions associated with a particular energy will become localized.
2.1.1 Localization

A wavefunction is localized if it is confined to a small region of space and falls off exponentially with distance, \( R \), as \( \exp(-\alpha R) \). This was first recognized by Anderson (1958) and is known as Anderson localization. The concept of localized wavefunctions for an electron in a trap below the conduction band was known before Anderson’s paper but what emerged was the possibility of a finite or continuous density of states \( N(E) \) in which all the states are localized; there may however exist a considerable overlap between wavefunctions of neighbouring states. If the Fermi energy \( E_F \) lies in a range of localized states the conductivity at \( E_F \), \( \sigma_{E_F} \), vanishes as the temperature approaches zero. Materials whose states at \( E_F \) are localized have been called ‘Fermi glasses’ (Anderson 1970).

In his paper Anderson (1958) uses a tight-binding approximation and a crystalline array of potential wells producing a narrow band of levels as shown in figure 2.1(a). It is assumed that there is little overlap between the atomic wavefunctions of adjacent wells. The bandwidth \( B \) is given by \( B=2zI \) where \( z \) is the coordination number and \( I \) is the transfer integral

\[
\int \phi^*(r-R_n) H(\phi(r-R_{n+1}) d^3x. \quad 2.2
\]

What happens to this band of energy levels when the potential energy function is no longer periodic? There are two ways in which the potential may not be periodic:

(i) By positional disorder caused either by lattice vibrations or the lack of long-range order as in a liquid.

(ii) The addition of a random potential to each well, Anderson used a random distribution for \( V \) letting it take on values between \( \pm V_o \).

If \( V_o \) is small, the electrons have a large mean free path. For large \( V_o \) the mean free path is reduced. However, from the rule of Ioffe and Regel, a mean free path such that \( kL < 1 \) is impossible.
The Ioffe–Regel rule then means that the shortest possible mean free path occurs when the wavefunction loses phase memory in going from atom to atom so that the wavefunction now has the form

$$\sum_n A_n \phi(r-R_n)$$

where the $A_n$ have random phases and amplitudes as in figure 2.2(a).

Thus there should be random fluctuations of the amplitude and phase of $\psi$ in going from well to well and, as $V_o/B$ increases further, the fluctuations become larger (figure 2.2(b)). However as $V_o/B$ becomes very large the interaction between neighbouring wells lessens and so $\psi$ will fall off exponentially with distance as in figure 2.2(c) and 2.2(d). Anderson found that, at the absolute zero of temperature, if $V_o/B$ is greater than a constant (dependent on coordination number $z$), an electron placed on one of the wells will not have diffused a large distance from the well after a long period of time has elapsed. Thus, if $V_o/B$ is greater than a critical value the wavefunctions are of the type shown in
CHAPTER TWO

Figure 2.2(c) and have the form

\[ \sum_{n} A_n \phi(x-R_n) \exp(-\alpha r) \]

where the coefficients $A_n$ have random phases as before.

\[ 2.4 \]

Any form of random potential, as in figure 2.1(b), will introduce a range of localized states in the band tails. Thus it is possible to have states which are localized in one range of energy and non-localized in another. Therefore an energy must occur at which localized and non-localized states are separated.

Figure 2.3 illustrates this separation between localized and non-localized states for the Anderson potential. Note that there is no
discontinuity in $N(E)$ or in its derivative at $E_C$ (Thouless 1970). As the disorder increases the energies $E_C$ and $E_C'$ move towards each other until at a critical amount of disorder all states in the band are localized.

![Density of States](image)

**Figure 2.3.** Density of states in the Anderson model. Localized states are indicated by the shaded regions and are separated from the extended states by the energies $E_C$ and $E_C'$ (after Mott and Davis 1979).

2.1.2 Density of States

As already pointed out the density of states is still a valid concept for amorphous materials. Like crystals the states lie in bands separated by energy gaps. If the short-range order is similar to that found in the crystalline phase then the gross features of the crystalline density of states are preserved in the amorphous phase.

As in crystals, states in the gap are a consequence of defects and are of great importance in determining the electrical and optical properties of non-crystalline materials. Several band models exist as will now be described.

**CFO Model**

Cohen, Fritzsche and Ovshinsky (1969) thought the band tails of amorphous materials would overlap because of the non-crystalline structure. The existence of mobility edges, critical energies separating
localized from extended states as proposed by Mott, were also a feature of this model. It is therefore sometimes referred to as the Mott-CFO model. The energy difference \( (E_C - E_V) \) between the two mobility edges is known as the mobility gap and contains only localized states. The model is thought to be more applicable to liquids because amorphous semiconductors and insulators which are transparent in the visible or infrared are thought not to have overlapping bands.

![Figure 2.4](image)

**Figure 2.4.** Various forms of the density of states for amorphous semiconductors. (a) the CFO model (see text) with overlapping band tails; (b) density of states for a continuous random network with no defects; (c) as (b) but with a band of defects; (d) the same as (c) but now showing the amphoteric nature of the defects (dangling bonds). (Note: localized states are indicated by the shaded regions) (after Mott and Davis 1979).

**Davis-Mott Model**

The band model shown in figure 2.4(c) was proposed by Davis and Mott (1970). Like the Mott-CFO model, the mobility edges lie at \( E_C \) and \( E_V \). A distinction however is made between localized states which originate from
the lack of long-range order and others which are due to defects in the structure. The number of such defect states at $E_f$ is greatly dependent on the preparation conditions. The model accounted for optical transparency if it was assumed that the density of such deep states was small.

Mott (1972) suggested that if the states at $E_f$ were from dangling bonds they could be amphoteric in nature. Such singly and doubly occupied bonds would give rise to two bands separated by a correlation energy $U$ (see figure 2.4(d)) with $E_f$ pinned between them.

2.1.3 Defects

Unlike the localized states forming the band tails, which are a consequence of the short-range order, states deeper in the gap arise from point defects. The density of these states depends greatly on the preparation conditions and post-deposition treatments. The principal point defect in amorphous silicon is the 'dangling bond', an undercoordinated silicon atom.

![Figure 2.5](image)

Figure 2.5. Shematic representation of possible defects in a tetrahedral network.

Figure 2.5 shows Ge (or Si) dangling bonds in various configurations in a continuous random network (CRN).

The presence of point defects in amorphous materials may seem rather surprising because any strain in the network, which may give rise to the
possibility of point defects, can be reduced by a rearrangement of the lattice. However overconstrained networks with an average coordination greater than 2.4 prefer to relieve strain by dangling-bond formation as shown by Phillips (1979).

![Defect configurations in a-Si:H](image)

Figure 2.6. Defect configurations in a-Si:H (after Robertson 1985)

The formation of silicon dangling bonds from sp hybridized orbitals is illustrated in figure 2.6. The energy difference between the \( \text{Si}_1^+ \) and \( \text{Si}_1^- \) configuration is the correlation energy \( U \) and is a measure of the energy required to place two electrons on the same site.

As the silicon dangling bonds normally contain one electron it is possible to detect them using electron spin resonance (ESR).

It was found that a-Si contains a large number of dangling bonds, but, by incorporating hydrogen into a-Si during deposition, the density of gap states is reduced markedly. The hydrogen therefore terminates any silicon dangling bonds by forming strong Si-H bonds. States associated with these lie towards the top of the valence band and hence introduction of hydrogen can be considered as removing states from the gap. This feature is an important one which permits doping of the material.
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2.2 Optical Properties

The first part of this section on optical properties deals with a general derivation of the optical constants of matter. This is followed by a discussion of the Lorentz model of optical absorption. This will be useful because the Lorentz description will be of use at a later stage; see chapter 7. To conclude the section, some general results illustrating the optical properties of amorphous semiconductors are mentioned.

2.2.1 Derivation of Optical Constants

From Maxwells equations it is possible to derive a wave equation for a plane wave propagating in an energy-absorbing medium

\[ \nabla^2 E = \frac{\varepsilon \mu}{c^2} \frac{\partial^2 E}{\partial t^2} + \frac{4\pi\sigma}{c^2} \frac{\partial E}{\partial t}. \]

2.5

The conductivity which appears in Eqn (2.5) is called the optical conductivity and approaches the ordinary dc electrical conductivity for isotropic materials. For anisotropic materials the optical conductivity and dielectric functions must be treated as tensors as the induced current and polarization generally lie in a direction different from that of the electrical field. A transverse electric field can induce a longitudinal current. Consider the propagation of a single plane wave within an isotropic medium

\[ E = E_0 \exp(i\mathbf{q}.r - \omega t) \]

2.6

where \( \mathbf{q} \) the wavevector is assumed to be complex and perpendicular to \( E_0 \).

Note that we assume a sinusoidal (plane wave) variation of \( E \) which is large compared with the lattice constant. Substituting Eqn. (2.6) into Eqn. (2.5) we find

\[ \mathbf{q}^2 = \mu \frac{\omega^2}{c^2} \left( \frac{\varepsilon_L}{\omega} + \frac{i\pi}{\omega} \right) = \omega^2 \frac{\varepsilon_L}{c^2}. \]

2.7
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since the complex dielectric function \( \varepsilon_L \) is defined by

\[
\varepsilon_L = \varepsilon_1 + i\varepsilon_2 = \varepsilon_L + i\frac{4\pi \sigma}{\omega} .
\]

2.8a

2.8b

A complex refractive index \( \hat{n} \) may be defined such that

\[
\varepsilon_L = \hat{n}^2
\]

2.9

where \( \hat{n} = n + ik \).

2.10

and \( n \) is the refractive index and \( k \) is the extinction coefficient; then from Eqn. (2.7)

\[
\hat{q} = \frac{\omega}{c} \hat{n} .
\]

2.11

and from Eqns (2.8a), (2.9) & (2.10)

\[
\varepsilon_1 = n^2 - k^2
\]

2.12

\[
\varepsilon_2 = 2nk .
\]

2.13

Thus Eqn (2.6) may be rewritten

\[
E = E_0 \exp\left(-\frac{\omega}{c} kr\right) \exp\left(\frac{\omega}{c} n\cdot r - \omega t\right) .
\]

2.14

The first exponential describes the attenuation of wave amplitude with distance. The second exponential describes a wave travelling with phase velocity \( c/n \).

The absorption coefficient \( \alpha \) which describes the decrease in intensity with distance is defined for one dimension as

\[
\alpha = -\frac{1}{I} \frac{dI}{dr}
\]

2.15

\[
\alpha = \frac{2\omega k}{c} = \frac{4\pi k}{\lambda}
\]

2.16

where \( \lambda \) is the wavelength of light in a vacuum. Thus

\[
\alpha = \frac{4\pi \sigma}{nc} = \frac{\omega \varepsilon_2}{nc} .
\]

2.17
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It is not possible to obtain $\varepsilon_2$ from transmission measurements above the fundamental absorption edge because the absorption is very high (typically $10^6$ cm$^{-1}$).

2.2.2 The Lorentz Oscillator

The optical constants derived above do not provide any indication of their actual values or of their frequency dependence. To do this we need a theory of absorption and dispersion. A simple classical model proposed by Lorentz and further developed by Drude and others may still be usefully applied to a number of problems and acts as a good starting point to the understanding of optical properties. Many features of these classical models have quantum mechanical counterparts. The assumptions of the model are that:

(i) the material contains charged particles bound to equilibrium positions by Hooke's law forces.
(ii) that these forces are isotropic.
(iii) the charged particles experience a damping force proportional to the velocity.

The equation of motion of such a particle of mass $m$ and charge $e$ subject to an oscillating electric field of the form $E_{\text{loc}} = E_0 \exp(-i\omega t)$ is written

$$m \frac{d^2 r}{dt^2} + mr \frac{d}{dt} + mw^2 r = -eE_{\text{loc}},$$  \hspace{1cm} 2.18

in which $\Gamma$ is the damping constant and $\omega_o$ is related to Hooke's constant $K$ by $\omega_o = (k/m)^{1/2}$. It has been assumed that the mass of the nucleus is infinite and the small force arising from the interaction of the electron with the magnetic field of the light wave is zero.

The solution of Eqn (2.18) is

$$\hat{r} = \frac{-eE_{\text{loc}}/m}{(\omega_o^2 - \omega^2) - i\Gamma \omega}$$  \hspace{1cm} 2.19

20
and the induced dipole moment is then
\[ \hat{p} = \frac{-\left(e^2 E_{\text{loc}}/m\right)}{(\omega^2 - \omega^2) - i\Gamma\omega} \quad 2.20 \]

Assuming the displacement \( r \) is small so that a linear relation exists between \( \hat{p} \) and \( E_{\text{loc}} \), i.e.
\[ \hat{p} = \alpha(\omega) E_{\text{loc}} \quad 2.21 \]

then
\[ \alpha = \frac{\left(e^2 / m\right)}{(\omega^2 - \omega^2) - i\Gamma\omega} \quad 2.22 \]

The macroscopic polarization for \( N \) atoms per unit volume is
\[ P = N\langle p \rangle = N\hat{\alpha}\langle E_{\text{loc}} \rangle \quad 2.23 \]

Writing
\[ \hat{\varepsilon} = 1 + 4\pi N\hat{\alpha} \quad 2.24 \]

and using Eqn (2.22) in Eqn (2.24) gives
\[ \hat{\varepsilon} = 1 + \frac{4\pi Ne^2}{m} \frac{1}{(\omega^2 - \omega^2) - i\Gamma\omega} \quad 2.25 \]

Extending this result to include atoms with more than one electron per atom yields
\[ \hat{\varepsilon} = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 - i\Gamma_j\omega} \quad 2.26 \]

where \( N \) is the number of electrons bound with resonance frequency \( \omega_j \) and \( \sum_j N_j = N \).
CHAPTER TWO

From the definitions of $\varepsilon_1$ and $\varepsilon_2$ it can be seen that

$$
\varepsilon_1 = \text{Re}(\tilde{\varepsilon}) = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 - i\Gamma_j \omega} \quad 2.27
$$

$$
\varepsilon_2 = \text{Im}(\tilde{\varepsilon}) = \frac{4\pi e^2}{m} \sum_j \frac{N_j \omega}{\omega_j^2 - \omega^2 - i\Gamma_j \omega} \quad 2.28
$$

Equating the derivative of eqn 2.28 to zero we find that $\varepsilon_2$ is a maximum when

$$
\varepsilon_2(\text{max}) = \frac{4\pi e^2}{m \Gamma \omega_0}. \quad 2.29
$$

It is possible to derive a similar expression using first-order perturbation theory (Wooten 1972; Harrison 1970)

$$
\tilde{\varepsilon} = 1 + \frac{4\pi e^2}{m} \sum \frac{f_{mo}}{\omega_{mo} - \omega^2 - i\Gamma \omega} \quad 2.30
$$

where $f_{mo}$ is defined as the oscillator strength and is a measure of the relative probability of a quantum mechanical transition.

Figure 2.7 shows the various regimes that are predicted by the Lorentz oscillator model.

For region (I) $\omega < \omega_0$, $\varepsilon_2 = 2nk > 0$ and $\varepsilon_1 = n^2 - k^2 > 1$ thus $k = 0$ and $n > 1$. Materials therefore will show a high transparency in this region with no absorption and a small reflectivity for insulators.

Region (II) is characterized by strong absorption; however, because $n$ and $k$ are high, a significant amount of reflectivity may still occur.

The electrons in region (III) may be considered as being free, because the photon energy is now much greater than the binding energy of the electron.

Region (IV) is characterized by $\varepsilon_1 = 0$ and the frequency at which this occurs is called the plasma frequency $\omega_p$. 

22
If it is assumed that the conduction electrons are no longer bound so that there is no restoring force acting on them, i.e. $\omega_0 \rightarrow 0$, the Drude model for metals is obtained. And as the electrons are not bound, local-field corrections are not necessary.

Using Eqns (2.27) & (2.28) with $\omega_0 = 0$ and replacing $\Gamma$ with $\tau^{-1}$ yields

$$\varepsilon_1 = 1 - \frac{\omega^2 \frac{\tau^2}{D}}{1 + \omega^2 \tau^2}$$ \hspace{1cm} 2.31

$$\varepsilon_2 = 1 - \frac{\omega^2 \frac{\tau^2}{D}}{\omega(1 + \omega^2 \tau^2)}$$ \hspace{1cm} 2.32

where $\tau$ is the mean carrier scattering lifetime (and also the relaxation time).
2.2.3 The Fundamental Absorption Edge

The selection rules which give rise to sharp features in the optical spectra of crystalline solids are no longer valid for disordered materials. Therefore amorphous materials do not possess the same sharp features seen in crystals, but exhibit broader features which mirror the overall crystalline spectra.

Figure 2.8 shows the absorption edge of glow-discharge a-Si:H deposited at $T_D=240^\circ$C. The absorption constant was obtained by a number of techniques; as can be seen, the agreement between the different methods is good.

![Graph of absorption edge](image)

Figure 2.8. Fundamental absorption edge of glow-discharge a-Si:H$_{0.16}$ prepared at $T_D = 240^\circ$C (Cody et al 1980 and Abeles et al 1980). Also shown are the absorption edges of evaporated hydrogen-free a-Si (Pierce and Spicer 1972) and of c-Si (Hulthen 1975) (as reported by Ley 1983).

Three regimes may be distinguished:

(A) A power-law regime ($\alpha>10^3\text{cm}^{-1}$) where $\alpha=(E-E_g)^F$.

(B) The so-called Urbach edge (Urbach 1953) where the absorption
coefficient depends exponentially on $\tau_0$.

(C) An absorption tail below 1.4eV ascribed to optical excitations from defect states deep in the gap. Absorption in this region is dependent on the sample preparation conditions (Connell 1979).

Figure 2.9 shows typical absorption spectra obtained from several types of amorphous semiconductors.

![Figure 2.9. Optical absorption edges for a number of amorphous semiconductors showing the Urbach region (after Mott and Davis 1979).](image)

2.2.2 Fundamental Vibrational Spectra

Infra-red spectroscopy provides a means of estimating the hydrogen content in a sample and can also determine the local bonding configuration of the hydrogen (Lucovsky 1979). An estimate for the overall hydrogen
content of a film (Brodsky et al 1977) is given by

\[ N = \frac{c n \omega_o \mu_o}{2 \pi^2 \varepsilon_s^2} \int \frac{\alpha(\omega)}{\omega} \, d\omega \]  

2.33

where \( c \) is the speed of light, \( n \) the refractive index, \( \omega_o \) is the frequency of the absorption band, \( \varepsilon_s^* \) the effective charge for Si-H in a Si-H matrix and \( \mu_o \) the reduced mass. Thus the concentration of hydrogen in a particular configuration can be estimated from its integrated absorption intensity \( \int (\alpha(\omega)/\omega) \, d\omega \).

<table>
<thead>
<tr>
<th>SiH</th>
<th>2000</th>
<th>630</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stretch</td>
<td>Bend (rock or wag)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiH₂</th>
<th>2090</th>
<th>890</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetric stretch</td>
<td>Scissors bend</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiH₃</th>
<th>2140</th>
<th>862</th>
<th>907</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetric Degenerate stretch</td>
<td>Symmetric Degenerate deformation</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 2.10. Local Si₃H vibrations for SiH, SiH₂, and SiH₃ groups (after Lucovsky et al 1979).](image-url)
CHAPTER TWO

Because the mass of hydrogen is much smaller than that of silicon the vibrational modes of the Si-H bonds can be regarded as arising solely from the vibration of the hydrogen atom; these are attached tetrahedrally to silicon and can occur in >Si-H, >Si-H$_2$ or -Si-H$_3$ configurations. The local vibrations for these groups are shown in figure 2.10.

As can be seen in figure 2.11 it is possible to detect small traces (~1ppm) of impurities, such as oxygen or hydrogen, in samples using infra-red spectroscopy. It therefore provides a quick and useful means for checking the sample purity.

![Figure 2.11. Infrared spectra of a-Si:H showing: (1) an oxygen-free film and (2) an oxygen-contaminated film, O/Si=0.15 (from Tardy and Meaudre 1983).](image)

2.3 D.C. Electrical Conductivity

At a finite temperature the total current can be written as

$$\sigma = -\int \sigma_E \frac{\partial f(E)}{\partial E} \, dE$$  \hspace{1cm} (2.34)

where $f(E)$ is the Fermi Dirac function and

$$\frac{\partial f(E)}{\partial E} = -f(E) \left( \frac{1-f(E)}{k_B T} \right)$$  \hspace{1cm} (2.35)
Conduction normally proceeds via extended states; however at lower temperatures contributions from localized state may become increasingly important especially if a large number of localized gap states exist. Conduction via localized states can occur only by phonon-assisted hopping.

### 2.3.1 Extended-State Conduction

An electron that has been excited to an extended state above the conduction-band mobility edge $E_c$ contributes to the conductivity in a way similar to that of a conduction electron in a metal. Eqn 2.34 can be written

$$
\sigma = e \int N(E)\mu(E)f(E)\left[1-f(E)\right]dE
$$

where $\mu(E)$ and $N(E)$ are the mobility and density of states at an energy $E$. An electron's motion within the extended states will be impeded by scattering and also by trapping and release events as shown in figure 2.12.

---

**Figure 2.12.** Schematic energy level diagram for the various conduction mechanisms in amorphous semiconductors (after Zallen 1983).
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If it is assumed that sharp mobility edges exist at $E_v$ and $E_c$ and that conduction takes place far enough away from $E_F$ so that

$$f(E)[1-f(E)] = \exp\left[-\frac{(E-E_F)}{k_B T}\right].$$  \hspace{1cm} 2.37

Eqn 2.36 may be integrated to give:

$$\sigma_{(ext)} = \sigma_{(ext)} \exp\left[-\frac{(E_c(T)-E_v(T))}{k_B T}\right].$$  \hspace{1cm} 2.38

where $\mu$ has been taken as zero in the mobility gap and to be some average value $\mu_e$ in the band. Eqn 2.38 may also be written as

$$\sigma_{(ext)} = \sigma_{(min)} \exp\left[-\frac{(E_c(T)-E_v(T))}{k_B T}\right].$$  \hspace{1cm} 2.39

Thus it would seem from equations 2.38 and 2.39 that extended state conduction is activated. It should be noted however, that the activation energy determined from experiment does not correspond to $(E_c-E_F)$ because the band gap (or mobility gap) is also a function of temperature and varies as

$$E_c(T)-E_v(T) = (E_c(E_F))_{T=0} - \gamma T$$  \hspace{1cm} 2.40

such that

$$\sigma_{(ext)} = \sigma_{(min)} \exp\left[-\frac{(E_c(E_F))_{T=0}}{k_B T}\right] \exp\left[-\frac{\gamma}{k}\right].$$  \hspace{1cm} 2.41

At lower temperatures ($< 77K$) the gap becomes gradually more temperature insensitive.

The pre-exponential is then

$$\sigma_o = eN(E_o)k_B \nu_e \exp\left[\frac{\gamma}{k}\right]$$  \hspace{1cm} 2.42

where, because $\mu_e \propto (1/T)$, $\sigma_o$ is temperature independent.
CHAPTER TWO

2.3.2 Thermally-Assisted Tunnelling Conduction

Thermally assisted tunnelling is sometimes observed in the localized gap states near the mobility edges $E_A$ and $E_B$ in figure 2.4 or in the donor or acceptor bands. It is found in a narrow temperature range in which $T$ is low enough to quench band conduction and permit the tunnelling mechanism to show up in the conductivity. The largest tunnelling contribution arises from jumps to unoccupied levels of nearest neighbours. Since it is unlikely to find such a level at the same energy the tunnelling process involves the emission or absorption of a phonon. Hence the thermally assisted tunnelling process involves a hopping energy $\Delta W_1$ in addition to the activation energy $(E-E_f)$ needed to raise the electron to the appropriate localized state at $E$. The conductivity will thus be of the form

$$\sigma = \sigma_1 \exp\left[-\frac{(E-E_f+\Delta W_1)}{k_B T}\right].$$  

2.43

For the Davis Mott Model $E = E_A$ and $\mu(E)$ drops sharply below $E_c$ so that $\sigma_1 \approx \sigma_0$.

2.3.3 Variable-Range Hopping Conduction

Two hopping transitions are schematically indicated by A and B in figure 2.12, where an electron tunnels from a filled state below $E_f$ to a nearly empty state above $E_f$. $R$ denotes the distance the electron hops while $W$ is the energy separation between the two states.

Tunnelling conduction near $E_f$ should be of the form

$$\sigma = \sigma_2 \exp\left[-\frac{\Delta W_2}{k_B T}\right].$$  

2.44

where $\Delta W_2$ has the same physical meaning as $\Delta W_1$. Since the density of states near $E_f$ and the range of their wavefunctions is probably smaller than near $E_A$ or $E_B$, one expects $\sigma_2 < \sigma_1$. As the temperature is lowered
the energy barrier \( W \) becomes increasingly more difficult to surmount, so that the probability for transition \( A \), figure 2.12, becomes less than that for transition \( B \), i.e. it becomes more favourable for centres which are not nearest neighbours but which instead lie energetically closer and within the range \( k_B T \). For this so called variable-range hopping process Mott (1972) derived the relation

\[
\sigma = \text{const} \exp \left[ - \left( \frac{T_T}{T} \right)^{\frac{1}{4}} \right].
\]

Ambegaokar et al (1971) find for \( T_s \)

\[
T_s = \frac{16\alpha^2}{k_B N(E_F)}
\]

where \( \alpha \), the coefficient of exponential decay of the localized state wavefunctions, was assumed to be independent of energy \( E \).

Figure 2.13 shows the various conduction mechanisms discussed in the text, and the region for which each mechanism dominates the conductivity.

![Figure 2.13](image)

**Figure 2.13.** (a)Schematic illustration showing how the dominant conduction mechanism changes with temperature, and (b) the temperature dependence of the conductivity along with the associated activation energies for the various regimes (after Mott and Davis 1979).
CHAPTER THREE

AMORPHOUS SILICON NITRIDE: A SHORT REVIEW

3.1 Introduction

3.2 Structure

3.3 Electronic Structure

3.3.1 Density of States

3.3.2 Evolution of the Valence Band with increasing Nitrogen Content

3.3.3 Defects

3.4 Doping

3.5 Optical Absorption

3.6 Luminescence
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AMORPHOUS SILICON NITRIDE: A SHORT REVIEW

3.1 Introduction

An extensive literature exists on the properties of silicon nitride. Because of its mechanical hardness, low thermal expansion and chemical reactivity it has found wide usage in the ceramics industry. Most applications involve the use of stoichiometric silicon nitride (Si$_3$N$_4$), a material which is an insulator with a band gap of ~5eV.

Silicon-based amorphous alloys such as a-SiC$_x$:H, a-SiO$_x$:H and a-SiN$_x$:H provide a means of controlling the optical band gap as well as the conductivity by changing the composition ratio x. These alloys have therefore opened up new possibilities in heterojunctions and graded-gap structures.

The first studies on amorphous silicon alloys were carried out by Anderson and Spear (1976), who prepared a-SiN$_x$:H by using a mixture of silane and ammonia and a-SiC$_x$:H films from C$_2$H$_4$. They found that the optical gap of a-SiN$_x$:H decreased from 5 to 2.5eV as the molar ratio of the gases NH$_3$/SiH$_4$ was reduced.

The electrical, optical and mechanical properties of plasma-deposited SiN$_x$ films are dependent upon deposition system parameters such as power, deposition temperature, gas pressure, gas composition and gas flows. Previous studies of film composition have shown that SiN$_x$ films produced at low temperatures are always amorphous but the Si/N ratio is dependent on the deposition conditions (Sinha et al 1978).

The incorporation of nitrogen into the films is strongly dependent on the nitrogen species, the uptake of nitrogen from NH$_3$ being more efficient than that from N$_2$. Use of higher powers in the deposition of the films leads to a small enhancement in the amount of nitrogen incorporated, whereas increasing the total pressure (Zhou et al 1985) or substrate
temperature (Herak et al 1985, Watanabe et al 1984) gives rise to lower nitrogen concentrations.

3.2 Structure

There are two possible hexagonal crystalline phases of Si$_3$N$_4$ as shown in figure 3.1.

![Hexagonal Crystalline Phases of Si$_3$N$_4$](image)

Figure 3.1. Illustration of the two forms of c-Si$_3$N$_4$ (α-Si$_3$N$_4$ and β-Si$_3$N$_4$).

Aiyama et al (1979) and Misawa et al (1979) have investigated the structural properties of amorphous stoichiometric Si$_3$N$_4$ and have established by using X-ray and neutron scattering that the short-range order in a-Si$_3$N$_4$ strongly resembles that of the crystalline phases, in particular that of β-Si$_3$N$_4$. Each silicon is tetrahedrally surrounded by

<table>
<thead>
<tr>
<th>TABLE 3.1. Bond angles and bond distances in various forms of Si$_3$N$_4$ (after Karcher et al (1984)).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length Bond angles (deg) Ref.</td>
</tr>
<tr>
<td>Si-N  N-N  Si-Si  Si-N-Si  N-Si-N</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>CVD a-Si$_3$N$_4$  1.729  2.83  3.01  121  109.8 a</td>
</tr>
<tr>
<td>CVD a-Si$_3$N$_4$  1.75  3.0 b</td>
</tr>
<tr>
<td>β-Si$_3$N$_4$  1.73-1.745  ~3.0  3.01  122-115 c</td>
</tr>
</tbody>
</table>

a Misawa et al 1979
b Aiyama et al 1979
c Wild et al 1972
four nitrogen atoms and each nitrogen occupies a planar triply coordinated site with silicon as its neighbour.

Films prepared by chemical vapour deposition (CVD) tend to be nearest to stoichiometry (Bailey and Kapoor 1982) whilst plasma-deposited films can either be silicon rich or nitrogen rich (Maeda and Arita 1982).

There is a high degree of chemical ordering in a-Si$_x$N$_y$ and a-Si$_x$N$_y$:H alloys but it is not absolutely perfect. With increasing $x$, Si-Si bonds are gradually replaced by Si-N bonds. Compositions above $x=1.33$ are possible through the formation of N-N and N-H bonds, although the former seems less likely.

There are three ways that nitrogen may be incorporated into the silicon network:

(i) Substitution of silicon atoms by nitrogen in the tetrahedrally bonded matrix thereby giving rise to n-type doping. A number of publications have reported doping (Smith and Milner 1983, Baixeras et al 1978, Xu et al 1981 and Bauer and Bilger 1982).

(ii) Random incorporation of nitrogen atoms with three-fold coordination into the silicon lattice as seen by Karcher et. al. (1984) and Bauer et. al. (1985).

(iii) Chemically ordered nitrogen incorporation in the form of Si$_3$N$_4$ clusters (for example see Della Sala et. al. (1985)).

3.3.1 Density of States

By using a tight-binding recursion method, Robertson and Powell (1985) calculated the local density of states (DOS) for Si$_3$N$_4$. Their results are shown in figure 3.2.

Robertson and Powell found that the Si-Si bonding state ($\sigma$) lies 0.1 eV above the valence band and the corresponding antibonding state($\sigma^*$) lies in the conduction band. The =N centres are also found not to produce any gap states. The results of Karcher, Ley and Johnson (1984) confirm the
results of Robertson and Powell apart from the fact that they find the top of the valence band is comprised of Np\(_\pi\) states rather than Si-Si antibonding states which are found in the gap as localized states.

Figure 3.2. The local density of states for a-Si\(_3N_4\) as calculated by Robertson et al (1985).

From the photoemission results of Karcher et al. (1984) and the calculations of Robertson the valence-band density of states of SiN\(_x=1.5\) is found to consist of a 12eV wide upper portion derived from Si3s, Si3p and N2p states. Separated from these is a peak solely from N2s electrons.

Figure 3.3. Partial densities of states of \(\beta\)-Si\(_3N_4\) as calculated by Robertson (1984)
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Figure 3.4 compares Robertson’s calculations for the partial density of states shown in figure 3.3 after correcting for the various photoemission cross-sections and the collection geometry, with the photoemission results of Karcher et al (1984).

There is a good agreement between the results implying therefore that the partial densities of states are correct. Karcher et al make the following assignments for the derived DOS: peak A is the N2p\(_n\) lone-pair band with some contribution from N2p\(_x,y\) states. Peak B comprises states of mainly N2p\(_x,y\) character with some contribution from Si3p states, as does peak C. The nitrogen 2s states are seen to lie 20eV below E\(_f\).

The N2p\(_n\) lone-pair band at the top of the valence band is not as well separated from the remainder of the valence band as in SiO\(_2\) because of the smaller polarity of the SiN bond (Fischer et al 1977). This agreement between the DOS for amorphous Si\(_3\)N\(_4\) and crystalline βSi\(_3\)N\(_4\) demonstrates how small deviations from stoichiometry have little effect on the DOS and
CHAPTER THREE

how the DOS primarily depends on the short-range order.

By adding the gap, the variation in the conduction-band edge (determined from optical measurements) was found relative to the valence band energy; a similar composition dependence in the conduction band was obtained from inverse photoemission measurements (Karcher et al 1984(b)). The position of the conduction band minimum derived from Si-Si $\sigma^*$ states is unaffected by the incorporation of nitrogen when $x \leq 1.0$. Above this the top of the conduction band changes from Si-Si $\sigma^*$ states to Si-N antibonding states, whereas Robertson and Powell find that Si-Si $\sigma^*$ states form the top of the conduction band throughout the entire range.

3.3.2 Evolution of the Valence Band with increasing Nitrogen Content

The 4eV wide peak at the top of the a-Si valence band is due mainly to Si3p states; Si3s states are observed between $E_f-5eV$ and $E_f-15eV$. The characteristic A-B-C structure is seen immediately nitrogen is introduced into the films, thus showing that, from the outset, nitrogen enters the films in the threefold planar configuration.

When $x \leq 0.9$, the top of the valence band is due to Si-Si 3p bonding states and above $x \sim 1.1$ the nitrogen lone-pair states form the top of the valence band with Si-Si $\sigma$ states corresponding to localized defects lying in the gap just above the top of the valence band. When the films contain hydrogen the transition of the top of the valence band from Si-Si $\sigma$ states to nitrogen lone-pair states occurs at $x = 0.9$ instead of $x = 1.1$.

Karcher et al found that the Si-H and N-H bonding states are 6.3 and 9.8eV below the valence band maximum respectively in stoichiometric silicon nitride. This is supported by the electron energy-loss measurements of Hezel and Leiske (1981) who found that Si-H bonds gave a peak at 8.5eV.
3.3.3 Defects

Defects are introduced into tetrahedrally bonded films (normally silicon based) because of the strain introduced by the constraints in the bond lengths and bond angles. The local strain is relieved by the creation of dangling bonds (undercoordinated atoms) which are usually neutral and have an unpaired spin i.e. positive $U$ defects. However, Kirk (1979) suggested that $\text{Si}_4\text{N}_4$ could have gap states with a negative correlation energy as in other lone-pair semiconductors because of their ability to overcoordinate like the defects in chalcogenide glasses (Kastner et al (1976)). He also proposed that nitrogen dangling bonds were responsible for the charge trapping in MNOS devices.

Robertson on the other hand has argued that overcoordination does not occur at the nitrogen site because of the nitrogen’s small size so that $N_4^+$ centres (as proposed by Kirk) are not present and $U_{\text{eff}}$ is positive. Another model for charge trapping in MNOS devices is due to Kapoor et al (1983) who thought that the memory trap was the Si-H bond because of the correlation between trap density and hydrogen content. However, the calculations of Robertson and Powell (1984) and the photoemission data of Karcher et al (1984) show that this level lies deep within the valence band and is not amphoteric. The write and erase operations involve the charging and discharging of trap states in $\text{Si}_3\text{N}_4$ (Arnett and Yun 1975) and therefore the state involved must be amphoteric in nature.

Robertson and Powell (1984) suggest that the long-term memory traps in MNOS devices are the silicon dangling bonds because of their amphoteric behaviour.
3.4 Nitrogen Doping

Nitrogen might be expected to act as a substitutional dopant (as do other group five elements) when small amounts are added to silicon. It is generally believed though that nitrogen does not act as an efficient dopant. However, doping has been reported in bulk a-Si:H by a number of authors (see for example Smith and Milner 1983, Baixeras et al 1978 and Dunnett et. al. 1986). Robertson and Powell (1984) noted that because of the small bond length, nitrogen atoms cannot be surrounded by four silicon atoms in a matrix. They do however suggest that doping could occur from nitrogen sites surrounded by three or possibly two hydrogen neighbours (Robertson and Powell 1985). Such donor sites are predicted to be shallow (Robertson 1985).

Noguchi et al (1982) have tried to explain the behaviour in the conductivity as the nitrogen is increased in terms of changes in the network structure of a-SiN\textsubscript{x}:H. They define four regimes:

(i) Substitutional doping by nitrogen atoms in the tetrahedral network which leads to an increase in the conductivity.

(ii) An increase in the number of silicon dangling bonds due to SiN bond breaking as a result of the three-fold coordination of nitrogen and its small size. Because of this bond breaking there is an increase in the number of midgap states which leads to trapping of the donor electrons thereby lowering the conductivity.

(iii) A decrease in the number of silicon dangling bonds due to an increase in hydrogen concentration and to the relaxation of the rigid tetrahedral network which leads to a rise in the conductivity.

(iv) The onset of insulating behaviour as seen by a decrease in the conductivity.
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Figure 3.5. Results of Watanabe et al (1983) showing the dark D.C. room temperature conductivity as a function of the gas molar ratio \( N_2 \) to \( \text{SiH}_4 \). The four regimes in the conductivity, as discussed in the text, can clearly be seen.

The results of Watanabe (figure 3.5) illustrates the various regions described; however behaviour of this sort is not typical of amorphous Si\( N_x \cdot H \) as is shown by the results of Dunnett et al (1986), Ibaraki and Fritsche (1984) and Kurata et al (1981) (figure 3.6).

Figure 3.6. Results of Dunnett et al (1986) showing the dark D.C. room temperature conductivity as a function of the gas molar ratio \( \text{NH}_3 \) to \( \text{SiH}_4 \). Also shown are the results of Ibaraki and Fritzsche (1984)(denoted by I-F) and Kurata et al (1981)( denoted by K).
3.5 Optical Absorption

The dependence of the optical gap and absorption edge with nitrogen content has already been extensively reported. The optical absorption edge is found to broaden with increasing x. It is generally agreed that there is an observed monotonic increase in the optical gap with nitrogen content x which is relatively independent of composition for x ≤ 1.0, but as stoichiometry is approached the gap opens up much more rapidly. For x < 1.0 the increase in the optical gap is due to a gradual recession of the valence band. The rapid increase in the gap for compositions greater than this is possibly due to the top of the conduction band changing from Si-Si σ* to Si-N anti-bonding states.

As pointed out by Searle et al (1987), small errors in determining the composition can lead to considerable scatter in plots of the optical gap versus composition, as is shown by Stutzel (1987) who compares the data reported by a number of authors, see figure 3.7.

Figure 3.7. Variation in the optical gap with nitrogen contents determined by various authors as reported by Stotzel (1987).
3.6 Luminescence

Austin et al (1986) have carried out a comprehensive study of the luminescence from a-SiN: alloys. They found that alloying with nitrogen broadens and shifts the main 1.3eV emission band seen in a-Si:H to higher energies as shown in figure 3.8, this is because the band gap of the material increases when nitrogen is introduced.

![Diagram of luminescence](image)

Figure 3.8. Variation in the photoluminescence peak energy $E_L$ with nitrogen content. Also shown is the peak width $\Delta E_L$ and the optical gaps $E_T$ and $E_{04}$ for comparison (after Austin et al 1986).

A small decrease in the luminescence efficiency occurs for low nitrogen concentrations (10% of the a-Si:H efficiency); at higher nitrogen concentrations the efficiency is found to be independent of $x$. This is in contrast to the rapid fall in efficiency observed when phosphorus or boron is introduced into a-Si:H as dopants, thus implying that nitrogen introduces fewer dangling bonds.

A blue shift in the main 1.3eV peak position with temperature is observed for a-SiN$_x$:H films, whereas a red shift is normally seen for a-Si:H, see figure 3.9. From this temperature dependence of the 1.3eV peak position and also from excitation spectra Searle et al (1987)
conclude that a composition variation in the gap exists, and thermal redistribution of trapped carriers gives rise to the blue shift as shown in figure 3.10.

Figure 3.9. Luminescence results of Austin et al (1986) showing the temperature dependent shift in the main emission band $E_L$ for a-Si$_x$N$_{1-x}$H films, (dashed lines show results obtained by using above band gap excitation, whereas solid lines indicate the use of below gap excitation).

Figure 3.10. Long range band fluctuation model of Searle et al (1987) used to describe the observed temperature dependent blue shift in the luminescence data.
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EXPERIMENTAL DETAILS

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4.1.1 Radio Frequency (RF) Sputtering

4.1.2 Sputtering Techniques

4.1.3 Sputtering System and Preparation Conditions

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4.1.5 Substrates

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4.2.1 Direct Mechanical Method

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4.2.3 Analysis using the Magnitude of Interference Fringes

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EXPERIMENTAL DETAILS

4.4  Electron Spin Resonance

4.5  Electrical Transport Measurements
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EXPERIMENTAL DETAILS

4.1 Sample Preparation Techniques

There are three main methods of producing a-Si; sputtering, evaporation and the glow-discharge technique.

Sputtering is not as extensively used to produce amorphous silicon as is the glow-discharge decomposition of silane. This is partly due to the fact that films deposited by sputtering tend to have electrical properties inferior to those produced by the glow-discharge technique. However, the advantage of sputtering over the glow-discharge technique is the possibility of uncoupling the two source materials silicon and hydrogen and independently optimising the role that each plays in determining the electrical and optical properties of the film. This control over the source materials is not possible for glow-discharge films because the silicon and hydrogen are chemically bonded in the starting material silane.

4.1.1 Radio Frequency (RF) Sputtering

Deposition by sputtering consists of removing material from a polycrystalline target and depositing the material on to a substrate where it forms an amorphous film. The atoms at the surface of the target are bombarded by fast-moving ions, normally argon; these surface atoms may then be knocked from the target into the plasma. They subsequently travel away from the target to condense on other surfaces some distance away from the target. A plasma is used to provide a source of bombarding ions. When the target is negatively biased, ions from the plasma are accelerated towards the target.

If an ac voltage is applied to the target then an electron current will flow towards the target during the positive half-cycle. Similarly,
an ion current flows towards the target during the negative half-cycle. At frequencies up to about 50kHz the two currents are equal. However, at higher frequencies, (radio frequencies RF), the ion current is smaller than the electron current. Owing to the difference in mobility between the electrons and ions and also because of the target capacitance, a negative bias builds up on the target surface. The potential on the target surface can then be described as an RF potential with a superimposed negative dc bias. It is this negative dc bias potential which attracts ions from the plasma towards the target, causing the bombardment of the target.

![Figure 4.1. Schematic diagram of an RF sputtering electrode arrangement and potential distribution](image)

The luminous region of the plasma consists of a sea of randomly moving ions and electrons. Ions that enter the target sheath are accelerated towards the target (essentially by the bias potential $V_B$) and bombard the target with an energy of the order $V_B$ electron volts, see figure 4.2 process 1. Several processes may occur following the ion impact (see Keller and Simmons 1979). The ions penetrate into the target and are brought to rest by colliding with the residual target atoms. Some of the
atoms situated at the surface may be emitted from the surface (process 2, figure 4.2) and travel through the plasma to the substrates; however, some backscattering occurs with the gas atoms (process 3 in figure 4.2). When the target material reaches the substrates, re-emission of the target material from the growing film may occur due to bombardment from ions accelerated towards the substrates by the substrate sheath (process 4 figure 4.2).

Figure 4.2 Physical processes involved in sputtering

By applying a d.c. bias to the substrate electrode the rate of emission of target material from the substrates can be controlled to some degree. This application of a bias to the the substrate electrode, known as bias sputtering, has been investigated by several groups (see for example Tardy and Meaudre 1983).
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If the target material is a conductor then it must be capacitively coupled to the RF voltage. This is achieved by including a capacitor in series with the power supply.

4.1.2 Sputtering Techniques

(i) Sputter deposition. Two methods are commonly used for straightforward RF sputter deposition. Either the substrates are held at ground potential or they are electrically isolated from ground such that they build up a negative self-bias. High quality films are often produced when the substrates are electrically isolated. The techniques are shown in figure 4.3(a).

Figure 4.3. Various sputtering techniques available with the Nordiko sputtering unit.
(ii) Sputter etch. If the RF power is applied to the work table instead of the target it is possible to sputter etch the substrates. This facility can then be used to clean the substrates prior to deposition or to remove small areas of the film necessary for integrated circuit construction (see figure 4.3(b)).

(iii) Bias sputtering. Bias sputtering is achieved by applying RF power to both the target and the substrates using a power splitter as shown in figure 4.3(c). The substrates which are receiving material from the target are also simultaneously sputter etched. Obviously the rate at which material arrives has to be greater than the etch rate; otherwise there would be no net film growth. One advantage that bias sputtering has over conventional sputtering is the ability to remove any gas trapped in the deposited film.

4.1.3 Sputtering System and Preparation Conditions

Sputtering System

A commercially available Nordiko NM-2000-T8-SE1 sputtering system was used to prepare the films and is shown in figure 4.4 and plate I. The stainless steel vacuum chamber, 22" in diameter and 15.8" high, contains a multielectrode turret consisting of a sputtering electrode, an evaporation source and a high-rate magnetron sputtering source. All the films were produced using the conventional 8" diameter sputtering electrode fitted with a 4" diameter polycrystalline Si target.

The substrate electrode was also 8" in diameter and its distance from the target could be adjusted from 1 to 5cm. A target substrate separation of 5cm was chosen. The substrates were held onto an 8" diameter copper platten by a contact mask and the platten was then locked in position on the substrate electrode. A heating element was situated in the substrate electrode and, to increase the thermal contact, thin deformable copper
PLATE I: The Nordiko Sputterer
Figure 4.4. Schematic diagram of the sputtering system.
gaskets were inserted between the platten and heater. The temperature was controlled by a Eurotherm temperature controller and one of two chromel-alumel thermocouples. One thermocouple was located on top of the heater outside the chamber; the other was inside the chamber and located into a hole drilled in the side of the substrate platten. Temperatures of up to ~400°C were attainable with this arrangement.

Various shutters could be moved into position between the target and substrate electrode to enable sputter cleaning of the target surface and substrate etching prior to deposition. A further contact mask could be rotated and locked onto the substrates to allow evaporation of contacts on to the films for electrical measurements.

The chamber was pumped by a Varian VHS-250mm oil diffusion pump fitted with a liquid-nitrogen cold trap and water-cooled baffle to reduce the diffusion of pump oil into the chamber. A Leybold Hereaus D30A direct drive rotary pump was used to back the diffusion pump. Chamber pressures of $2 \times 10^{-7}$ Torr were attainable with this arrangement; pressures below $10^{-7}$ Torr could be reached if the copper Meisner coils, located around the substrate electrode, were filled with liquid nitrogen.

A VSW Vacuum Analyst quadrupole mass spectrometer was used prior to sputtering to examine any residual gases remaining in the chamber after pumping. It was not possible to examine the gases during sputtering because the sputtering pressure is too high for the mass spectrometer to operate, and also because of the inherent screening problems introduced from using R.F. power.

Pumpdown time was minimised by using oxygen-free nitrogen to vent the chamber and also ensuring that the chamber was up at atmospheric pressure for only short periods.

The sputtering gases, zero-grade hydrogen, argon and nitrogen were admitted into the chamber through piezoelectric valves controlled by a Vacuum General 78-7 flow ratio and pressure control system. The signal
from a Vacuum General CM capacitive manometer monitoring the chamber pressure during sputtering was fed back to the gas control units to maintain the correct pressure and ratio of the gases. As the gas controller could only handle two gases, a gas mixing vessel was built to enable the introduction of a third gas, nitrogen, into the system (see figure 4.5). The gas mixing vessel was evacuated to a pressure of 100mbar by a rotary pump. It was then filled to an over pressure of 1900mbar with equal amounts of nitrogen and argon. The vessel was again evacuated and the whole procedure repeated a number of times. After the final evacuation the vessel would be filled with nitrogen and argon in the required ratio. The gas mixture from the vessel was then fed into one of the gas lines of the gas control unit. There was enough gas in the gas mixing vessel for the production of four films.

Figure 4.5. Gas handling unit showing the gas mixing vessel which enabled the use of three gases.
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Preparation Conditions

Prior to the deposition of a film, the mass spectrometer was used to check the chamber for any contamination. Shown in figure 4.6(a) is a typical trace from the mass spectrometer taken before deposition. From this the main contaminants are seen to be water and nitrogen. Figure 4.6(b) shows a spectrum of the sputtering gases used in depositing a silicon nitride film. Because the sputtering pressure is much greater than the achievable base pressure, no contaminants are seen in this trace.

Figure 4.6. Typical spectra of (a) the residual gases in the vacuum chamber and (b) the sputtering gases.

The gas lines and chamber were flushed through several times with the required gases. The target was then etched for ~30 minutes with 200 Watts R.F. power (~2.47W/cm²) and an argon pressure of ~15mtorr. This was done to remove the SiO₂ layer which will have formed on the target surface.

Following the sputter etch of the target the pressure was reduced to
10 mtorr and hydrogen was introduced if required. Without extinguishing the plasma, the shutter covering the substrates was moved out of the plasma and the film was deposited. A film thickness of the order of one micron required a deposition time of approximately three hours. After deposition the chamber was again pumped down to its base pressure of \(10^{-7}\) mbar.

Two methods of producing multilayers were tried. The first method was simply to feed nitrogen into the chamber along with argon and hydrogen and to deposit a silicon nitride layer. The thickness of the layer was estimated from the known deposition rate of silicon nitride and the deposition time. After deposition of the layer a shutter was moved into the plasma to prevent further depositions and the flow of nitrogen into the chamber was stopped. After a suitable time interval the shutter was moved out of the plasma and the silicon layer was then deposited. The plasma was sustained throughout the whole procedure.

The second method of producing multilayers used a rotating substrate table described later, (see p.57) and two simultaneously powered targets (see figure 4.7). This required the replacement of the high-rate (magnetron) electrode with a conventional RF target electrode and the use of a power splitter (see figure 4.3(c)). Power from the power supply was divided to the two electrodes by the power splitter and a shutter with two adjustable-size apertures was used (see figure 4.7). The apertures were positioned in such a way that they were directly over the two targets and did not allow any cross contamination. The substrates were rotated directly over the two targets by mounting the substrates around the perimeter of the rotating substrate table. Individual layer thicknesses could be varied by altering the speed of rotation or the size of the apertures, or by changing the ratio of the power to the two targets. The targets used were silicon and silicon nitride. Several superlattice structures were grown using this technique. However, owing to lack of
time, this investigation was not pursued to its full conclusion.

4.1.4 Rotating Substrate Table

A rotating substrate table was designed and built to replace the stationary table supplied as standard in the sputtering system. As previously mentioned the purpose of the rotating substrate table was to enable the production of multilayer films and to also improve the thickness uniformity of the standard type films.

In addition completely homogeneous alloys can be deposited from two or more targets with the desired composition being attained by adjusting the rates of deposition from each target. The requirement for making homogeneous alloys is that in each revolution of the substrate less than a monolayer of each component of the alloy is deposited.
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Several reports have been published describing rotating substrate holders used in MBE and sputtering systems to try and improve the uniformity of the layers (Cho and Cheng 1981, Huggins and Gurvitch 1983). As these designs were incompatible with the Nordiko NM-2000-T8-SE1 sputtering system and did not meet all our requirements, another approach had to be taken. The rotating substrate table was designed such that it could be easily interchanged with the original substrate table.

The schematic layout of the rotating substrate holder is shown in figure 4.8. A stepper motor was mounted to the existing top flange of the vacuum vessel. The drive from this was transmitted via an 'O' ring belt to an Ultra High Vacuum (UHV) rotary drive attached to the vacuum vessel top flange with copper-gasket-sealed UHV flanges. This method of achieving rotation inside the vacuum system using a rotary drive was chosen because of the greater reliability gained over the more usual 'O' ring Wilson seal. A coupling shaft connected the rotary drive to the drive chain wheel. This drive wheel was mounted in two stainless steel bearings located in an aluminium block, which in turn was attached to the mounting plate. Two chain wheel tensioners, to allow rotation in either direction, were also fixed on the mounting plate. The tensioners could be released to allow removal of the rotating substrate holder without having to split the chain.

A stainless steel roller chain passed round the drive chain wheel, tensioners and substrate chain wheel. The substrate chain wheel was fixed to an aluminium bearing housing containing a stainless steel bearing. This was held onto the copper platten with a bearing retaining plate. The copper platten was fitted to the standard mounting column using the existing bayonet type fittings and locked in position by two screws so enabling rotation of the bearing housing in either direction. The copper substrate holder was bolted to the bearing housing.

Before final assembly, all the components were cleaned using standard
FIGURE 4.8. SCHEMATIC LAYOUT OF THE ROTATING SUBSTRATE HOLDER AND DRIVE SYSTEM.
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UHV techniques.

Heating of the substrates was achieved using the existing heater element located within the mounting column. Initially two thermocouples were used to monitor the temperature of the table while it was stationary. One thermocouple was placed in good thermal contact with the surface of the substrate holder and the other was located within the mounting column such that it did not interfere with the rotation. The time taken for the substrate holder to reach the required temperature was then noted along with the temperature in the mounting column. This eliminated the need to measure the temperature at the substrate holder, a procedure which would have required a thermocouple to be mounted in contact with the substrate holder during rotation or some external radiation monitor.

4.1.5 Substrates

Various substrates were used, depending on which measurements were to be made on the films.

(i) Optically flat 7059 Corning glass slides: highly resistive barium-alumino silicate, alkali-free glasses were used for the electrical and optical (visible/uv) measurements.

(ii) Crystalline silicon wafers 0.75mm thick were used for the infra-red measurements.

(iii) Freshly cleaved lithium floride was also used a number of times so that transmission electron microscopy could be used to examine the films.

4.2 Determination of Composition and Thickness of the Films

The composition of the glow discharge films and a number of the sputtered films was determined by electron microprobe analysis carried out at Harwell. In addition, Rutherford backscattering (RBS) carried out at the SERC facility at the University of Surrey was also used to find the
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composition of several sputtered films.

Three methods have been used to determine the geometrical thickness $d$ of the films.

4.2.1 Direct Mechanical Method

A Talystep was used to scan across the edges of the film and across any pin-holes appearing in the film. Grooves were also produced in the central region of the film by a sharp tool. Measurement of several groove and edge heights reveals any non-uniformity in film thickness over the track scanned by the Talystep probe. The accuracy of the method is $\pm 0.1 \mu m$.

4.2.2 Tolansky Method

This is an interferometric technique and again requires the presence of a groove or step in the film. In addition the sample surface must be highly reflecting and, for $SiN_x$, this was achieved by coating it with evaporated aluminium. A half-silvered mirror was placed on top of the sample, and the interference fringes produced by light reflected from this and the sample were photographed (see figure 4.9 and plate 4.2). The displacement of the fringes at a step or groove was measured in terms of the wavelength of the light used (mercury $\lambda = 546.1nm$). The accuracy of the technique is $\pm 0.2 \mu m$.

4.2.3 Analysis using the Magnitude of Interference Fringes in Reflection.

This method, proposed by Cisneros et al (1983), provides a means of determining $n$ and $d$ independently. For its application, both the film and the substrate are assumed to be transparent, i.e. non-absorbing. The criterion for this is that the sum of the measured reflectivity $R$ and transmission $T$ of the film plus substrate combination be unity.
Figure 4.9. Diagram showing the experimental arrangement of the Tolansky technique used in determining the thickness of the films.
PLATE II: Fringes Produced by the Tolansky Method
this condition the values of the reflectivity at the extrema (R$_{\text{min}}$ and R$_{\text{max}}$) of the interference fringes are given by

$$R_{\text{even}} = \left(\frac{1-n_1}{1+n_1}\right)^2$$  \hspace{1cm} 4.1
$$R_{\text{odd}} = \left(\frac{n_1-n_2}{n_1+n_2}\right)^2$$ \hspace{1cm} 4.2

where 'even' and 'odd' correspond to the order of the fringes and $n_3$ is the refractive index of the substrate. In these equations, maxima occur for odd-integer orders when (R$_{\text{max}} > R_{\text{substrate}}$) and for even-integer orders when (R$_{\text{min}} < R_{\text{substrate}}$), since (R$_{\text{even}} = R_{\text{substrate}}$). For Corning 7059 glass, $n_3 = 1.53$ and $R_{\text{even}} = 0.044$. From figure 4.9, we see that (R$_{\text{max}}$) and (R$_{\text{min}}$) are both greater than this value; hence (R$_{\text{odd}}$) = (R$_{\text{max}}$) and we can write:

$$R_{\text{max}}^{1/2} = \pm \frac{(n_1-n_2)}{(n_1+n_2)}$$ \hspace{1cm} 4.3

The positive roots of this equation are

$$n' = n_3 \left(\frac{1-R_{\text{max}}^{1/2}}{1+R_{\text{max}}^{1/2}}\right)^{1/2}$$ \hspace{1cm} 4.4

$$n'' = \frac{n_3}{n'}.$$ \hspace{1cm} 4.5

In this work, n' was found to be less than unity and hence could be rejected as a solution. Knowing n' (n'') and using the value of nd determined by the method described in section 4.3.1, d can be calculated.

4.3 Optical Measurements

A Perkin Elmer double-beam 580B spectrophotometer was used for transmission and reflectance measurements in the range 2.5$\mu$m to 50$\mu$m (0.496-0.0248eV). Reflection measurements were made with a Perkin Elmer specular reflectance accessory. To prevent absorption from water and carbon dioxide, a model CD3 air dryer was used to purge the air flowing
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around the sample compartment.

The reflectivity $R$ and transmission $T$ of the films in the range 200 nm to 2500 nm were measured at room temperature using a double-beam Perkin Elmer 330 spectrophotometer. This instrument was well matched to the Perkin Elmer 580B infra-red spectrophotometer. Near-normal incidence reflection measurements were carried out by using two Perkin Elmer reflection attachments, one in the reference beam containing an Al mirror and one in the sample beam of the spectrometer carrying the film under study. To determine absolute values, the reflectivity of the standard mirror must be taken into account. An integrating sphere was used to check the absolute reflectivity of the aluminium standard.

Typical spectra obtained from a-$\text{SiN}_x$:$\text{H}$ ($x=1.34$) is shown in figure 4.10.

4.3.1 Multiple Reflections

If there is little or no absorption of light in a film and the sides of the film are sufficiently parallel for the thickness to vary by only a small fraction of the wavelength of light over the area, then constructive and destructive interference will occur because of the multiple reflections from the film surfaces.

If the path difference between rays $R_1$ and $R_2$ are equal to $m\lambda$ then $R_1$ and $R_2$ will combine constructively, i.e. $2d\cos\theta=m\lambda/n$ where $\lambda/n$ is the wavelength of light in the material of refractive index $n$.

MULTIPLE REFLECTIONS

Thus a series of fringes will be seen in reflection and transmission measurements (see figure 4.10) and from these it is possible to determine the refractive index of the film. Finding $n$ by this method is not
Figure 4.10. Room temperature reflectivity and transmission versus wavelength for a-Si$_{x}$N$_{y}$H (x=1.34) (Davis et al 1987)
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straightforward because m, the order of the fringe, is not known. This is sometimes overcome by measuring the wavelengths at two successive maxima and applying the conditions:

\[ 2n_2 = m\lambda_1 \quad \text{4.6a} \]
\[ 2n_2 = (m+1)\lambda_2 \quad \text{4.6b} \]

On eliminating m, one obtains

\[ 2n_2 = (\lambda_2^{-1} + \lambda_1^{-1})^{-1} \quad \text{4.7} \]

However, this procedure is only correct if n is known to have no linear wavelength dependence. If n varies with \( \lambda \) and is expressed by

\[ n = n' + b\lambda + c\lambda^2 \quad \text{4.8} \]

then, using Eqn. 4.8 for n in Eqns. 4.6a and 4.6b, will lead to an expression similar to Eqn. 4.7 after m has been eliminated:

\[ 2n'd = (\lambda_2^{-1} - \lambda_1^{-1}) \quad \text{4.9} \]

As b has also been eliminated it may take on any value and eqn 4.9 will not give the correct value for n. It may be argued that there is no linear term in \( \lambda \) for the dispersion of n when it is described by a single oscillator but in practice, approximate linear wavelength dependencies may be produced from the combined effect of various contributions.

One way to find the order m is to make a guess at the value and then compute nd. Incorrect values for m lead to an unphysical diverging behaviour in n as a function of increasing wavelength as shown in figure 4.11.
Another method for determining $m$ is to eliminate $nd$ by assuming that in transparent regions $n$ does not vary with wavelength i.e. when no absorptive processes are occurring $nd$ can be assumed constant and so the position of the two consecutive maxima or minima in the reflection or transmission data can be used to find $m$:

$$m\lambda_1 = (m+1)\lambda_2$$

$$m = \frac{\lambda_2}{\lambda_1 - \lambda_2}$$

where $\lambda_2 < \lambda_1$.

Figure 4.11. Dispersion of refractive index with photon energy. Unphysical behaviour is observed when the wrong value for the order of the fringe is chosen, as is the case above when $m=1$ and $3$. 
4.3.2 Refractive Index

The long-wavelength refractive index was determined by a method proposed by Cisneros et al (1983) and is described in 4.2.

Thus knowing d the thickness of the film, m the order and the wavelength \( \lambda_m \) of the corresponding fringe it is possible to determine \( n \) as a function of wavelength.

The dispersion of the refractive index \( n \) is shown in figure 4.12 for various a-SiN\(_x\)(::H) films. Similar behaviour was observed for all the films, with \( n \) approaching the long-wavelength refractive index value \( n(0) \) as the photon energy is decreased, and increasing with photon energy as the fundamental absorption edge is approached.

Figure 4.13 shows the value of the long-wavelength refractive index \( n(0) \) plotted as a function of \( x \) for all the films. Results of other workers (Lowe et al, 1986; Stein et al, 1979) are included for comparison.

4.4.3 Fundamental Absorption Edge

The optical absorption edges were obtained using the measured values of \( R \) and \( T \) in the expression

\[
T = C(1-R_{\text{meas}})\exp(-\alpha d) .
\]

This expression is not the full form of the equation describing the transmission of light through a film supported on a substrate. The expression for the actual transmission, ignoring reflections from the substrate air/interface (assumed to be negligible), is

\[
T = \frac{(1-R_1)(1-R_2)e^{-\alpha d}}{1-R_1R_2e^{-2\alpha d}}
\]

where \( R_1 \) and \( R_2 \) are the reflection coefficients at the air/film interface and the film/substrate interface respectively. Because it is not possible
Figure 4.12. Refractive index $n$ versus photon energy for various $a$-$\text{SiN}_x$:H films: $x$, films without hydrogen; $o$, 3–6 vol% hydrogen in the plasma. (Davis et al 1987)
Figure 4.13. Static refractive index $n(0)$ versus nitrogen content $x$ for $\text{a-SiN}_x(:\text{H})$ films: $\times$, films without hydrogen; $+$, 1 vol% hydrogen in the plasma; $\circ$, 3-6 vol% hydrogen in the plasma; $\Delta$, glow-discharge films; $\bullet$, results of Lowe et al (1986); $\blacksquare$, results of Stein et al (1979) determined at 632.8nm (Davis et al 1987)
to find $R_1$ and $R_2$, an approximation has to be made. It is usually assumed that $R_1$ and $R_2$ are both equal to the measured reflectivity $R_{\text{meas}}$ so that equation 4.13 becomes

$$T = \frac{(1-R_{\text{meas}})^2 e^{-\alpha d}}{1-R_{\text{meas}}^2 e^{-2\alpha d}}.$$  

4.14

However, some workers (see for example Al-Shabarty 1974), neglect multiple reflections altogether and just use the expression

$$T = (1-R_{\text{meas}}) e^{-\alpha d}.$$  

4.15

The constant $C$ in equation 4.12 is an approximation to account for the multiple reflections occurring within a film and is given the value of 0.8.

In the wavelength region when the Corning 7059 substrate begins to absorb, about 450nm or less, the transmission relative to the substrate alone was used.

Figure 4.14 shows the absorption edges for various a-Si$_x$N$_y$(:H) films prepared by sputtering. It can be seen that the edge moves to higher energies with increasing nitrogen content.

4.4 Electron Spin Resonance

Films were deposited onto polished quartz solely for the purpose of studying defect states by electron spin resonance (ESR).

Three series of films were produced:

(i) Sputtered a-Si$_x$N$_y$ without hydrogen deposited at 20°C.
(ii) Sputtered a-Si$_x$N$_y$:H with hydrogen deposited at 20°C.
(iii) Sputtered a-Si$_x$N$_y$:H with hydrogen deposited at 200°C.

A further set of samples prepared by glow discharge decomposition of silane and ammonia were kindly provided by Professor Spear (University of
Figure 4.14. Optical absorption coefficient $\alpha$ versus energy for various $\alpha$-SiN$_x$(::H) films: $\times$, films without hydrogen; $\circ$, 3-6% vol hydrogen in the plasma; $\Delta$, glow-discharge films. (Davis et al 1987)
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Dundee). The measurements were carried out at 77°C using a Bruker X Band spectrometer, Chemistry Department University of Leicester.

4.5 Electrical Transport Measurements

Gold electrodes were evaporated in a co-planer gap-cell configuration onto the samples. Either the four-probe or two-probe method for conductivity measurements was employed. Fine copper wires were attached to the electrodes with (RS) silver loaded electrically conducting paint. The samples were mounted onto a cryostat, which in turn fitted into a Delta Design Environmental Temperature Control Cabinet, which was capable of controlling the temperature to within ±0.5°C of the required temperature. By using an internal heater and a flow of circulating liquid nitrogen vapour from a pressurised liquid-nitrogen dewar a temperature range of 100 to 470K was accessible.

Two copper-constantan thermocouples, both attached to the surface of the substrate with conducting paint were used to measure the temperature of the sample. The e.m.f. developed was displayed on two voltmeters accurate to ±0.2μV with BCD outputs.

The cryostat was evacuated to below 10^{-6} Torr at which point the cryostat was flushed through with helium several times and finally filled with an overpressure (~1-2psi) of helium.

A Coutant 50V d.c. stabilized power supply was used for the supply voltage with the current being read by a Keithley 616 digital electrometer. The voltage dropped across the sample was measured by a Keithley 181 nanovoltmeter.
CHAPTER FIVE

PHOTOEMISSION

5.1 Introduction

5.2 Photoelectron Spectroscopy

5.2.1 The Three-step Model of Photoemission

5.2.2 Core Level Spectra

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5.4 Results and Discussion

5.4.1 Core Level Spectra

5.4.2 Valence Band Spectra
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PHOTOEMISSION

5.1 Introduction

Photoemission experiments were performed on a series of sputtered silicon nitride films. Both hydrogenated and non-hydrogenated films were studied. The position and strength of the core levels were determined, along with the plasmon energies as a function of $x$.

5.2 Photoelectron Spectroscopy

If a metal is illuminated with light of frequency greater than a critical value, electrons will be emitted from filled states of the metal, thus giving rise to the 'photoelectric effect'. The escaping electrons carry useful information about the energy depth of states from which they originate. Photoelectron spectroscopy provides information similar and sometimes complementary to other spectroscopic techniques such as X-ray fluorescence and photon absorption.

Photoemission is very surface sensitive due to the small escape depths (10-50Å) of photoemitted electrons. All measurements therefore have to be taken with the sample situated in an ultra-high vacuum, so that contamination of the surface occurs at a relatively slow pace.

As shown in figure 5.1, photoelectron spectroscopy uses photons as the incident species and electrons are the detected outgoing particles. The energy difference of the sample before losing an electron (ground state) and after losing the electron (excited state) must equal the energy of the annihilated photon. However, due to its complexity, the photoemission process is not usually treated in such a rigorous fashion. A simpler one-electron picture is used, whereby the emitted electron is viewed as coming from a one-electron orbital within the sample, without losing energy on escaping into the vacuum.
Figure 5.1. The photoemission process
In this case the energy of the emitted electron is given by

\[ K.E_{\text{electron}} = h\omega - \phi - B.E_{\text{bound state}} \] 5.1

where the binding energy is measured from the Fermi level. See figure 5.1.

By measuring the energies of the escaping electrons using a retarding potential method and knowing the incoming photons energy, it is possible to determine the energies of the bound states within the sample.

5.2.1 Three-Step Model of Photoemission

Valence band spectra obtained by experiment can be interpreted by the 'three-step model' of photoemission. As its name implies, the model describes photoemission in terms of three separate processes:

(i) Optical excitation.

(ii) Transport of the electron through the solid. This step includes the possibility of inelastic scattering by other electrons present in the sample.

(iii) Escape through the sample surface into the vacuum.

The energy distribution curve (EDC) of photoemitted electrons \( I(E,\omega) \) is the sum of a primary distribution of electrons \( I_p(E,\omega) \) which have not suffered any collisions and a secondary distribution of electrons \( I_s(E,\omega) \) which have suffered an energy loss in one or more collisions

\[ I(E,\omega) = I_p(E,\omega) + I_s(E,\omega) \] 5.2

Because of multiple scattering, the secondary distribution \( I_s(E,\omega) \) is expected to be structureless with the possible exception of peaks due to plasmon losses (see §5.2.4). Berglund and Spicer (1964) have derived an expression to describe this secondary electron distribution.

The primary distribution \( I_p(E,\omega) \) can be represented by a convolution
of the distribution of photoexcited carriers $P(E, \omega)$, a transmission
function $T(E)$ and an escape function $D(E)$

$$I_p(E, \omega) = P(E, \omega)T(E)D(E) \quad .$$  5.3

The transmission function $T(E)$ and the escape function $D(E)$ both vary
slowly with energy and so neither are expected to give rise to any
structure in $I_p$. They may, however, distort the background energy
distribution to some degree.

A distribution of photoexcited electrons $P(E, \omega)$ is obtained from the
bulk optical excitation of electrons from occupied states $n$ into empty
states $n'$

$$P(E, \omega) = \sum_{nn'} \int d^3k |<n' | p | n>|^2 \delta(E_n(k)-E_n(k)-\hbar\omega) \delta(E_n(k)-E_n(k)) \quad 5.4$$

where $p$ is the momentum operator and $\delta$ denotes the delta function. $E_n$ and
$E_{n'}$ are the energies of the initial and final states and $k$ is the
wavenumber, which is the same for both states.

Equation 5.4 is closely related to $\varepsilon_2(\omega)$, the imaginary part of the
dielectric function

$$\omega^2 \varepsilon_2 = \sum_{nn'} \int d^3k |<n' | p | n>|^2 \delta(E_n(k)-E_n(k)-\hbar\omega) \quad .$$  5.5

The additional $\delta$ term in equation 5.4 selects from all possible
transitions that contribute to $\varepsilon_2$ at $\hbar\omega$ those with final energies $E_{n'}$
equal to the energy $E$ selected by the electron energy analyser.

If the dipole matrix element $M_{n'n} = <n' | p | n>$ is assumed to be constant
then we obtain the joint density of states (JDOS)

$$J(\omega) = \frac{1}{8\pi^3} \sum_{nn'} \int d^3k \delta(E_{n'}(k)-E_n(k)-\hbar\omega) \quad .$$  5.6

$J(\omega)$ counts the number of transitions possible at photon energy $\hbar\omega$
subject to energy and wavevector conservation. Assuming constant dipole matrix elements, \( P(E,\omega) \) reduces to the so called energy distribution of the joint density of states (EDJDOS)

\[
P(E,\omega) \sim \sum_{nn'} \int \delta(E_{n'}(k) - E_n(k) - \hbar \omega) \delta(E_{n'}(k) - E(k)) .
\]

Thus by the three-step model, the photoelectron spectrum is essentially a distorted form of \( P(E,\omega) \): see Ley (1984) p.61 and Wooten (1972) p.155.

5.2.2 Core Level Spectra

Each element has its own characteristic set of core level states which can be probed in the X-ray region. Knowing the binding energies of these states permits the chemical characterization of a material.

5.2.3 Chemical Shift

The binding energies of an element depend on the local chemical environment of the element. For example, aluminium has a binding energy of 72.6eV in Al metal and 75.3eV in \( \text{Al}_2\text{O}_3 \). The shift in binding energy is due to a spatial rearrangement of the valence electrons of the atom and a different potential created by the nuclear and electronic charges on all the other atoms in the compound.

An expression for the binding energy difference, \( \Delta E_i^{C}(A,B) \) of a core level \( c \) measured for an atom \( i \) in two different compounds \( A \) and \( B \) with valence charges \( q_i^A \) and \( q_i^B \) is

\[
\Delta E_i^C = K_c (q_i^A - q_i^B) + (V_i^A - V_i^B)
\]

where \( V_i^A = \sum q_j^A/R_{ij} \) with \( R_{ij} \) the separation between atoms \( i \) and \( j \) and \( q_j \)
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is the charge on atom j.

The first term describes the difference in the electron-electron interaction between core orbital c and the valence charge $q_A$ and $q_B$ respectively. Frequently the q's are treated classically as if they were screening charges which leads to a screening potential:

$$k_c q_i = \frac{q_i}{r_{v,i}}$$  \hspace{1cm} \text{(5.9)}

$$r_{v,i} = \left( \frac{1}{r_v} \right)^{-1}$$  \hspace{1cm} \text{(5.10)}

where $r_{v,i}$ is the average radius of the valence shell of atom i.

The second term has the character of a Madelung potential. In the point-charge approximation the $V_i$'s are expressed as sums over potentials arising from ionic charges $q_i$ centred at positions $R_{ij}$ relative to atom i.

Equation 5.8 does not fully describe the situation as it does not account for the rearrangement of charge that occurs after an atom has been ionized. Electrons move nearer to the positive hole created in photoemission and so screen the positive charge which lowers the measured binding energy.

5.2.4 Plasmons

A plasma is a medium with equal numbers of positive and negative charges and where at least one of the types of charge is mobile. If the charge is made to oscillate as a whole then a plasmon is created. The frequency at which the sea of charge oscillates is the plasma frequency and is dependent on the binding energies of the charges. For a metal the valence electrons are only loosely bound to the positive ion cores forming the lattice and the frequency for the collective plasma oscillation is correspondingly small. For an insulator, however, the frequency required to induce plasma oscillations is much greater because the electrons are more tightly bound to their respective ion cores.
Consider a region in which charge is displaced a small distance whilst the rest of the system remains unperturbed. This produces two regions of net charge density, opposite in polarity, which attract each other. If the electrons are essentially free, i.e. there is negligible damping in the system, the charges overshoot and the positions are reversed. The system can be considered as a wash of charge flowing backwards and forwards at the characteristic plasma frequency.

As the electrons all tend to vibrate in sympathy the wavelength of such oscillations is large. The plasma frequency occurs when $\varepsilon_1=0$ and $\varepsilon_2<1$ see Wooten (1972).

The passage of an electron through a solid or the reflection of an electron or photon from a film may lead to the excitation of a plasmon. The charge of the electron couples with the electrostatic field fluctuations of the plasma oscillations. The energy of the reflected or transmitted electron will show an energy loss equal to integral multiples of the plasma energy.

Plasmons are created by the outgoing core-level photoelectron and are seen on the high binding energy side of XPS core lines (Figs 5.4 and 5.5). Assuming a free-electron approximation, the plasma energy ($h\omega_p$) is given by (Wooten 1972)

$$ (h\omega_p)^2 = \left(\frac{e^2}{\epsilon_0 m}\right)N_v $$.  \hspace{5cm}  \text{(5.11)}

where $m$ is the electron mass. For an alloy e.g. Si$N_x$, the density of valence electrons $N_v$ is related to the nitrogen content $x$ and the density $\rho$ according to

$$ N_v = \rho \left(\frac{n_{Si} + n_{N}}{A_{Si} + xA_N}\right) \Lambda_A. $$ \hspace{1cm}  \text{(5.12)}

The atomic weight and number of valence electrons are denoted by $A_{Si}$, $A_N$ and $n_{Si}(=4)$, $n_{N}(=5)$ respectively and $\Lambda_A$ is the Avogadro number.
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5.3 Experimental Procedure

The experiments were carried out using an ESCA spectrometer, the main components of which are shown in Figure 5.2.

The differentially pumped helium lamp enabled valence-band studies to be undertaken using the He(I) line (21.2eV) for photoexcitation. Monochromatized Al Kα(1486.6eV) radiation was used for the X-ray source. Electrons emitted from the sample were collected and energy analysed by an integrating retarding-field hemispherical analyser.

![Figure 5.2. Schematic of the photoelectron spectrometer](image)

Because of the surface sensitivity of photoemission, it is essential that clean surfaces are used. All surface contaminants normally present must therefore be removed before measurements are made. Cleaning of the sample surface was achieved by use of an argon sputter gun. Working at a pressure of 10⁻¹⁰ Torr increases the time required for a monolayer of residual gas to form on the sample surface.

All samples were prepared by RF sputtering as previously described (see §4.1.3). The samples were deposited onto aluminium foil at room temperature. Aluminium was used as the substrate material to prevent charging of the samples. However, because of the excellent insulating properties of silicon nitride, it was inevitable that the samples built up
a surface charge. This charge led to a distortion of the field between the sample and analyser, thereby leading to a distortion in the UPS spectrum. Two methods were tried to counteract this charging: either the sample was flooded with electrons or a negative bias was applied to the sample. The latter method proved to be the more successful, but neither procedure was able to produce reasonable results from the most highly insulating films.

After deposition the films were stored under vacuum until ready for use. Three samples were then mounted on a linear drive carriage, which in turn was attached to the end flange of the spectrometer vacuum chamber. This mounting procedure was done in air, taking no longer than fifteen minutes before the samples were back under vacuum. A pressure of $10^{-10}$ Torr was readily achieved after the system had been baked for 24 hours at a temperature of 150°C.

Any surface contamination was observed in the core level spectra. Figure 5.3 shows the core level spectra of a-Si:H taken before and after argon bombardment. Peaks at 284, 543 and 409 eV are assigned to the carbon, oxygen and nitrogen core states and are surface contaminants, as evidenced by their disappearance after argon bombarding. The two peaks at 150 and 99 eV are the Si 2s and 2p levels respectively. Also shown in figure 5.3 is a typical XPS trace from a-SiNx:H. The small peak at 250 eV is from the argon 2p state which arises from the argon bombardment or perhaps from incorporation during deposition of the sample. No signs of further contamination were seen in the films after surface cleaning had taken place.

The nitrogen content of the films was determined from the optical gap.
Figure 5.3. TYPICAL XPS SPECTRA OF a-Si$_x$N$_y$(H) FILMS BEFORE AND AFTER CLEANING THE SURFACE BY ARGON ION BOMBARDMENT
5.4 Results and Discussion

5.4.1 Core Level Spectra

As can be seen from figures 5.4 and 5.6, the binding energy of the silicon 2p level increases monotonically from 99eV in a-Si to 104eV in stoichiometric silicon nitride (x=1.33). There is also a corresponding shift in the Si 2s core level (see figures 5.5 and 5.6). This shift can arise because either the Fermi level moves within the band gap or there is a charge transfer from the silicon to the more electronegative nitrogen.

Also shown in figure 5.6 is the shift in the N 1s level. As pointed out by Karcher and co-workers (1984), nitrogen should always be fully coordinated with three silicon neighbours; therefore, no shift in the nitrogen 1s level should be observed. A shift to higher binding energies is however possible if the nitrogen bonds with the more electronegative species hydrogen and nitrogen. Karcher et al find that for near stoichiometric films the number of such 'wrong bonds' is no more than 12% of the total bonded nitrogen. They infer that this should lead to an asymmetry, or the presence of a satellite or shoulder in the spectra. As no such features were observed by them or in this study, the origin of the shift is ascribed to the movement of the Fermi level within the band gap. The shift in the Si 2s and 2p core levels can therefore be ascribed to both a movement of the Fermi level and a chemical shift.

A gradual increase in the linewidth is also observed. However, unlike in Karcher and Ley (1984), there is no observed decrease in the line width when x > 0.7 or any evidence of a shoulder in the Si 2p core level. Karcher et al fit the Si 2p core level with a superposition of chemically shifted components. A fit of five chemical components was used, Si_{0}', Si_{1}.....Si_{4} corresponding to silicon atoms with no nitrogen bonds, one nitrogen bond, etc respectively, until all four Si-Si bonds have been replaced by Si-N bonds.
Figure 5.4. Binding energies of the Si 2p core levels.
Figure 5.5. Binding energies of the Si 2s core levels.
Figure 5.6. Binding energies of Si 2p 2s and N 1s levels as a function of nitrogen content $x$. 
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The proposed description by Coleman and Thomas (1968) that non-stoichiometric silicon nitride (ie $x \neq 4/3$ in $a$-$SiN_x$) is a mixture of $a$-$Si_3N_4$ and $a$-$Si$ regions can be rejected from our XPS data. Two Si 2p core levels split by ~3eV would be expected if the model were correct, one line arising from Si in a pure $a$-$Si$ environment and the other from Si surrounded by four N atoms. As this is not the case it must be assumed that the samples are homogeneous.

The plasma energies determined from the XPS data are shown in figure 5.7. It can be seen that the plasma energy increases from 16.5eV in $a$-$Si:H$ to 23eV in $a$-$Si_3N_4$.

Figure 5.8 shows the density of the samples obtained from the plasma energies, see 5.2.4. The result for $x=0$ agrees reasonably well with the known density of $a$-$Si$ (2.1-2.3g/cm$^3$, Ley 1984), and the results for higher $x$ also compare favourably with the results of other workers (Sinha et al 1978 and Aiyama et al 1979) as is shown in figure 5.8.

From the ratio of the areas of the Si 2p peaks and N 1s peak it is possible to determine the composition $x$, because the area of each peak is proportional to the number of atoms giving rise to the corresponding peak. Figure 5.9 shows the value of $x$ in $a$-$SiN_x$ determined from the optical gap and the ratio of the Si 2p and N 1s peaks. This curve was used to determine $x$ for near-stoichiometric films.

5.4.2 Valence Band Spectra

Results from the valence band studies are shown in figure 5.10. Spectra typical of that for $a$-$Si(:H)$ were obtained (see also Roedern, Ley and Cardona 1977; Smith and Strongin 1981).

The top of the valence band is dominated by emission from the Si 3p states for non-hydrogenated silicon. With the addition of hydrogen a new peak is observed at 6.4eV and is due to H 1s states. The peak at 9.5eV is attributed to the argon 3p orbital. A recession of the valence band is
Figure 5.7. **Plasma frequencies from core level data as a function of nitrogen content x.**

(x) Sputtered a-SiN$_x$ without hydrogen, (◯) sputtered a-SiN$_x$:H, (□) results of Nishijina et al (1977), (△) results of Hezel et al (1982)
Figure 5.8. Density of the samples determined from the plasma energy as a function of nitrogen content $x$. 

(\textcircled{\textbullet}) results of Aiyama et al (1979),
(\textcircled{\textsquare}) results of Sinha et al (1982)
Figure 5.9. Nitrogen content $x$, determined from the optical gap versus the ratio of the N1s and Si2p peak areas.

$\frac{\text{N1s}}{\text{Si2p}}$

Ratio of areas of N1s and Si2p core levels

Nitrogen content $x$ (a-Si$_N$X ($:H$))

- $x$ a-Si$_N$X
- $\bigcirc$ a-Si$_N$X:$H$

Figure 5.9. Nitrogen content $x$, determined from the optical gap versus the ratio of the N1s and Si2p peak areas.
Figure 5.10. Valence band spectra \((h\nu=21.2\text{eV})\) from a number of \(\text{a-SiN}_x(:\text{H})\) films.
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observed but because of the surface charging a quantitative study was not possible. Also, lower lying nitrogen related features were not seen because of the steeply rising background of secondary electron emission.

Thus in conclusion, valence band studies proved unsuccessful for two reasons:

(i) charging of the sample lead to highly distorted spectra.

(ii) The limitations of using the He(I) line for excitation makes the observation of characteristic features difficult because of the rapidly rising background.

Normally a synchrotron radiation source is used to provide a whole range of energies. With a knowledge of the various photoemission cross-sections and their energy dependence it is possible to identify characteristic features in the EDC.
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RESULTS FROM ESR, INFRA-RED AND ELECTRICAL MEASUREMENTS

6.1 Introduction

6.2 Electron Spin Resonance Measurements

6.3 Electrical Measurements

6.3.1 D.C. Electrical Conductivity

6.3.2 Pre-Exponential Factor

6.4 Infra-Red Absorption Measurements
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RESULTS FROM ESR, INFRA RED AND ELECTRICAL MEASUREMENTS

6.1 Introduction

This chapter contains the results from electron spin resonance (ESR), infra-red and electrical measurements. The ESR measurements are of use in discussing the number and types of defects present in various types of a-SiN_x:H film and their variation with composition x.

Measurements of the D.C. dark conductivity of sputtered a-SiN_x films with and without hydrogen have been made. The results from the two types of film have been compared and discussed in the light of what is known from other chapters. Using the results from a number of a-Si films with varying amounts of hydrogen, an estimate for the minimum metallic conductivity has been determined.

Infra-red measurements have been used to help characterize a-SiN_x:H samples in terms of nitrogen and hydrogen content and sample homogeneity.

6.2 Electron Spin Resonance

Magnetic resonance may be detected from systems which have a magnetic moment \( \mu \) as a consequence of having an angular momentum \( \hbar G \), where \( G \) is either a nuclear (I) or electron spin (S). The magnetic moment \( \mu \) is related to \( G \) by

\[
\mu = \gamma_g \hbar G
\]

6.1

where the constant \( \gamma_g \) is the gyromagnetic ratio,

\[
\gamma_g = g \left( \frac{e}{2m_0} \right)
\]

6.2

and \( m_0 \) is either the electron mass or the proton mass depending on whether electron spin resonance (ESR) or nuclear magnetic resonance (NMR)
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is being considered. If a strong magnetic field $H$ is applied, there is a Zeeman interaction between the magnetic moment $\mu$ and the field and is given by

$$E = -\mu \cdot H = -g \left( \frac{e\hbar}{2m_o} \right) G \cdot H = -g \left( \frac{e\hbar}{2m_o} \right) mH$$  \hspace{1cm} 6.3

where $m$ is the required magnetic quantum number. Resonance occurs when a field of frequency

$$\omega = -g \left( \frac{e\hbar}{2m_o} \right) \frac{H}{\hbar}$$  \hspace{1cm} 6.4

is applied.

The $g$ values measured using eqn (6.4) normally differ from the free-spin value ($g_s = 2.0023$). This is because of the coupling between the motion of the other charges present.

The sample is placed in a microwave cavity and the magnetic field is swept. Resonance is observed as an absorption of the applied microwave power.

The spin density $N_s$ is determined from the area underneath the absorption band and is calibrated using a sample with a known number of spins, usually manganese which has five unpaired electrons per atom.

Shown in figure 6.1 are the derivatives of the electron spin resonance (ESR) absorption signal from the glow-discharge samples. A weak signal is observed for $x = 0.48$ and $x = 1.0$, but no signal is seen at all for $x = 1.33$. Much stronger signals are obtained from sputtered films containing no hydrogen over the entire compositional range.

A reduction in the 'g' value and an increase in the line width ($\Delta H_{pp}$), defined as the separation in gauss between the maximum and minimum turning points in the derivative of the absorption spectrum, is seen for all types of films with increasing nitrogen content $x$, see figures 6.2 and 6.3. Similar results have been reported by other workers (see for example Lowe et al 1985).
Figure 6.1. ABSORPTION DERIVATIVE OF THE ESR SIGNAL OBTAINED FOR THREE a-Si$_{1-x}$H FILMS PREPARED BY GLOW DISCHARGE DECOMPOSITION

$\chi=1.33$ NO SIGNAL DETECTED

$\chi=1.0$ $N_e=4.5\times10^{17}$ cm$^{-3}$

$\chi=0.48$ $N_e=3.8\times10^{17}$ cm$^{-3}$
Figure 6.2. Variation of the 'g' value with nitrogen content x.

(x)SP-SiNₓ, (Δ)SP-SiNₓ:H, (*)GD-SiNₓ:H (Shimizu, 1984); (▲)GD-SiNₓ:H (Lowe, 1986); (o)GD-SiNₓ:H, (a)SP-SiNₓ:H, present work.
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The dependence of \( g \) and \( \Delta H_{\text{pp}} \) with composition has been discussed by Shimizu et al (1984). They point out that any interaction between the ground and excited states of the defect (assumed to be silicon dangling bonds) decreases due to the opening of the energy gap, such that the \( g \) value moves closer to the free-spin value.

As more nitrogen is introduced into the films there is an increased hyperfine interaction between neighbouring nitrogen nuclei \(^{14}\text{N} I=1\) and the silicon dangling bonds, which leads to an increase in the line width \( \Delta H_{\text{pp}} \). Shimizu et al (1982) have performed \( 'Q' \) band measurements and found little change in \( \Delta H_{\text{pp}} \) as compared with the \( X \) band spectra thus supporting the view that the broadening is indeed due to a hyperfine interaction.

The observed signal is thought to arise from Si dangling bonds only. Any signal from the nitrogen dangling bonds would be split into three lines because of the large hyperfine interaction with the nitrogen \(^{14}\text{N}\) nucleus as observed in figure 6.4. A splitting into three lines has also been observed from crystalline silicon with substitutional nitrogen impurities (Brower, 1980, 1982).

Figure 6.4 shows the spectra taken from a glow discharge \( \text{a-SiN}_x:\text{H} \) film \((x=0.75)\). The spectra exhibits many triplet lines which arise from the different chemical environments the nitrogen nuclei find themselves in. The results presented in figure 6.4 are not typical of the results usually obtained from \( \text{a-SiN}_x:\text{H} \) films and in fact suggest that this particular sample may contain crystalline regions.

Figure 6.5 shows the variation in spin density with nitrogen content for the different types of films. A gradual decrease in \( N_S \) occurs with increasing \( x \) for the non-hydrogenated films, whereas the hydrogenated films deposited at room temperature show a slight increase in \( N_S \) with \( x \). An increase in \( N_S \) occurs when \( x \leq 1.1 \) in both hydrogenated films sputtered at 200°C and glow-discharge films. Whilst any further increase in \( x \) leads to a reduction in \( N_S \) for both types of films, this reduction however, is
Figure 6.4, ESR Spectrum for glow-discharge a-SiN_x:H (x=0.75) showing the triplet lines from nitrogen dangling bonds superimposed on the signal from silicon dangling bonds.
RESULTS OF SHIMIZU FOR SPUTTERED FILMS ARE INDICATED BY DASHED LINES (Top curve, no H; bottom curve, with H)

Figure 6.5. Variation of spin density \( (N_s) \) for a-Si\( N_x \):H films as a function of \( x \).
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less marked in sputtered material. Similar trends in \( N_s \) for glow-discharge films have been reported elsewhere (see for example: Shimizu et al (1982), Makino (1986) and Hasegawa (1987)).

A decrease in the spin density \( N_s \) for non-hydrogenated films with \( x \) is attributed to a reduction in the average coordination number of each atom and so an overall relaxation of the highly strained network.

However, the opposite appears to be the case for hydrogenated films. Introducing nitrogen into the films increases the defect density for \( x \leq 1.1 \) implying an increase in the strain present in the films. This may not be surprising when it is considered that the three-fold coordinated nitrogen atoms having a shorter covalent bond length are expected to enter into an essentially fourfold coordinated tetrahedral network of silicon atoms. The decrease in \( N_s \) for \( x \geq 1.1 \) has yet to be explained. It was originally thought that the decrease in \( N_s \) was in some way related to the hydrogen content of the samples. However, some workers report an increase in hydrogen content up to \( x \leq 0.7 \) (Searle, (1987)), followed by a decrease, whereas others find that the hydrogen content has little or no compositional dependence (Lowe et al, (1986); Makino et al, (1986)). Therefore the total hydrogen content of the films is not believed to play an essential part in the reduction of \( N_s \).

Figure 6.6 shows the dependence of \( N_s \) with annealing at two different temperatures as reported by Makino (1986). At low \( x \), \( N_s \) is greatly increased by annealing. When \( x=1.0 \), there is a decrease in \( N_s \) for a 700\(^\circ\)C anneal and \( N_s \) increases to its pre-anneal value when the annealing temperature is further increased to 900\(^\circ\)C. When \( x=1.1-1.2 \), \( N_s \) is also reduced by annealing at 700\(^\circ\)C; however annealing at 900\(^\circ\)C only serves to increase \( N_s \) by a small amount. Yokayama et al (1981) also find that \( N_s \) decreases by over an order of magnitude with annealing at a temperature of 500\(^\circ\)C for a glow-discharge film of composition \( x=0.84 \), and that annealing stoichiometric films has no effect on \( N_s \).
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Thermal annealing at high temperatures causes a reconstruction of the film structure, with new Si-Si or Si-N bonds being formed, and a dissociation of hydrogen.

![Graph showing the effect of annealing at two different temperatures on $N_\text{S}$ for a-SiN$_x$:H films (after Makino 1986).]

Figure 6.6. Effect of annealing at two different temperatures on $N_\text{S}$ for a-SiN$_x$:H films (after Makino 1986).

Thus from these studies it may be concluded that the role of hydrogen in reducing $N_\text{S}$ becomes less significant as $x$ is increased. This is further supported by our own studies on hydrogenated and non-hydrogenated stoichiometric films.

Shown in figure 6.7 is the defect density for CVD grown material as reported by Robertson and Powell (1985). The value for $x=0$ is from Hirose (1981) whilst the other values are from Fujita et al (1985) using the results of Bailey et al (1982) to convert the gas ratio into film composition. It can be seen that $N_\text{S}$ decreases monotonically with $x$ and that the decrease is much faster when $x > 1.1$. The gradual decrease in $N_\text{S}$ is again attributed to a reduction in the average coordination number, and
consequently to a general relaxation of the strain inherent in CVD material.

It is thought that the process leading to the rapid decrease in \( N_s \) for \( x > 1.0 \) in CVD material may be the same process giving rise to the reduction of \( N_s \) in glow-discharge material.

![Diagram](image)

**Figure 6.7.** Dependence of spin density with nitrogen content for CVD alloys. The value of \( N_s \) for a-Si is from Hirose (1981) and the remaining results have been adapted from Fujita et al. (1985) by converting the gas flow ratio to film composition using the data of Bailey et al. (1982) (from Robertson and Powell 1985).

The behaviour in \( N_s \) can be explained in terms of a model proposed by Robertson and Powell (1984) for low nitrogen concentrations and later used by Makino et al. (1986) to explain the dependence of \( N_s \) for nitrogen rich films. Robertson calculated the density of states for a-Si\(_2\)N\(_4\) and proposed that the nitrogen dangling bonds \( N_2^- \) produce the density of states at the valence band maximum, see figure 6.8, while silicon dangling
bonds $\text{Si}_3^0$ and nitrogen dangling bonds $\text{N}_2^-$ give gap states. The single electron from the silicon dangling bond falls into the lower lying nitrogen dangling bond, so converting the $\text{N}_2^-$ to $\text{N}_2^-$ and the $\text{Si}_3^0$ to $\text{Si}_3^+$, both of which are undetectable by ESR.

![Energy levels](image)

**Figure 6.8.** Schematic density of states in plasma deposited a-$\text{Si}_3\text{N}_4$ showing the position of the silicon and nitrogen dangling bonds (after Robertson and Powell 1985).

Thus there are then two competing processes:

(i) An increase in the number of $\text{Si}_3^0$ centres due to the increased strain arising from the incorporation of triply coordinated nitrogen atoms into a tetrahedral network.

(ii) A reduction in $\text{Si}_3^0$ dangling bonds by conversion to $\text{Si}_3^+$ via the nitrogen dangling bond.

When $x \ll 1.1$, the concentration of silicon dangling bonds is more than the nitrogen dangling bond concentration. Therefore process (i) above is dominant and $N_s$ increases accordingly. For $x \gg 1.1$ the number of nitrogen dangling bonds is similar to the number of silicon dangling bonds and so most $\text{Si}_3^0$ centres will be converted to $\text{Si}_3^+$ centres. Thus process (i) is outweighed by process (ii), thereby leading to a reduction in $N_s$.  

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This model also explains why annealing reduces $N_s$ for $x<1$. Any N-H bonds or Si-H bonds would be broken by annealing thus increasing the number of nitrogen and silicon dangling bonds. As the N-H concentration is larger than the Si-H concentration, nitrogen dangling bonds outnumber the silicon dangling bonds. Therefore, any silicon dangling bonds either form bonds with nearby nitrogen dangling bonds, or they become positively charged due to the electron transferring from the silicon to the nitrogen dangling bond. If this model is correct, then a light-induced spin signal (LESR) should be seen through a conversion of $Si^+_3$ centres to $Si^0_3$.

Figure 6.9 shows the increase in the ESR signal for a glow discharge film ($x=0.48$) when illuminated with light from a tungsten bulb using an infra-red blocking filter. As can be seen, there is no change in the 'g' value or line width $\Delta H_{pp}$. After the light source is switched off the signal returns to its pre-illumination value. Samples with higher nitrogen concentrations were illuminated with UV light from a mercury lamp: this was necessary because light from a tungsten bulb is not of sufficient energy to excite carriers across the large band gap of the material.

As $x$ increases $\Delta N_s$, the change in the ESR signal due to illumination should increase. However, because the dark ESR signal $N_s$ increases faster, the ratio $(\Delta N_s/N_s)$ decreases and therefore any LESR signal becomes increasingly more difficult to observe with increasing $x$. Because $N_s$ has decreased for stoichiometric films, it should be possible to observe a LESR signal. No increase was seen, but this may have been because the signal was below the detectability of the spectrometer ($\lesssim 10^{16}$ cm$^{-3}$), remembering also that no signal was detected for near stoichiometric films, or the linewidth was so large that even though a signal may be present it could not be integrated.

A photoinduced spin signal has been reported by Krick et al (1987) for PECVD silicon nitride films. However, the signal remained after cessation of the illumination, suggesting the mechanism to be defect creation (analogous to the Staebler-Wronski effect in a-Si:H) rather than LESR.
Figure 6.9. Increase in the absorption derivative of the ESR signal due to illumination.
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Conclusions

(i) The increase of $N_s$ with $x$ up to $x \approx 1.1$ arises from incorporating smaller threefold coordinated nitrogen atoms into a fourfold tetrahedral network of silicon atoms.

(ii) The rapid decrease in $N_s$ for $x > 1.1$ in glow discharge and CVD films may be from a conversion of the paramagnetic centre $\text{Si}_3^O$ to a diamagnetic centre $\text{Si}_3^+$. However no LESR signal is seen to verify this mechanism.

(iii) No decrease in $N_s$ is observed for non-hydrogenated films because the number of silicon dangling bonds always exceeds the number of nitrogen dangling bonds.

6.3 Electrical Measurements

6.3.1 D.C. Electrical Conductivity

Figure 6.10 shows an Arrhenius plot of the dark conductivity for non-hydrogenated a-$\text{SiN}_x$ films. Curves typical of hopping conduction were obtained for films with low $x$; however, as $x$ increased, so the linearity of the curves improved.

The variation of the room-temperature conductivity with $x$ is shown in figure 6.11 for both hydrogenated and non-hydrogenated films. With increasing $x$ the conductivity is seen to decrease due to the films becoming more insulating and also the difference between the non-hydrogenated and hydrogenated films becomes smaller. When $x \approx 1.0$ the values obtained for the two types of film are very similar.

The conductivity pre-exponential (see next section) is shown in figure 6.12. Again the difference between hydrogenated and non-hydrogenated films for low $x$ gradually lessens as $x$ is increased.

The conductivity data presented above provide further evidence that the importance of hydrogen in these films lessens as $x$ is increased.
Increasing Nitrogen Content

Figure 6.10. D.C. Conductivity of a-SiN$_x$ films.
Figure 6.11. Variation of the room temperature conductivity $\sigma_{RT}$ with nitrogen content. (*) films without hydrogen; (□) films with hydrogen.
Figure 6.12 Variation of the pre-exponential factor $\sigma_0$ with nitrogen content for a-SiN$_x$(:H) films.

(*) films without hydrogen; (□) films with hydrogen.
6.3.2 Conductivity Pre-Exponential Factor

Remembering that the conductivity may be written

\[ \sigma(T) = \sigma_0 \exp \left( -\frac{(E_C(T)-E_F(T))}{k_B T} \right) \]  \hspace{1cm} 6.5

where \( E_C(T)-E_F(T) \), the activation energy, is given by

\[ E_C(T)-E_F(T) = (E_C-E_F)_{T=0}^{T=0} (\gamma_C-\gamma_F) T. \]  \hspace{1cm} 6.6

Thus values of \( \sigma_0 \) obtained from plots of \( \sigma \) versus inverse temperature are not the actual values for the constant \( \sigma_0 \) because the activation energy \( (E_C-E_F) \) changes with temperature. However, because of the high density of defects within the band gap of a-Si, the position of the Fermi level is pinned and therefore temperature insensitive, i.e. \( \gamma_F=0 \).

A series of films were produced with varying degrees of hydrogen content, it was hoped that a composition would be achieved whereby the Fermi energy was just pinned so enabling an accurate determination for \( \sigma_0 \). The values of \( 1.82 \times 10^3 (\Omega \text{cm})^{-1} \) and \( 2.51 \times 10^3 (\Omega \text{cm})^{-1} \) were obtained from a-Si and a-Si:H films respectively. Dersch (1983) obtained a similar value of \( 2.3 \times 10^3 (\Omega \text{cm})^{-1} \) for \( \sigma_0 \) from an undoped sample which had been irradiated with 3MeV electrons so as to increase the defect density and thereby pin the Fermi energy. Dersch's value agrees reasonably well with that found for evaporated a-Si \( (1 \times 10^3) (\Omega \text{cm})^{-1} \) by Beyer and Stuke (1973).

If the temperature dependence of the mobility edges with respect to \( E_F \) \( (\gamma_C) \) is known and taken into account it is possible to find a value of \( \sigma_{\text{min}} \), the minimum metallic conductivity, from \( \sigma_0 \). Thus, the value obtained for \( \sigma_0 \) from the present films must be divided by \( \exp(\gamma_C/K) \), the factor which accounts for the shift in the mobility edge with temperature.

Cody (1984) finds from optical measurements a value for the shift of the optical gap with temperature of \( 2.4 \times 10^{-4} \text{eVK}^{-1} \). Since \( E_F \) lies near mid gap \( \gamma_C \) can then be taken to be approximately one half of this value, i.e.
1.2x10^{-4} \text{eV}\text{k}^{-1}. Using this yields the result

\[ \sigma_0 = 112(\Omega\text{cm})^{-1} \]

which is in good agreement with the results from other workers (Kakalios and Street 1986) and the theoretical result predicted by Müller and co-workers (1984) of ~100(\Omega\text{cm})^{-1} and by Mott (1988) of 100-200(\Omega\text{cm})^{-1}.

Figure 6.13 shows that \( \sigma_{\text{min}} \) is expected to be independent of the activation energy for conduction \( E_C - E_F \). However the results shown in figure 6.10 illustrate that this behaviour is not the case for SiN\(_x\) (:H) films. The reason for the variation of \( \sigma_0 \) with \( x \) (the so-called Meyer-Neldel behaviour) could be related to a varying value of \( \gamma_C \) or \( \gamma_F \) but this idea has not been pursued.

![Figure 6.13. Schematic diagram illustrating \( \sigma_{\text{min}} \) (after Elliott 1983).](image)

6.4 Infra-red Absorption Measurements

Typical infra-red spectra are presented in figure 6.14. The spectra show no signs of the presence of impurities. Note that the curve corresponding to \( x=0 \) has been shifted up by 20\% for clarity. The stretching absorption bands due to the Si-H bond at 2090cm\(^{-1}\) and Si-N bond (840cm\(^{-1}\)) are clearly observed, along with the SiH wagging mode at
Figure 6.14 Typical Infrared Transmission spectra from three sputtered a-SiN$_x$H films.
(Note that the spectra for x=0.0 has been shifted up by 0.2 for clarity).
For very high nitrogen concentrations ($x \sim 1.3$) a further absorption band at $3340\text{cm}^{-1}$ is seen, which arises from N–H bond stretching (not shown). The absorption band seen at $1100 \text{cm}^{-1}$ is due to an oxide layer on the substrate surface and is observed prior to film deposition.

An appreciable shift in the position of the Si–H stretching mode from $2090\text{cm}^{-1}$ up to $2200\text{cm}^{-1}$ occurs with the addition of nitrogen into the films (see figures 6.15 and 6.16). This shift can be attributed to the presence of Si–N bonds which increases the electronegativity sum of the Si–H bond, leading to a decrease in the Si–H bond length. A similar trend has been reported by other workers (Lowe et al (1986), Morimoto et al (1983), Knolle and Osenbach (1985)).

![Diagram of Si–H stretching modes](image)

**Figure 6.15.** Schematic illustration of the various frequencies of the Si–H stretching mode when the Si–H bond is located in a number of different chemical environments (after Chayahara et al 1985).

The gradual random replacement of H atoms in Si–H bonds by N atoms should lead to the eventual disappearance of Si–H bonds, as observed in the present films. This, along with the fact that there is a gradual
Figure 6.16 Position of the Si-H stretching mode versus nitrogen content for sputtered a-Si$_x$N$_y$:H films.

(*) present work; (o) results of Lowe et al (1986).
shift in the band to higher wavenumbers and that no features are observed due to a-Si:H, provides further evidence that the films are homogeneous.

The position of the SiH bond stretching mode of vibration for x=0 is 2090cm⁻¹. Jeffrey et al (1979) report that films with superior electronic properties tend to exhibit SiH stretching modes at 2000cm⁻¹. However, Moustakis (1982) concludes that the position of the SiH stretching mode in no way influences the quality of the film and that film quality depends only on the overall hydrogen content.

Recently, Morimoto et al (1986) have compared the Si-H absorption intensity with the content of incorporated H atoms derived from hydrogen evolution and nuclear magnetic resonance (NMR). It was shown that the intensity of the stretching mode (2000cm⁻¹) gives a better correlation with the H content than that from the corresponding wagging mode (650cm⁻¹).

Lowe finds that for low x there is an increase in the number of Si-H bonds. At higher x the hydrogen content increases slightly due to the formation of NH, but the overall content of SiH bonds remains constant. Hasegawa et al (1987) and Morimoto et al (1983) find a similar trend in the SiH content up to x=0.5, but at higher x, they find that the number of Si-H bonds decreases.

Figure 6.17 shows the compositional dependence of the SiN (840cm⁻¹) absorption band. The relative amounts of hydrogen and nitrogen were obtained from the expression \( \int \alpha(\omega) / \omega d\omega \) and by using the corresponding absorption bands (2100cm⁻¹ for hydrogen and 840cm⁻¹ for nitrogen). Figures 6.18 and 6.19 show the absorption intensity (\( \int \alpha(\omega) / \omega d\omega \)) obtained from the 2100cm⁻¹ (SiH) and the 840cm⁻¹ (SiN) modes respectively.

Results similar to Hasegawa's (1987) were found, in that the number of SiH bonds up to x=0.6 increased after which point a rapid reduction occurred. Hasegawa et al (1987) find that a linear relation exists.
Figure 6.17. Absorption of the Si-N stretching mode at 840 cm\(^{-1}\) for sputtered a-Si\(_{x}\)N\(_y\)H films.
Figure 6.18. Integrated area of the Si-H, 2100cm\(^{-1}\), stretching mode \(\int (\omega/\\omega)d\omega\) against nitrogen content \(x\).
Figure 6.19. Integrated area of the Si-N, 840 cm\(^{-1}\), stretching mode \(\int (\alpha/\omega) d\omega\) against nitrogen content \(x\).
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between the absorption intensity and $x$, namely

$$N_N = xN_{Si} = A \int \frac{\alpha(\omega)}{\omega} d\omega.$$ \hspace{1cm} 6.8

In their estimation they assumed that the density of silicon atoms ($N_{Si}$) was constant over the entire compositional range, and that the constant $A$ had the value $6.5 \times 10^{18} \text{cm}^{-2}$ for one series of films and $7.1 \times 10^{18} \text{cm}^{-2}$ for another series with $x < 0.9$. Sasaki et al (1982) determined $A$ to be $7.7 \times 10^{18} \text{cm}^{-2}$ from a pyrolytic a-SiN$_{1.3}$ sample and Yadav (1979) obtained the value of $9.2 \times 10^{18} \text{cm}^{-2}$. From the known density of the present films measured from photoemission (see p.90) the atomic density was found to vary with $x$. Thus Eqn 6.8 does not hold for the present samples and the value of $A$ rises from $3.19 \times 10^{18} \text{cm}^{-2}$ when $x=0.26$ up to $1 \times 10^{19} \text{cm}^{-2}$ for stoichiometric films ($x=1.33$).
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CHARACTERISTIC ENERGIES

7.1 Introduction

A discussion of the various characteristic energies derivable from optical data is presented in the first section of this chapter. These characteristic energies have varying degrees of physical significance and can be of use in describing a material. The latter section of this chapter contains the results of some of these energies obtained from films of silicon nitride with various compositions.

7.2.1 The Electronic Dielectric Constant

The first energies discussed are derived by considering the real part of the electronic dielectric constant. An expression for the frequency dependence of the real part of the electronic dielectric constant can be derived by using time-dependent perturbation theory (see Wooten 1972 p.72)

\[ \epsilon_1(\omega) = 1 + \frac{8\pi N e^2}{\hbar^2} \sum_m \frac{|x_{m0}|^2 \omega_m (\omega_m^2 - \omega^2)}{\left(\omega_m^2 - \omega^2\right)^2 + \Gamma^2 \omega^2} \]

where \( N \) is the number of non-interacting atoms per unit volume. If we let

\[ f_{mn} = \left(\frac{2\pi \omega_m}{\hbar^2}\right) |x_{mn}|^2 \]

where \( f_{mn} \) is defined as the oscillator strength, and is a measure of the relative probability of a quantum mechanical transition. Thus equation 7.1 can be rewritten as

\[ \epsilon_1(\omega) = 1 + \frac{4\pi N e^2}{\hbar^2} \sum_m \frac{f_{mn}}{\omega_m^2 - \omega^2} \]

We now consider two approximations to Eqn (7.3) which contain parameters which can be measured experimentally.
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#### 7.2.1 Static Dielectric Constant and Penn gap \( E_g \)

Penn (1962) has shown that by using an isotropic free-electron model containing a single energy gap \( E_g \), i.e. the distribution of transition energies are replaced by one average energy gap, \( E_g \), it is possible to calculate the static dielectric constant of a semiconductor. Penn's results can be obtained by letting \( \hbar \omega_{mn} = E_g \) in Eqn (7.3) where \( E_g \) is an average gap. Eqn (7.3) becomes

\[
\varepsilon_1(0) = 1 + \frac{4 \pi e^2 h^2}{m E_g} \sum_m f_{mn} N \tag{7.4}
\]

A schematic diagram showing \( E_g \) is illustrated in figure 7.1.

![Figure 7.1](image.png)

**FIGURE 7.1.** Schematic diagram of the energy gap between the valence and conduction bands, \( (\Delta E_{cv}) \) and the average gap \( (E_g) \) (from Phillips 1973).

Using the sum rule

\[
\sum_m f_{mn} = Z \tag{7.5}
\]

where \( Z \) is the number of electrons per atom, Eqn (7.4) reduces to

\[
\varepsilon_1(0) = 1 + \left( \frac{\hbar \omega}{E_g} \right)^2 \tag{7.6}
\]
where \( \omega_p^2 = \frac{4nNe^2}{m} \) is the plasma frequency of the electrons.

Phillips (1968) and Phillips and Van Vechten (1969) decomposed \( E_g \) into homopolar and heteropolar parts, \( E_h \) and \( C \) respectively, such that they are related by

\[
E_g^2 = E_h^2 + C^2 . \tag{7.7}
\]

If homopolar bonds are formed then the hybridized orbitals have the same energy \( E_A \). By using the free-atom energies \( E_s \) and \( E_p \) for s and p electron levels it is possible to make an estimate for the average energy of a \( sp^3 \) hybridized orbital centred on atom A

\[
E_A = \frac{E_s(A) + 3E_p(A)}{4} . \tag{7.8}
\]

In this case \( V_{\text{ionic}} \) is zero i.e. there is no ionic potential (\( C=0 \)), so the average homopolar energy gap \( E_g \), is \( E_h \) and Eqn (7.6) may be written

\[
\varepsilon_1(0) = \frac{(\hbar \omega_p)^2 +1}{E_h^2} . \tag{7.9}
\]

The energy gap \( E_h \) should depend only on the bond length \( l \) and it can be shown that \( E_h \propto l^{-2\frac{1}{2}} \) for silicon and nitrogen (Phillips 1973).

For two different atoms A and B, differences in \( E_A \) and \( E_B \) will lead to a charge transfer from one atom to the other when they are bonded together. It is not possible to use \( E_A \) and \( E_B \) to estimate any ionic contribution because the formation of bonds alters the energy levels to such an extent that the atomic values used for \( E_A \) and \( E_B \) are no longer accurate.
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Band theory can be used to show that the ionic and covalent contributions to $E_g$ are $90^\circ$ out of phase; therefore the total energy gap $E_g$ associated with the A-B bond has the form

$$E_g = E_h + iC$$

7.10

where $E_h$ represents the average energy gap produced by $V_{covalent}$ and $C$ represents the magnitude of the energy gap produced by $V_{ionic}$. The ionic contribution $C$, to the energy gap $E_g$, is related to the potential $V_{ionic}$ and therefore must also be related to the atomic potentials $V_A$ and $V_B$.

To find the total potential it is assumed that the inner valence electrons screen the ion core potential. Therefore each potential must be multiplied by a screening factor $\exp(-K_g r)$ as given by Thomas-Fermi theory: $K_g = (4K_f / \pi l)^{1/2}$ and is proportional to $l^{-1/2}$ ($l$ being the bond length), $K_f$ is the Fermi wavenumber of the valence electron gas, $K_f = 3\pi^2 n$ and $n$ corresponds to 8 electrons per diatomic volume.

Because $C$ depends on $V_{A-V_B}$ we can write

$$C(A,B) = b \left( \frac{Z_A e^2}{r_A} - \frac{Z_B e^2}{r_B} \right) \exp\left( -\frac{K_s l_{AB}}{2} \right)$$

7.11

where $l_{AB}$, the A-B bond length, is given by $r_A + r_B$ and $b$ is a dimensionless constant of order unity. Eqn (7.11) is found to be quite accurate when $b$ has the value 1.5.

For the amount of ionic and covalent character of a bond between A and B we can write

$$f_i = \frac{C}{E_g}$$

7.12

$$f_h = \frac{E^+}{E_g}$$

7.13
7.2.2 Single Oscillator Energy $E_o$

In the region of transparency, the important interband transitions can be approximated by non-interacting single oscillators where each valence electron contributes one such oscillator. Eqn (7.3) can then be written as

$$
\varepsilon_1(\omega) = 1 + \omega^2 \frac{f_n}{\omega_n^2 - \omega^2} 
$$

where $f_n$ is the electric dipole oscillator strength associated with transitions at frequency $\omega_n$. By isolating the first (strong) oscillator term and combining the remaining terms in the form

$$
\sum_{n \neq 1} \frac{f_n}{\omega_n^2} \left(\frac{1+\omega^2}{\omega_n^2}\right)
$$

the summation can be sensibly carried out for $\omega < \omega_n$. By including terms up to $\omega^2$ yields the single oscillator approximation

$$
\varepsilon_1(\omega)-1 = \frac{F}{E_o^2-(\hbar\omega)^2} 
$$

where $E_o$ and $F$ are related to all the $f_n$ and $\omega_n$ in Eqn (7.15).

Wemple and DiDomenico (1971) further showed that a simple empirical relationship exists between $F$ and $E_o$

$$
E_d = \frac{F}{E_o} 
$$

where $E_d$ is a dispersion energy. Equation (7.16) can therefore be rewritten as

$$
(n^2-1) = \frac{E_d E_o}{E_o^2-(\hbar\omega)^2} 
$$

which is essentially the formula appropriate for a single oscillator of energy $E_o$. 

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Values of $E_o$ and $E_d$ may be determined from the gradient and y intercept of a plot of $(n^2-1)^{-1}$ versus $(\omega \mu)^2$.

Can the long wavelength dielectric constant of a solid really be described in such a simple manner as the single oscillator? Figure 7.2 shows plots of $(n^2-1)^{-1}$ versus $(\omega \mu)^2$ for a number of our films; similar results were obtained for all the films studied. Wemple and DiDomenico (1969) have reported similar behaviour for over fifty widely different ionic and covalent non-metallic crystals. From the linearity of the curves it would seem that Eqn (7.18) does accurately describe the frequency-dependent dispersion of the dielectric constant. At long wavelengths the curves may cease to be linear because of the negative contributions of lattice vibrations to the refractive index. Similarly at short wavelengths a negative deviation from linearity may be seen due to the onset of the fundamental absorption edge or possible excitonic effects.

7.2.3 Dispersion Energy $E_d$

The dispersion energy $E_d$, which is a measure of the strength of interband optical transitions, is found to depend on the charge distribution and is thus closely related to the chemical bonding. Wemple (1973) and Wemple and DiDomenico (1971) proposed the empirical relation $E_d = \beta Z_a N_e$ where $N_c$ is the coordination of the 'cations' (silicon in the present case) surrounding an 'anion'. $Z_a$ is the formal chemical valence of the anion and $N_e$ is the effective number of valence electrons per anion. The $\beta$ parameter was shown to have the numerical value for crystals containing a single anion species and to be two-valued taking on the ionic value $\beta_i = 0.26 \pm 0.04 \text{eV}$ for most oxides and halides and the covalent value $\beta_c = 0.37 \pm 0.05 \text{eV}$ in the zinc blende and diamond structures.

Crystals with a wurtzite structure appear to have intermediate values of $\beta$ with ZnO taking on the ionic value and ZnS the covalent value.
Figure 7.2. $E^2$ versus $(n^2 - 1)^{-1}$: To determine the single oscillator energy $E_0$ and the dispersion parameter $E_d$

- $\circ$ films with hydrogen
- $\times$ films without hydrogen

Increasing nitrogen content

$E^2$

$(n^2 - 1)^{-1}$
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$E_d$ does not depend on the volume density of valence electrons, and so on the internuclear spacing, which is in marked contrast to the Penn gap $'E_g'$.  

7.2.4. Hopfield Energy Gap Parameter, $E_a$

Hopfield (1970) derived a further energy $E_a'$, which is the band-gap parameter in a high-frequency sum rule. The derivation of the Hopfield energy is not considered in the present text.

Relationships exist between the various energies so that we have $(\hbar \omega_p)^2 = E_a^2 = F_a E_0$ and $E_o = 1.5 E_T$. Further, it may also be noted $E_T < E_o < E_g < E_a'$, where $E_T$ is the direct optical gap.

7.3.1 Optical Gap

The simplest procedure to define the optical gap ($E_c - E_v$, see figure 7.1) is to use the value of the photon energy at which the absorption coefficient equals $10^4 \text{cm}^{-1}$; this energy is usually denoted $E_{o4}$ (Freeman and Paul 1979). Values of $E_{o4}$ determined from material prepared by the glow-discharge technique are found to be similar to those values obtained from the Tauc definition of the optical gap $E_T$ (see next section). However, for sputtered material, the photon energy at which the absorption coefficient equals $10^3 \text{cm}^{-1}$ i.e. $E_{o3}$ is found to give a better correspondence with the Tauc gap $E_T$ (see Derbyshire 1987).

7.3.2 Tauc Gap

As described earlier in Chapter Two, the position and shape of the fundamental absorption edge in amorphous materials is dependent on the preparation conditions; for example the hydrogen content as described earlier can have a marked effect (see §2.1.3). The power-law regime of the absorption curve ($\alpha > 5 \times 10^3 \text{cm}^{-1}$) is then used to define the optical gap $E_g$ (region A of figure 2.8, p.24) because the absorption in this
region is least affected by preparation conditions.

A definition for the optical gap $E_g$ which assumes that the electronic transitions giving rise to the absorption region $A$ of figure 2.8 take place between delocalised states was introduced by Tauc et al (1966).

The absorption is given by

$$\alpha(\omega) = \varepsilon_2(\omega) \frac{\omega}{nc} = \frac{8m^2\pi \hbar a}{\pi \omega c^2} \int \frac{|P(\omega)|^2 N_v(E) N_c(E+\hbar \omega)}{\hbar \omega} \, d\omega .$$  \hspace{1cm} 7.19

If $N_v(E)$ and $N_c(E+\hbar \omega)$ follow a simple power law behaviour as a function of energy

$$N_v \propto (E_v-E)^{r_1}  \hspace{1cm} 7.20a$$

$$N_c \propto (E-E_c)^{r_2}  \hspace{1cm} 7.20b$$

then

$$\alpha = \frac{\text{const}}{\varepsilon_2(\omega)} |P(\omega)|^2 (\hbar \omega-E_v)^{r_1+r_2+1} \hspace{1cm} 7.21$$

where $E_G = E_v-E_c$.

Assuming a constant matrix element for all interband transitions and a free-electron-like density of states, i.e. $r_1 = r_2 = \frac{1}{2}$, yields the result originally proposed by Tauc et al (1966)

$$\alpha \varepsilon_2(\omega) = \text{const} (\hbar \omega-E_v)^{\frac{1}{2}} . \hspace{1cm} 7.22$$

Plotting $(\alpha \varepsilon_2)^{\frac{1}{2}}$ against $\hbar \omega$ yields $E_G$ from a linear extrapolation of the curve, see figures 7.3 and 7.4. The linearity of the plot is not affected by omitting the refractive index and $E_G$ changes by no more than 50meV (see Cody et al, 1980 and Klazes et al, 1982). When this definition is used $E_G$ is commonly referred to as 'Tauc gap' and is denoted $E_T$.

Curves obtained from the Tauc plot exhibit a limited linear region as
can be seen in figures 7.4; over wider energy ranges the data deviate markedly from a straight line. The value of $E_G$ therefore depends on the region used for the extrapolation (see Cody et al 1980, Klazes et al 1982 and also Thutupalli and Tombin, 1977).

If the densities of non-localized states have a linear dependence on energy ($r_1=r_2=1$) as suggested by Klazes et al (1982), or there exists a linear distribution function $N(E)$ in the region of localized states as discussed by Mott and Davis (1970) and assuming transitions between localized states occur with the same probability as other transitions, it follows that

$$\alpha \omega n(\omega) = c(\hbar \omega - E_G)^3.$$  \hspace{1cm} \text{7.23}

Note that a linear fit over a wider range is obtained from Eqn (7.23) (see figure 7.4). Fagan and Fritsche (1970) found that Eqn (7.23) was more applicable for multi-component glasses. In general $E_G$ determined from Eqn (7.23) is 0.2-0.3eV smaller than that obtained from the Tauc definition $E_T$. 
Figure 7.4. Plots of \((\alpha \nu)^{1/2}\) versus photon energy for a-Si:H to determine the Tauc gap \(E_T\) assuming parabolic bands (Tauc et al 1966) and \((\alpha \nu)^{3/2}\) to determine the optical gap using a linear density of states for the bands as proposed by Klazes et al (1982). After Ley 1984).

Finally it must be mentioned that a-Se satisfies the relation

\[
\alpha(\omega)\nu = \text{const.}(\nu - E_G). \tag{7.24}
\]

Summarizing: an optical gap \(E_G\) may be defined from the absorption edges of many amorphous semiconductors. However, without prior knowledge of the form of the densities of states or the energy dependence of the matrix elements, it can only be surmised as to whether \(E_G\) represents a true gap in the DOS or is just another characteristic energy related to the mobility gap.
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7.4 Results and Discussion

7.4.1 Variation in Band Gap $E_T$ with Composition

A plot of $(\alpha\omega)^2$ versus photon energy to determine the Tauc gap of several silicon nitride films is shown in figure 7.5. With increasing nitrogen content the curves are seen to shift to higher energies as might be expected knowing that the optical gap is widening.

Figure 7.6 shows the increase in the Tauc gap for silicon nitride alloys with increasing nitrogen content $x$. Similar results have been reported elsewhere (see for example Knolle and Osenbach 1985 and Kurata et al 1981). The curve can be split into two distinct regions: the first region up to $x=0.7$ is characterized by a relatively slow increase in the Tauc gap with $x$. In contrast to this, the second region is seen to have a much greater dependence on nitrogen content, with the band gap opening rapidly and approaching 4eV for near stoichiometric films. Non-hydrogenated films or films produced with less than 1 vol% hydrogen in the plasma have a band gap approximately 0.3eV lower than corresponding hydrogenated films when the nitrogen content of these films is low. It is known that the incorporation of hydrogen into a-Si films causes a recession of the top of the valence band to lower energies and thereby increases the gap. This difference in the optical gap between hydrogenated and non-hydrogenated films gradually lessens with increasing nitrogen content and when $x \geq 1.0$ the gaps merge to similar values. The reason for this is the replacement of Si$3p$ states, forming the top of the valence band with N$2p$ lone-pair states.

7.4.2 Variation in $E_0$ and $E_g$ with Composition

Shown in figure 7.7 is the variation of $E_0$ with increasing nitrogen content; plotted on the same figure (lowest curve) is the variation of the band gap $E_T$, which is seen to vary less rapidly than $E_0$. Also shown are
Figure 7.5. Plot of $(\alpha h\nu)^2$ versus photon energy to determine the Tauc gap $E_T$ for non-hydrogenated films.
Figure 7.6. Tauc gap $E_T$ versus $x$ for $\text{a-SiN}_x(:\text{H})$ films: $\times$, films without hydrogen; $+$, 1vol% hydrogen in the plasma; $\circ$, 3–6vol% hydrogen in the plasma; $\triangle$, glow-discharge films. (Davis et al 1987)
Figure 7.7. Single-oscillator energy $E_0$ versus $x$ for a-SiN$_x$(:H) films; $x$, films without hydrogen; $+$, 1vol% hydrogen in the plasma; $\circ$, 3-6vol% hydrogen in the plasma, $\triangle$, glow discharge films (from Piggins et al 1987).
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the variations in the maxima of the Si3p, N2p_z and the N2p_{xy} levels relative to the conduction-band edge from the photoemission data of Karcher et al (1984) using the assignments of Robertson (1984).

We believe $E_o$ represents the energy of interband electronic transitions from the dominant peak in the valence band to the conduction band as illustrated schematically in figure 7.8. When $x=0$ the transitions are from Si3p states lying about 3.5eV below the conduction band. As nitrogen is introduced into the films, the number of Si-Si or N-N bonds increases and the valence band contains an increasing proportion of nitrogen derived states. Thus the centre of gravity of the valence band shifts to lower energies much more rapidly than does the top of the valence band. Remembering that transitions from the top of the valence band states determine the onset of the fundamental absorption edge and therefore the minimum band gap energy, it would seem reasonable that $E_o$ is larger and varies much more rapidly with $x$ than does $E_T$. When $x > 1$ lower-lying nitrogen 2p_{xy} states will shift $E_o$ to even higher values.

Penn Gap $E_g$

The Penn gap $E_g$ and its variation with composition is shown in figure 7.9. It was determined from the long-wavelength refractive index $n(0)$, (see figure 4.13, p.70) and values of the plasma energy $\hbar\omega_p$ determined by Karcher et al (1984); their values for the plasma energy were found to be similar to the values obtained for the present films (see figure 5.7 p.90). A monotonic increase in $E_g$ with increasing nitrogen $x$ is observed; it is not clear however, whether $E_g$ can be related to any specific features in the valence band density of states. It may be possible however, to use $E_g$ to find the degree of ionic character the Si-N bond has over the entire compositional range.

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Figure 7.8. Schematic illustration of the density of states and inter-band electronic transitions in a-Si$_x$H: (a)x=0; (b)x=0.5; (c)x=1. (Davis et al. 1987).
Figure 7.9. Penn gap $E_g$ versus $x$ for a-$\text{Si}_n\text{N}_x(:H)$ films: $x$, films without hydrogen; + 1 vol% hydrogen in the plasma; o, 3-6 vol% hydrogen in the plasma; Δ, glow discharge films. (Davis et al 1987)
7.4.3 Variation in $E_d$ with Composition

From the very good fits to the long-wavelength refractive index data
(see figure 7.10) and the $E_o$ data (see figure 7.7), the dispersion energy
$E_d$ has been evaluated using the limiting form of equation (7.18) namely

$$n(0) = \left(\frac{E_d}{E_o} + 1\right)^{1/2}. \tag{7.25}$$

Note that no attempt has been made to distinguish between the results from
the different types of films. The values of $E_d$ obtained are shown in
figure 7.11 and, in spite of the scatter in $n(0)$ and $E_o$, it is clear that
$E_d$ falls monotonically with increasing $x$.

For diamond-type structures Wemple and DiDomenico (1971) take $N_c=4,$
$Z_a=4$ and $N_e=8$. Using the same values of $N_c$ and $N_e$ for the alloys and
allowing $Z_a$ to vary according to

$$Z_a = \frac{Z_{Si}}{1+x} + \frac{Z_{N}x}{1+x}. \tag{7.26}$$

The observed fall in $E_d$ requires a non linear change in $\beta$ from 0.25 to
0.22eV between $x=0$ and $x=1.5$. The low value of $\beta$ is not expected
according to the simple expression proposed by Wemple and DiDomenico
(1971).

There may however be some small reduction in $N_c$ associated with
incomplete or dangling bonds at void boundaries. The presence of voids
would reduce the density and so $E_d$ should be scaled with the crystalline
to amorphous density ratio. However, density measurements made both from
direct measurement and from photoemission results (see p.91) showed that
the density of the present films were similar to the corresponding
crystalline values and is therefore not the reason for this low value of
$\beta$. 

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Figure 7.10. Variation of $n(0)$ with $x$ for a-Si$_{x}$N$_{y}$(:H).
Films sputtered without hydrogen ($x$), with 1% hydrogen (+) and with 3-6% (o) hydrogen in the plasma. Glow discharge films (●). Values of $n(0)$ used in determining the dispersion energy $E_d$ were obtained from the curve drawn through the data (Piggins et al 1987).
Figure 7.11. Variation of the dispersion energy $E_d$ with $x$ for a-Si$_x$N$_{1-x}$ films.
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REFLECTION MEASUREMENTS FROM AMORPHOUS SILICON NITRIDE FILMS

8.1 Introduction

8.1.1 Reflection Measurements

8.1.2 Dispersion Relations

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8.1.4 Quantum Theory of Absorption

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REFLECTION MEASUREMENTS FROM AMORPHOUS SILICON NITRIDE

8.1 Introduction

Reflection measurements have been made in the range 0.5eV to 12eV on silicon nitride films with varying degrees of nitrogen concentration. Films prepared by sputtering, with and without hydrogen, were studied along with films prepared by the glow-discharge technique. From the reflection measurements $\varepsilon_2$ spectra were determined by using Kramers-Kronig analysis. The optical joint density of states and its variation with alloying were derived from the $\varepsilon_2$ data and its behaviour discussed in relation to the valence-band density of states.

8.1.1 Reflection Measurements

The reflection coefficient $\hat{r}(\omega)$ is a complex function defined at the sample surface as the ratio of the reflected electric field to the incident electric field

$$\hat{r}(\omega) = \frac{E(\text{ref})}{E(\text{Inc})} = |r(\omega)|e^{i\theta} .$$

The amplitude $r(\omega)$ and phase components $\theta(\omega)$ of the reflectivity have been separated out.

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ are related to the reflectivity at normal incidence by

$$\hat{r}(\omega) = \frac{(\hat{n}(\omega)-1)}{(\hat{n}(\omega)+1)} = \frac{(n(\omega)+ik(\omega)-1)}{(n(\omega)+ik(\omega)+1)} .$$

The measured reflectance intensity $R(\omega)$ is defined as the product of the reflection amplitude

$$\hat{R}(\omega) = \hat{r}(\omega)^*\hat{r}(\omega) .$$
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From eqn (8.1) it can be shown that \( n(\omega) \) and \( k(\omega) \) cannot be directly determined from normal-incidence measurements

\[
R(\omega) = \left| \frac{n(\omega)-1}{n(\omega)+1} \right|^2 \quad 8.4a
\]

\[
= \frac{(n(\omega)-1)^2+k(\omega)^2}{(n(\omega)+1)^2+k(\omega)^2} \quad 8.4b
\]

Upon reflection there is an accompanying change in phase \( \theta \) as given by

\[
\tan \theta = \frac{2k(\omega)}{n(\omega)^2-1+k(\omega)^2} \quad 8.5
\]

Thus only by knowing the reflection intensity and phase at each wavelength is it possible to determine \( n(\omega) \) and \( k(\omega) \).

The optical constants are obtainable by measuring the reflectivity at different angles of incidence and using the Fresnel equations. However, this is a difficult experiment to perform. The dispersion relations (K-K analysis) can be used to find the optical constants from the reflectivity alone, provided the reflectivity of the sample is known over a large energy range.

8.1.2 Dispersion Relations

A dispersive process can be related to an absorption process through an integral formula relating the two processes. Thus the dispersion of the refractive index of a material with photon energy can be related to the extinction coefficient \( k \).

Dispersion relations follow from causality, the requirement that no effect can occur before the stimulus has taken place (see Toll 1956 and Wu 1962). The dispersion relations that can be derived for linear systems subject to causality (Toll 1956, Wu 1962) can be used to obtain the optical constants from normal-incidence reflectivity data and to derive sum rules.

The relationship of the response to the stimulus is given by a response function. In the case of an electromagnetic field acting on
electrons we have

\[ E = \varepsilon^{-1}(q, \omega) E^{\text{ext}} \]  \hspace{1cm} \text{(8.6)}

where the response function is \( \varepsilon^{-1}(q, \omega) \).

The dielectric function \( \varepsilon \) links the macroscopic optical properties with the microscopic electronic structure of the solid. A semiclassical approach using Maxwell's equations can be used to relate the dielectric function to experimental observables (e.g. reflectivity and transmittance).

The dispersion relations for the dielectric constants are

\[ \varepsilon_1(\omega)-1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_1(\omega')}{(\omega'^2 - \omega^2)} \, d\omega' \]  \hspace{1cm} \text{(8.7)}

\[ \varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega')-1}{(\omega'^2 - \omega^2)} \, d\omega' \]  \hspace{1cm} \text{(8.8)}

where \( P \) denotes the Cauchy principal value (see Wooten 1972 and Stern 1963). Three assumptions have been used in deriving Eqns (8.7) and (8.8) boundedness, linearity and causality. Singularities at finite frequencies or divergences at infinite frequency can be treated by modified relations containing extra constants. An example would be conductors where the imaginary part of \( \varepsilon_r (\sigma/\omega) \), is not bounded as \( \sigma \neq 0 \) and has a non-vanishing dc value for when \( \omega \to 0 \) (Stern 1963; Toll 1956).

From Eqn (8.1) we can write

\[ \ln \hat{r}(\omega) = \ln |r(\omega)| + i\Theta(\omega) \]  \hspace{1cm} \text{(8.9a)}

\[ = \ln |R(\omega)| + i\Theta(\omega) \]  \hspace{1cm} \text{(8.9b)}

It can be seen that a linear relationship exists between the amplitudes of incident and reflected light. The real and imaginary parts of the reflection coefficient are thus connected by Kramers-Kronig
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dispersion relations

\[ \theta(\omega) = -\frac{\omega}{\pi} \int_0^\infty \ln \left[ \frac{R(\omega')/R(\omega)}{(\omega^2 - \omega'^2)} \right] d\omega' \]  \hspace{1cm} 8.10

Eqn (8.10) is the usual method of determining the optical constants. It does, however, require a knowledge of the reflectivity over the entire spectral region. The integral of eqn (8.10) can be evaluated by Simpson's rule since it is a smooth and well-behaved function. It must be noted that any systematic error in the reflectance measurement does not affect the phase because the ratio \( R(\omega')/R(\omega) \) is used to calculate the phase and thus any systematic errors cancel. Regions of constant reflectivity contribute nothing to the phase and so the absorption is zero. Using eqns (8.1) and (8.2) it is possible to write \( n \) and \( k \) as

\[ n(\omega) = \frac{1-R(\omega)}{1+R(\omega)-2\cos(\theta(\omega))R(\omega)}^{\frac{1}{2}} \]  \hspace{1cm} 8.11

\[ k(\omega) = \frac{2\sin(\theta(\omega))R(\omega)}{1 + R(\omega) - 2\cos(\theta(\omega))R(\omega)}^{\frac{1}{2}} \]  \hspace{1cm} 8.12

Since the reflectivity can only be measured over a limited range, an extrapolation of the data is necessary to extend the data set. A significant contribution to the integral can occur at frequencies far removed from \( \omega \) if \( dR/d\omega \) is large and so the extrapolation used must be chosen with care. If it is assumed that the dielectric constant is given by the Drude formula (see §2.2.2, p.23) for frequencies above the plasma frequency \( \omega_p \), then \( \varepsilon = 1 - \omega_p^2/\omega^2 \). At high frequencies \( \varepsilon_1 \to 1, \varepsilon_2 \to 0 \) and \( k \to 0 \) so that \( n = k = \frac{\omega}{\omega_p} - \frac{1}{2} \) and \( R = (n-1/n+1)^2 = 1/16(\omega_p/\omega)^4 \). If the last measured point \( \omega_1 \) is larger than \( \omega_p \) it would seem logical to extrapolate \( R(\omega) \) by \( R = R_1(\omega_1/\omega)^4 \) where \( R_1 \) is the last measured reflectance value at \( \omega_1 \).

A further approach in extrapolating data is to assume that

\[ R = R_{ef} \left( \frac{\omega_{ef}}{\omega} \right)^s \]  \hspace{1cm} 8.13

where \( \omega > \omega_{ef} \) and is the frequency of the last measured reflectance
value $R_{ef}$ and $s > 0$ is an empirical parameter chosen to give best agreement with the experimental results.

Another extrapolation procedure is to use

$$R = R_{ef} \exp \left[ B(\omega_{ef} - \omega) \right] \quad 8.14$$

where the constant $B$ is chosen to make the derivative of the extrapolated reflectivity equal to the measured derivative at $\omega_{ef}$. However, the integral will diverge if the integration range is not cut off at a certain frequency.

8.1.3 Sum Rules

Sum rules can be derived from the Kramers-Kronig relations and are very useful in the interpretation of optical data (Wooten (1972) and Stern 1963). At frequencies higher than those of the highest absorption band we can rewrite Eqn (8.7) as

$$\varepsilon_1(\omega) = 1 - \frac{2}{\pi\omega^2} \int_0^\omega \frac{\omega' \varepsilon_2(\omega')}{(\omega^2 - \omega'^2)} d\omega' + \frac{2}{\pi} \int_{\omega_c}^{\infty} \frac{\omega' \varepsilon_2(\omega')}{(\omega^2 - \omega'^2)} d\omega' \quad 8.15$$

where $\omega_c$ is the frequency for which no further absorption occurs, i.e. $\varepsilon_2 = 0$ for $\omega > \omega_c$. Also at high frequencies $\omega'$ can be neglected in the denominator of the first integral because $\omega > \omega_c$ and thus Eqn (8.15) becomes

$$\varepsilon_1(\omega) = 1 - \frac{2}{\pi \omega^2} \int_0^{\omega_c} \frac{\omega' \varepsilon_2(\omega')}{(\omega^2 - \omega'^2)} d\omega' \quad 8.16$$

for $\omega > \omega_c$.

At very high frequencies all the valence electrons may be treated as if they are essentially free and the dielectric constant is described by the Drude result.

$$\varepsilon_1(\omega) = 1 - \left( \frac{4\pi ne^2}{m} \right) = 1 - \left( \frac{\omega_p}{\omega} \right)^2 \quad 8.17$$
where \( m \) is the free-electron mass and \( N \) is the number of electrons per unit volume in the solid. Comparing Eqns (8.16) and (8.17) shows that
\[
\int_0^\infty \omega \varepsilon'_\text{r}(\omega) d\omega = \left( \frac{4\pi Ne^2}{m} \right) = \frac{i\hbar n}{p^2}. \tag{8.18}
\]

This sum rule can be related to the number of effective electrons \( n_{\text{eff}} \) contributing to the optical properties
\[
\int_0^\infty \omega \varepsilon'_\text{r}(\omega) d\omega = \left( \frac{4\pi Ne^2}{m} \right) n_{\text{eff}}(\omega_c) \tag{8.19}
\]
where \( N_a \) is the density of atoms.

Eqn (8.18) is related to the rate of energy absorption by transverse fields (photons).

Dispersion relations also exist between the reciprocal of the dielectric function
\[
\text{Re} \left( \frac{1}{\varepsilon(\omega)} \right) = 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega' \text{Im} \left[ \frac{1}{\varepsilon(\omega')} \right]}{\omega^2 - \omega'^2} d\omega'. \tag{8.20}
\]

Again for frequencies high enough so that no further absorption takes place (\( \varepsilon'_\text{r}(\omega)=0 \)), Eqn (8.21) becomes
\[
\text{Re} \left( \frac{1}{\varepsilon(\omega)} \right) - 1 = \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2} - 1. \tag{8.21}
\]

where \( \varepsilon'' \gg \omega \).

A further sum rule for the static dielectric constant can be obtained directly from Eqn (8.7) by simply setting \( \omega=0 \)
\[
\varepsilon(0) = 1 - \frac{2}{\pi} \int_0^\infty \frac{\varepsilon'_\text{r}(\omega')}{\omega'} d\omega' \tag{8.23}
\]
for \( \omega \gg \omega_c \).
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This provides a useful check as to the completeness with which \( \varepsilon_2(\omega) \) is known.

There is yet another sum rule which is related to plasma excitation. When an electron enters a solid it produces the field \( D \). The rate of energy absorption per unit volume from an electric field is

\[
\frac{de}{dt} = \text{Re}(E \cdot \frac{\partial D}{\partial t}). \tag{8.24}
\]

If the dielectric displacement for a particle of charge \( e \) and velocity \( \mathbf{v} \)

\[
D(r,t) = -\nabla \frac{e}{r-vt} \quad \tag{8.25}
\]

is substituted into Eqn (8.24) we obtain

\[
\frac{de}{dt} = \frac{\omega \varepsilon_2 |D|^2}{\varepsilon_2^2} = -\omega \text{Im}(\varepsilon^{-1}) D^2 \quad \tag{8.26}
\]

where

\[
\text{Im} \left( \frac{1}{\varepsilon} \right) = -\frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \quad \tag{8.27}
\]

is the electron energy loss function and describes the loss of energy by a charged particle passing through a solid. A maximum in the energy loss occurs at the plasma frequency \( \omega_p \).

The sum rule is analogous to Eqn (8.18) and is written

\[
-\int_0^\infty \omega \text{Im} \left( \frac{1}{\varepsilon} \right) d\omega = \frac{1}{2} n \omega_p^2 \quad \tag{8.28}
\]

8.1.4 Quantum Theory of Absorption and Dispersion

The crystalline phase provides a useful starting point for a discussion of interband transitions in the amorphous state.

The transition probability for an electron from a filled valence band state to an empty conduction-band state results from the perturbation of
the system by the time dependent vector potential of the electromagnetic field. The total Hamiltonian is then
\[ H = \frac{1}{2m}(p+eA)^2 + V(r) \]  
8.29

where \( p \) is the momentum, \( V(r) \) the potential experienced by the electron and \( A \) the vector potential.

The light wave can be described by the vector potential
\[ A = \hat{\mathbf{a}} \left( \exp(i \mathbf{q} \cdot \mathbf{r} - \omega t) + \exp(-i \mathbf{q} \cdot \mathbf{r} - \omega t) \right) \]  
8.30

where \( \hat{\mathbf{a}} \) is the unit polarization vector and \( \mathbf{q} \) is the photon wavevector.

The first-order perturbation operator is then
\[ H'(r,t) = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} \]  
8.31

The transition probability from an initial valence-band state \( \psi_v \) to a final conduction band state \( \psi_c \) is
\[ W(\omega, t', k, k') = \frac{e^2}{m^2 \hbar^2} \left| \int_0^t dt' \int \mathbf{r} \langle \psi_c | \mathbf{A} \cdot \mathbf{p} | \psi_v \rangle \right|^2 \]  
8.32

For crystals \( \psi_v \) and \( \psi_c \) are Bloch-type wavefunctions and may be written
\[ \psi_v = \exp \left( -i \frac{E_v(k) t}{\hbar} \right) \exp(i \mathbf{k} \cdot \mathbf{r}) u_v(k, \mathbf{r}) \]  
8.33

where \( u_v(k, \mathbf{r}) \) has the periodicity of the lattice; a similar expression holds for \( \psi_c \). These two equations and Eqn (8.30) when put into Eqn (8.32) yield
\[ W(\omega, t', k, k') = -\left( \frac{e}{m \hbar} \right)^2 A^2 \left| \int_0^t dt' \exp \left( i \frac{E_v(k) - E_v(k') - \hbar \omega}{\hbar} \right) M_{vc} \right|^2 \]  
8.34

where \( M_{vc} \) the Matrix Element and is an integral over all space
\[ M_{vc} = \int \mathbf{r} \left( \exp -i (k' - \mathbf{q}) \cdot \mathbf{r} \right) u^*_c(k', \mathbf{r}) \hat{\mathbf{a}} \cdot \nabla \left( \exp(i \mathbf{k} \cdot \mathbf{r}) \right) u_v(k, \mathbf{r}) \]  
8.35

The first selection rule is based on conservation of crystal momentum in a periodic medium. \( M_{vc} \) disappears unless \( k' - \mathbf{q} = k \) and since \( \mathbf{q} \ll k, k' \),
q may be ignored so that $k = k'$ such that only vertical transitions are allowed in the dipole approximation.

This leads to the transition probability per unit time and unit volume (Bassani 1966)

$$W_{vc}(\omega) = -4\pi \hbar \left(\frac{e}{m}\right)^2 A^3 \int \frac{dk}{4\pi^2} |M_{vc}|^2 \delta(E_C - E_V - \hbar\omega) .$$  \hspace{1cm} 8.36

The $\delta$ function is a consequence of the conservation of energy, such that the probability of a transition is non zero only when $E_C - E_V = \hbar\omega$ and thus

$$\varepsilon_2(\omega) = -\frac{8\pi}{\varepsilon_0} \left(\frac{m\hbar}{\omega}\right)^2 \int \frac{dk}{4\pi^2} |M_{vc}|^2 \delta(E_C - E_V - \hbar\omega) .$$  \hspace{1cm} 8.37

The imaginary part of the dielectric constant at a frequency $\omega$ is given by all vertical interband transitions between states of energy difference $\hbar\omega$ and by the matrix element $M_{vc}$ which depends on the wavefunctions of initial and final states. Using the property of the $\delta$ function

$$\int_a^b g(x) \delta[f(x)] dx = \sum_{x_o} g(x_o) \left| \frac{df}{dx} \right|^{-1}_{x = x_o}$$  \hspace{1cm} 8.38

where $f(x_o) = 0$ and $a < x < b$ and assuming $M_{vc}$ slowly varies with $K$ the integral in Eqn (8.37) can be rewritten

$$\varepsilon_2(\omega) = -\frac{8\pi}{\varepsilon_0} \left(\frac{m\hbar}{\omega}\right)^2 \int \frac{dS}{4\pi^2} \frac{|M_{vc}|^2}{\sqrt{\nu(E_C - E_V) E_C - E_V - \hbar\omega}}$$  \hspace{1cm} 8.39

where the surface integral is over the surface in $k$ space for which $E_{cv}(k) = E_C(k) - E_V(k) = \hbar\omega$.

Calculations have shown that $M_{vc}$ is indeed a slowly varying function compared with

$$J_{vc}(\omega) = \int \frac{dS}{4\pi^2} \frac{|M_{vc}|^2}{\sqrt{\nu(E_C - E_V) E_C - E_V - \hbar\omega}}$$  \hspace{1cm} 8.40

the so-called optical joint density of states (ODJOS). Points in $k$ space
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for which $\mathbf{v}_{k} \cdot \mathbf{E}_{vc} = 0$ are called critical points or Van Hove singularities (Van Hove 1953; Phillips 1956) and give rise to sharp features in the JDOS and optical constants.

The wavefunctions $\psi_{v}(=|i>)$ and $\psi_{c}(=|f>)$ of the valence and conduction bands can be expanded in terms of a set of orthonormal, localized wavefunctions $|nv> \text{ and } |nc>$ centred on different atoms $n$. Thus

$$|i> = \sum_{n} a_{inv} |nv>$$

8.41a

and

$$|f> = \sum_{n} a_{inc} |nc> .$$

8.41b

When $|i>$ and $|f>$ are localized they will both be of the same order of magnitude.

For a crystal the $a$'s are plane waves and $|nv>$ are Wannier functions. Writing $a = Ae^{i\delta}$, for an amorphous solid the phases $\delta$ vary randomly from site to site because the uncertainty in $k$ is of the order of the wavevector itself $\delta k = k$ (for strong scattering). Furthermore, the amplitudes of the $a$'s may vary from atom to atom and for localized states one of the $a$'s will dominate over the others. This random phase approximation (RPA) is not exact since it does not take into account the considerable degree of short-range order still persisting within the molecular units. It does however, provide a useful starting point in describing the optical properties of amorphous semiconductors.

The momentum matrix element for transitions between extended states can be averaged over an ensemble of random systems

$$\left< |f|p|i> \right>_{\text{ensemble}} = \frac{a^3}{V} \left< \sum_{n'} |n'c|p|nv> \right>_{\text{ensemble}}$$

8.42

where $a$ is the interatomic spacing. The term $<nc|P|nv> \neq P_{cv} \neq 0$ will dominate the sum and so

$$\left< |f|p|i> \right>_{\text{ensemble}} = \frac{a^3}{V} |nc|p|nv> \right|^2 = \frac{a^3}{V} P_{cv} \cdot |P_{am}(\omega)|^2$$

8.43
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where \( P_{cv} \) is of the order \( \hbar/a \).

Thus for the amorphous phase \( \varepsilon_2(\omega) \) is given by

\[
\varepsilon_2(\omega) = \frac{2}{V} \left( \frac{2ne}{m\omega} \right)^2 |P_{am}(\omega)|^2 \sum_{E_f-E_1-\hbar\omega} \delta \delta
\]

and when the one electron density of states \( g(E) = \frac{1}{V} \delta(E-E_n) \) is introduced eqn (8.44) becomes

\[
\varepsilon_2(\omega) = 2 \left( \frac{2ne}{m\omega} \right)^2 a^2 P_{cv}^2 \int_0^{\hbar\omega} dE g_1(-E)g_f(\hbar\omega-E) .
\]

The critical points associated with \( k \) conservation in the crystalline case are absent in the amorphous case as illustrated in figure 8.1.

Figure 8.1. Nonzero optical matrix elements for a-Si:H and c-Si from a particular valence-band state. Because there is no \( k \) conservation in a-Si:H all transitions are allowed (after Jackson et al 1985).
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Amorphous solids exhibit features in the spectra only at energies where the joint density of states has structure.

![Figure 8.2. Fundamental absorption band of a-Ge and c-Ge (after Spicer and Donovan 1970).](image)

From figure 8.2 it can be seen that amorphous Ge shows no sign of the peak observed at 4.5eV in crystalline Ge. This peak is, however, made more pronounced due to an Umklapp enhancement of the slowly decreasing matrix element. These matrix element may be described by the Penn model of a semiconductor and are found to have a $\omega^{-2}$ dependence.

$$|P_{\text{Penn}}(\omega)|^2 = \frac{\hbar}{\pi k_f} \left( \frac{\omega}{\omega_0} \right)^2$$  \hspace{1cm} 8.46

where $k_f$ is the magnitude of the wavevector at the Fermi level. The optical joint density of states can be determined from $\varepsilon_2$ spectra either assuming the matrix elements are described by the Penn model (Eqn (8.46))
or a suitably averaged crystalline value. The valence band density of states can be obtained by using a step function to approximate the conduction-band density of states. Theoretical calculations tend to suggest that the conduction band density of states should be smooth and featureless (Joannopoulos and Cohen 1973).

8.2 Experimental Procedure

Three types of sample were used:

(i) a-SiN:H prepared by glow-discharge decomposition of silane and ammonia
(ii) Sputtered a-SiN without hydrogen
(iii) Sputtered a-SiN:H with hydrogen.

The near-normal-incidence reflection measurements were taken at room temperature over the range 0.5 to 12eV. The Perkin Elmer 330 spectrophotometer (see §4.3 p.63) was used to find the reflectances between 0.5eV and 5eV. Reflection measurements in the vacuum ultraviolet were kindly taken by Dr T. Shen (University of Cambridge) and a description of the spectrometer used can be found in Shen (1987).

To perform Kramers-Kronig analysis a knowledge of the reflectance over a large energy range is necessary (see§8.1.2). Two extrapolations were used to extend the data range. For energies below the first data point $E_1$, a constant reflectivity was assumed. This was justified since $E_1$ was at least 1eV below the band gap. At high energies the extrapolation used was of the form $(energy)^{-4}$.

8.3 Results and Discussion

Figure 8.3 shows the reflectivity for the three types of samples used. The peak observed at 4eV for all types of film slowly decreases with increasing x and shifts to higher energies. Using Kramers-Kronig analysis $\varepsilon_1(E)$ and $\varepsilon_2(E)$ were obtained from the reflectivity data along with
Figure 8.3 Reflection of Glow Discharge a-SiN_x:H
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\( n_{\text{eff}}(E) \), the number of electrons taking part in optical transitions. To show the validity of the extrapolations used in finding \( \varepsilon_1 \) and \( \varepsilon_2 \), \( n_{\text{eff}}(E) \) has been calculated up to to an energy \( E \) and has been compared with the expected number of valence electrons.

Figure 8.4 shows that for \( x=0 \), \( n_{\text{eff}} \approx 3 \) at 12eV as would be expected since the plasma energy \( E_p \) was found to be 17eV from photoemission experiments performed on the same set of samples (see figure 5.7 p.90). A reduction in \( n_{\text{eff}} \) at 12eV is observed from films with increasing \( x \). This is hardly surprising knowing that \( E_p \) moves to higher energies with increasing nitrogen concentration.

The behaviour of \( \varepsilon_1(E) \) with increasing \( x \) is shown in figure 8.5. Similar results were obtained for all the hydrogenated films with an overall broadening of the line shape as the films become more insulating (increasing damping factor \( \Gamma \) in the Lorentz model). \( \varepsilon_1 \) shifts to higher energy with \( x \), supporting the increase in \( \hbar \omega_p \) with \( x \).

Figure 8.6 shows the variation in \( \varepsilon_2 \) with increasing \( x \). The \( \varepsilon_2 \) spectra obtained for \( x=0.01 \) is typical of the spectra from a-Si:H (see for example Sotiropoulos and Weiser 1987 and Connell 1979). As \( x \) increases the peak at 4eV broadens and its centre of gravity shifts to higher energies.

From the \( \varepsilon_2 \) spectra the optical joint density of states (OJDOS) were determined by assuming constant matrix elements and are shown in figure 8.7. It can be seen that for \( x>0.6 \) the peak at 4eV associated with transitions from Si-Si levels weakens and a peak at \(-11eV\) from N2p\(_2\) levels evolves slowly, as already suggested previously in chapter seven (see also Davis, Piggins and Bayliss 1987). Above \( x=1 \) the 4eV peak has almost vanished and hence the number of Si-Si bonds has decreased sharply: by alloying we expect either a shift of the 4eV peak to higher energies if the different bonds mix or the appearance of new features in the spectra if there is little intermixing between the Si-Si and nitrogen states.
Figure 8.4 Effective number of electrons taking part in optical transitions for glow discharge a-Si:H.
Figure 8.5 Epsilon 1 for glow discharge a-SiN$_x$:H

Increasing Nitrogen Content
Figure 8.7: Joint Density of States for Glow Discharge a-SiN_x.
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The results indicate that nitrogen atoms do not simply replace silicon atoms in a tetrahedrally coordinated lattice because such a model predicts a majority of Si–N bonds at \( x = 0.44 \) and the peak in the OJDOS should have shifted to higher energies. For the case of little mixing, a new peak should be seen at higher energies, together with a rapid decrease in the peak at 4eV. This is the case however for \( x \approx 1 \) and so suggests that the structure is more like an ordered bond network rather than a random bond network (Piggins et. al. 1987) at high nitrogen concentrations. Similar effects were seen by Sotiropoulos and Weiser (1987) in a-Si\(_{1-x}\)C\(_x\):H alloys, and were attributed to the effect of hydrogenation of the carbon in a silicon lattice for low \( x \). Thus the carbon has little effect on the silicon–silicon states because it bonds with the hydrogen. This effect of hydrogenation at low \( x \) is not found in Si\(_N\)\(_x\)(:H). However, for \( x > 0.6 \) it seems as though a new electronic structure does exist with much mixing of the silicon and nitrogen levels, since a gradual shift in position of the peak in the OJDOS from 4eV to ~8eV occurs for \( x \approx 0.6 \) to 1.4 respectively.

Shown in figure 8.8 is the optical joint density of states when the Penn model is used to describe the matrix elements. The only observed difference between figures 8.7 and 8.8 is a faster reduction in the OJDOS at energies higher than the main peak when the Penn model is used to describe the matrix elements.
Figure 8.8 JOINT DENSITY OF STATES FOR GLOW DISCHARGE a-Si$_x$N$_{1-x}$
(Assuming the matrix elements are given by the Penn Model)
CHAPTER NINE

SUMMARY and CONCLUSIONS

9.1 Introduction

9.2 Summary

9.3 Suggestions for Further Work
CHAPTER NINE

SUMMARY AND CONCLUSIONS

9.1 Introduction

This chapter contains a summary of the results arising from the present work. For an in-depth discussion of the results, the reader should refer to the relevant chapter. Some suggestions for further work are also presented.

9.2 Summary

Photoemission measurements were made on a-Si$_{1-x}$N$_x$ (:H) to investigate both core-level and valence-band spectra. Core-level spectra exhibit a monotonic shift of all levels to higher binding energies as $x$ is increased, although the shift in the N 1s level is smaller than that for the Si 2p and Si 2s levels. From the plasma energies the density of the films was determined and was found to increase with nitrogen content $x$, in contrast to the results of Karcher et. al. (1984).

Valence-band studies by photoemission were not successful owing to the insulating nature of silicon nitride and the limitation of having only one photoexcitation energy (HeI line).

ESR results using glow-discharge films showed an increase in the number of dangling bonds with $x$ up to $x=1.0$. No further rise was observed for $x>1.0$ and a rapid decrease was seen when $x=1.3$. The reason for this rapid decrease is still unclear, but it is generally agreed that hydrogen plays no part in it. A possible explanation could be the conversion of Si$_3^-$ centres to Si$_3^+$ via electron transfer to the nitrogen dangling bond states. However an LESR signal, predicted by this model, was not found. Sputtered hydrogenated films deposited at 200°C show a similar behaviour whereas hydrogenated and unhydrogenated films deposited at room temperature show a less marked behaviour with $x$. 

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Trends in the infra-red results were found to be similar to those of other workers with the SiH stretching mode shifting to higher wavenumbers with increasing x. There is evidence that the hydrogen content of the films, determined from the SiH stretching mode, may increase with x up to x = 0.7, after which point the hydrogen concentration decreases.

The incorporation of nitrogen into a-Si:H leads to a monotonic increase in the band gap $E_T$. At first the gap increases slowly, from 1.7eV in a-Si:H, up to -2.0eV for when x = 0.7, at which point any further increase in x leads to a rapid opening of the gap. Results for hydrogenated films prepared by sputtering are similar to those obtained from films deposited by the glow-discharge technique.

The relationship proposed by Wemple and DiDomenico (1971) to describe the wavelength dependence of the refractive index, and from which a single oscillator energy $E_0$ can be found, was obeyed by all alloys regardless of the composition or hydrogen content. The single oscillator energy $E_0$ was found to be about 3.5eV for a-Si:H and corresponds to the difference between the Si2p states and the bottom of the conduction band as determined from photoemission. With increasing x, $E_0$ is found to increase at a greater rate than the band gap, suggesting that the centre of gravity of the valence band density of states shifts to lower energies much faster than the band edge. One explanation would be the emergence of lower lying nitrogen-related features in the DOS, thereby leading to a lowering in energy of the centre of gravity in the valence band.

The optical joint density of states derived from ultraviolet reflection measurements tend to support this explanation for the behaviour of $E_0$ with increasing nitrogen content. As the concentration of nitrogen in the films is gradually increased, the peak in the optical joint density of states (ODJOS) at 4eV (associated with transitions from Si-Si levels), weakens and a new peak at 11eV from N 2px levels evolves slowly.

Because the peak in the OJDOS does not rapidly decrease or shift to
higher energies for $x < 1$ we predict that nitrogen atoms do not simply replace the silicon atoms randomly in a tetrahedrally coordinated network. Such a model predicts a majority of Si–N bonds at $x=0.44$ and so the peak in the OJDOS should have shifted to higher energies for this composition. However when $x \geq 1$ there is a rapid decrease in the peak at 4eV, suggesting that the structure is now more like an ordered bond network.

It can easily be shown that for a random bond network the number of Si–Si bonds is overtaken by the number Si–N bonds at 41% ($x=0.67$) whereas for the ordered bond network, Si–N bonds outnumber Si–Si bonds at 31% ($x=0.44$) (see figure 9.1).

![Figure 9.1](attachment:image.png)

**Figure 9.1.** Number of bonds per atom of each type present in $\text{SiN}_x$ ($\text{Si}_{1-y} \text{N}_y$) as a function of $x$ ($y$) according to the random bond network (---) and the ordered bond network (—) models. For the RBN: $\text{Si-Si} = 8(1-y)/(4-y)$; $\text{Si-N} = 2y(1-y)/(4-y)$; $\text{N-N} = 9y^2/(4-y)$. (After Piggins et al 1987)

The Penn gap $E_g$ increases monotonically with increasing $x$ and could possibly be used to define the degree of ionic character the Si–N bond has.
The dependence of the dispersion energy \( E_d \) with alloying has been determined from the long wavelength refractive index \( n(0) \) and the single oscillator energy \( E_0 \) and is found to decrease with \( x \). The observed non-linear decrease in \( E_d \) with increasing \( x \) is not expected according to the simple expression proposed by Wemple and DiDomenico (1971).

From the compositional dependence of the infra-red, photoemission and reflection measurements it can be inferred that the films are homogenous and do not consist of phase-separated regions.

The importance of hydrogen in determining the properties of a-Si\( N_x \) gradually decreases with increasing \( x \), as shown by the optical and conductivity measurement.

In conclusion figure 9.2 shows a schematic illustration of the density of states for a-Si\( N_x \):H it also illustrates the silicon and nitrogen dangling bonds.

9.3 Suggestions for Further Work

An understanding of the dependence of the spin density with nitrogen content has yet to be fully resolved. Work is in hand to try and understand why \( N_s \) decreases rapidly for stoichiometric films and if the origin of the decrease is indeed due to a conversion of \( \text{Si}_3^0 \) defect centres to \( \text{Si}_3^+ \) via the nitrogen dangling bond or if there is some other mechanism. It may be possible to observe a small signal from stoichiometric \( \text{Si}_3 N_4 \) if larger quantities of sample are used.

Results from ESR should be related to defect concentrations obtainable from other experiments such as luminescence and photothermal deflection spectroscopy (PDS) to see if a corresponding decrease in the number of defects is also observed for near stoichiometric films. Stewart and Jones
(1988) however, have made some PDS measurements on a-SiN$_x$ films prepared by the glow-discharge technique and found that $N_S$ has the same variation with $x$ as found by ESR but is approximately a factor of eight times lower.
APPENDIX

Reflection measurements along with $n_{\text{eff}}$, $\varepsilon_2$ and the ODJOS from sputtered films are presented below for comparison and completeness sake. It was felt that it was not necessary to show these results in the corresponding chapter as they do not really contribute anything more to the discussion of the electronic properties of the material.
Figure A1. REFLECTION OF SPUTTERED a-Si$_x$H (With $H_2$)
Figure A3. EFFECTIVE NUMBER OF ELECTRONS TAKING PART IN OPTICAL TRANSITIONS FOR SPUTTERED a-Si\textsubscript{N\textsubscript{x}:H}
Figure A4. Effective number of electrons taking part in optical transitions for sputtered a-SiN$_x$ (No H$_2$).
Figure A7. JOINT DENSITY OF STATES FOR SPUTTERED a-SiN$_x$:H$_2$
REFERENCES
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REFERENCES


PHILLIPS J C (1973) in Bonds and Bands in Semiconductors (Academic Press,
New York).


1394.


Telecommunications, Vol. 16 Amorphous Semiconductors, Ed. Hanakawa
(North Holland, Amsterdam) p.21.


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REFERENCES


A STUDY OF

THE OPTICAL AND ELECTRONIC PROPERTIES OF AMORPHOUS SILICON NITRIDE

by N. Piggins

ABSTRACT

Amorphous a-Si$_x$N$_{3-x}$(:H) films have been prepared by radio-frequency sputtering in an argon-nitrogen-hydrogen atmosphere. Both hydrogenated and non-hydrogenated films were studied along with films prepared by the glow-discharge decomposition of a gaseous mixture of silane and ammonia.

Photoemission experiments were performed on the sputtered samples. The position and strength of the core levels were determined, along with the plasma energies as a function of $x$.

A comprehensive study of the number and types of defects present within a-SiN(:H) was undertaken. Films sputtered at room temperature and at 200°C, both with and without hydrogen, were studied along with films prepared by the glow-discharge technique. The results obtained are discussed in the light of existing models.

Certain characteristic energies obtainable from optical data have been found for hydrogenated and non-hydrogenated films. These results are then related to other experimental results, in particular those from photoemission measurements.

Reflection measurements have been made in the range 0.5eV to 12eV on the sputtered and glow-discharge films. From the reflection measurements $\varepsilon_2$ spectra were determined by Kramers-Kronig analysis. The dependence of the optical joint density of states with alloying was found from the $\varepsilon_2$ data. It was found from these measurements that the top of the valence band gradually changes from Si3p states to N 2p$_z$ states.