Structure and Properties of Amorphous Ge$_x$Se$_{1-x}$ and Related Alloys

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

by

Jaeho Choi  BSc. (Seoul)
Department of Physics and Astronomy
University of Leicester

December 1996
To my parents
Structure and Properties of Amorphous Ge$_x$Se$_{1-x}$ and Related Alloys

Abstract

Un-hydrogenated and hydrogenated a-Ge$_x$Se$_{1-x}$ films (0.2<x<1) have been prepared by radio-frequency sputtering at room temperature employing an r.f. power of 240 W and an Ar pressure of 3-6 mTorr. Zn-alloyed films, a-Ge$_x$Se$_y$Zn$_z$, were deposited under the same conditions, with Zn concentrations up to 27%. The compositions of the films were determined by an energy dispersive X-ray analyser (SEM-EDAX) attached to a scanning electron microscope.

Optical absorption edges of the a-Ge$_x$Se$_{1-x}$ samples have been deduced from reflection-transmission (R-T) spectra and photo-thermal deflection spectroscopy (PDS) measurements. The optical bandgaps, other parameters related to the edges, and the real part of the refractive index were determined and analysed. The effects of hydrogenation on the a-Ge$_x$Se$_{1-x}$ films are investigated by analysing their optical absorption edges and measurements of the d.c. electrical conductivity as a function of temperature.

The optical and electrical properties of a-Ge$_x$Se$_y$Zn$_z$ films were studied and the effects of Zn addition to GeSe films analysed from the behaviour of the optical gap and the activation energy in the d.c. electrical conductivity.

Extended X-ray absorption fine structure (EXAFS) measurements have been performed on both a-Ge$_x$Se$_{1-x}$ and a-Ge$_x$Se$_y$Zn$_z$ films. Information on the local atomic structure, e.g. the nearest-neighbour bond length and the coordination number, has been extracted from the data and is discussed in detail. In particular, the experimentally determined partial coordination numbers are compared with those predicted by two models, the chemically ordered bond network (OBN) and random bond network (RBN) structures. The results reveal that the a-Ge$_x$Se$_{1-x}$ films have a chemically ordered 4-2 covalent bond network structure throughout the whole composition range and that Zn replaces the Ge atoms and is four-fold coordinated.

The dielectric functions of the a-Ge$_x$Se$_{1-x}$ alloys is modelled and the calculated optical properties compared with the experimental results. Good agreement is found.
Acknowledgements

I am most grateful to my supervisor, Professor E. A. Davis, for his guidance, encouragement and support throughout the course of this research. His patience and assistance, especially during the writing of the thesis, are very much appreciated.

I would like to express my gratitude to Dr. S. J. Gurman for introducing me to the Daresbury Laboratory and its facilities. His guidance in analysing EXAFS data and his considerable assistance with the modelling described in § 6.4 are gratefully acknowledged.

I would like to thank to Dr. A. Singh, Dr. S. H. Baker, Dr. N. Elgun, Dr. B. T. Williams and Mr. M. Kay for valuable discussions and kind assistance when it was needed. Many thanks are also due to Mr. G. L. C. McTurk for the SEM-EDAX measurements, and to Mr. S. Thornton and the staff of the Electronic and Mechanical Workshops for technical assistance.

I wish to send my sincere love and gratitude to my parents. Without their patience, understanding and financial support, this work would not have been completed.

Finally, I thank my wife, Hae-Kyung, for her self-sacrificing support and bearing with me for such a long time, and to my little son, Uh-Young, who has been a great source of moral support.
Structure and Properties of Amorphous Ge\textsubscript{x}Se\textsubscript{1-x} and Related Alloys

Abstract
Acknowledgements
Contents

Chapter 1  General introduction

1.1 Amorphous solids 2
1.2 Applications of amorphous solids 3
1.3 Preparation of amorphous solids 5
  1.3.1 Melt-quenching 5
  1.3.2 Thermal evaporation 6
  1.3.3 Sputtering 7
  1.3.4 Glow-discharge decomposition 8
  1.3.5 Chemical vapour decomposition 8
1.4 Classification of amorphous semiconductors 9
1.5 Chalcogenide glasses 10

Chapter 2  Theoretical background 12

2.1 Effects of disorder 13
2.2 Localization 14
2.3 Band models for amorphous materials 16
2.4 Defects and their electronic structure 18
  2.4.2 Lattice relaxation at defects 18
  2.4.3 Correlation energies 20
2.5 Optical properties 21
  2.5.1 Definition of absorption coefficient 21
  2.5.2 Fundamental absorption edges 23
  2.5.3 Various markers for the optical bandgap 25
2.6 Electronic transport 26
  2.6.1 Extended-state conduction 26
  2.6.2 Band tail conduction 27
  2.6.3 Variable-range hopping conduction 28
    at the Fermi energy
2.7 Thermoelectric power 28
2.8 The Hall effect 29

Chapter 3 Ge$_x$Se$_{1-x}$ glasses and amorphous thin films: a brief review 31

  3.1 Optical absorption 32
  3.2 Structure 33
    3.2.1 The Phillips' raft model 33
    3.2.2 Continuous random network model 35
    3.2.3 Structure-related works 37
  3.3 Density of states 41
  3.4 Photo-induced effects 44

Chapter 4 Sample preparation techniques 47

  4.1 Radio-frequency sputtering 48
5.1.5 Data analysis 68
5.2 Infra-red spectroscopy 69
5.3 Scanning electron microscopy with EDAX 72
5.4 Optical measurements 73
  5.4.1 Reflection-Transmission spectroscopy 73
  5.4.2 Refractive index and film thickness 73
  5.4.3 High absorption coefficients 76
  5.4.4 Photothermal Deflection Spectroscopy 77
    5.4.4.1 Introduction 77
    5.4.4.2 Theory 78
    5.4.4.3 Experimental setup 82
    5.4.4.4 Measurement and signal analysis 86
5.5 D.c electrical conductivity measurements 88

Chapter 6 Results: Optical and electrical properties of a-Ge\textsubscript{x}Se\textsubscript{1-x} and related alloy thin films 90

6.1 Optical properties of a-Ge\textsubscript{x}Se\textsubscript{1-x} thin films 91
  6.1.1 Optical absorption edges 91
  6.1.2 Refractive index 93
  6.1.3 PDS data 96
6.2 Effect of hydrogenation 96
6.3 Ternary alloys of a-Ge\textsubscript{x}Se\textsubscript{y}Zn\textsubscript{z} 98
6.4 Modelling the dielectric function 99
  6.4.1 Introduction 99
  6.4.2 Background theory 101
  6.4.3 Results 105
  6.4.4 Discussion 111
<table>
<thead>
<tr>
<th>Chapter 7</th>
<th>Results: Structural properties of a-Ge$<em>x$Se$</em>{1-x}$ and related alloy thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>EXAFS spectroscopy: a-Ge$<em>x$Se$</em>{1-x}$ thin films</td>
</tr>
<tr>
<td>7.2</td>
<td>EXAFS spectroscopy: a-Ge$_x$Se$<em>y$Zn$</em>{2}$ thin films</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 8</th>
<th>Summary and suggestions for future work</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Summary</td>
</tr>
<tr>
<td>8.2</td>
<td>Suggestions for future work</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>References</th>
</tr>
</thead>
</table>
Chapter 1  General introduction

1.1 Amorphous solids
1.2 Applications of amorphous solids
1.3 Preparation of amorphous solids
   1.3.1 Melt-quenching
   1.3.2 Thermal evaporation
   1.3.3 Sputtering
   1.3.4 Glow-discharge decomposition
   1.3.5 Chemical vapour decomposition
1.4 Classification of amorphous semiconductors
1.5 Chalcogenide glasses
1.1 Amorphous solids

The main research described in this thesis concerns the properties of amorphous alloys of germanium-selenium. Materials in this system are called chalcogenides which form a major class of non-crystalline or amorphous solids. What are amorphous solids and why are they important? Literally speaking, 'amorphous' describes materials that have no regular form or structure; in other words, they do not have long-range order in the positions of their atomic constituents. If we refer to amorphous solids as being 'disordered', we need a standard which can be called 'ordered'. The standard is the perfect crystal. In solid-state physics books, this is defined in the following way:

A perfect crystal is one in which the atoms (or groups of atoms or 'motifs') are arranged in a pattern that repeats periodically in three dimensions to an infinite extent.

If we follow this definition, even small concentrations of defects or other kind of perturbations from perfect crystallinity, for example, vibrational disorder, vacancies, dislocations, etc., should be considered. However, when we call a solid amorphous, we assume more drastic changes of crystallinity such as a large topological disorder of the atoms.

If amorphous materials do not have regularity in their atomic positions, how can we analyse their structure? Fortunately these materials still possess some degree of local order, such as bond lengths and bond angles, which remain similar to those in the crystalline counterparts. Hence several of the experimental techniques used for probing the structure of crystals, for example X-ray and electron diffraction as well as EXAFS, can still be used. If we remember that the short-range order
determines many semiconductor properties, such as electrical conductivities or optical absorption edges, we can easily realise how important it is to undertake research on amorphous counterparts of crystalline materials that have been used in device technology. Also when amorphous materials are used as commercial components in industrial markets, the benefit of low fabrication costs compared with crystalline materials is a distinct advantage. Thus research on amorphous materials has become a large activity in solid-state physics.

1.2 Applications of amorphous solids

Amorphous solids have been used in many applications for several decades. Silicate glasses can be regarded as one example of commonly used materials. Apart from this well known utilization, a variety of applications have been realized relatively recently following the discovery that many other types of material can be produced in amorphous form, i.e. as bulk glasses or thin films.

One world-wide current application is in the area of electrophotography, alternatively known as xerography, as used in document copying machines. The first material used in this application was a-Se in thin-film form. More recently this material has been replaced by a-Si:H (Shimizu 1985).

Spear and Le Comber (1976) discovered that a-Si:H could be doped either n-type or p-type when prepared by the glow-discharge decomposition method. This opened the horizon that a-Si:H could be used as the active elements in electronic devices. A review of recent works on electronic device applications of a-Si:H has been given by Hamakawa (1987).
We encounter small TV or notebook computer screens everyday. In these screens, TFTs (Thin Film Transistors) are used as switching elements. These TFTs have been made using a-Si:H thin films as the base material. A review of activities in this area has been given by Madan and Shaw (1988).

In addition we should not neglect the important usage of a-Si:H in solar cells, which directly convert sunlight to electrical power. This element is met in small personal calculators and for the generation of electricity in remote locations.

In the presence of an electric field or a concentration gradient, certain ions, such as Li⁺ or Ag⁺, can diffuse into oxide or chalcogenide glasses. This has made some amorphous materials useful in electrochemical applications. Solid-state batteries, displays or chemical sensors are representative examples of these. Gabano (1985) and Souquet (1988) have given reviews of research on solid-state batteries. Also Owen (1980) and Tohge and Tanaka (1986) have demonstrated useful examples of using chalcogenide glasses as chemical sensors.

More recently certain amorphous materials have been used in fibre optics. Special halide or chalcogenide glasses have shown good characteristics in this field.

In addition to the applications mentioned above, amorphous materials have been used for other purposes and have potential for new applications.
1.3 Preparation of amorphous materials

1.3.1 Melt-quenching

Cooling the molten form of certain materials sufficiently quickly can produce amorphous materials easily. This method is called melt-quenching. Materials made by this method have been termed 'glasses' in the past. However, glasses are not necessarily made only by this method and a more general definition of a glass is a material that exhibits a glass-transition temperature (Elliott 1984).

The melt-quenching method has the advantage of making amorphous materials easily by a continuous hardening of the melt, but it has the drawback that some portion of materials may be crystallized during the process. Therefore, a sufficiently high cooling rate is essential for precluding crystal nucleation and growth. This matter is discussed well in Turnbull (1969). The most usual way of producing samples is to seal the constituent elements in a fused silica ampoule under a good vacuum ($10^{-6}$ Torr), and to hold the melt for several hours in a rocking furnace at a sufficiently high temperature. The melt can be quenched by simply turning off the oven switch or plunging the ampoule into a liquid which has a high thermal conductivity and a high latent heat of vapourisation. Since the material produced in this manner normally is in the form of a rod or plug, for making thinner form it is sometimes compressed between two parallel plates after heating it up to beyond its glass-transition temperature.

In the case of metal samples, a faster cooling rate ($10^6$ Ks$^{-1}$) is required to prevent crystallisation. Such a method was achieved in the pioneering work of Duwez in 1959 (Klement et al 1960). The technique uses a copper chill-block to cool the melt rapidly by intimate contact. Alternatively the
melt is squirted on to a rapidly rotating copper wheel. However, these techniques cannot produce material in bulk form, but only as ribbons with a thickness of a few hundreds of microns.

1.3.2 Thermal evaporation

If a solid is heated above its vapourisation temperature in vacuum, it will evaporate and the atoms will travel in straight lines until they meet a suitable substrate in their path to condense upon. This is the principle of thermal evaporation which is perhaps the most widely used method to produce amorphous thin films because of its simplicity and fast deposition speed.

A typical arrangement is shown in Fig 1.1. Normally the vacuum chamber pressure is obtained by a diffusion pump with a liquid nitrogen trap to better than $10^{-6}$ Torr during the process. The boat between two electrodes contains the material either in powder or thin-foil form. High-melting-point metals, such as tungsten or molybdenum, are most commonly used as this boat material. A large d.c. current is applied between the electrodes. Since the vapour condenses onto a relatively cold substrate, the atoms are essentially frozen into random positions when they arrive. The large effective cooling rate ensures that crystallisation of the material is inhibited.

A major problem with conventional evaporation is the inhomogenous nature of the resulting films. Many factors influence this drawback, e.g. lack of control over substrate temperature, base gas pressure in the chamber, boat and filament temperature, etc. Also it is difficult to produce multicomponent alloys this way because of differences in the evaporation rates of the individual components. Flash evaporation, in which powdered material is dropped steadily on to a heated source thereby
almost instantaneously vapourising it, is sometimes used to overcome this problem.

Nevertheless, the technique can produce films of order of tens of microns thickness easily with good deposition rates of the order of 0.1-1.0 \( \mu m \) per second. Hence it has been used in commercial applications for several decades.

1.3.3 Sputtering

Sputtering is a popular method of deposition because of its versatility and ease of control over parameters for making a relatively homogeneous material.

The principle of sputtering is rather straightforward. Inert gas is introduced in a vacuum chamber and a plasma struck. Energetic ions from this plasma bombard a target and ejected atoms travel to a substrate where they are deposited.

There are three major types of sputtering; d.c. sputtering, radio-frequency sputtering and magnetron sputtering. The method chosen depends on target materials. D.c. sputtering is only feasible for metal targets, but r.f. sputtering can be used for either metallic or insulating materials (see Fig 1.2). Magnetron sputtering, in which a permanent magnet situated below the target concentrates the plasma bombardment of the target, is useful when high rates of deposition are required. The samples used in this work have been made by r.f. sputtering. Further details of the sputtering processes and the techniques used will be presented in Chapter 4.
Figure 1.1  Schematic illustration of a thermal evaporation chamber. B is a high-melting point metallic boat and S a substrate attached to a heater (H). The entire apparatus is placed in a vacuum chamber pumped to a high vacuum (V) (after Elliott 1984).

Figure 1.2  Schematic illustration of an r.f. sputtering apparatus. The r.f. power is applied between the target (T) electrode and the substrate (S) electrode. A sputtering gas is introduced into the chamber and a plasma (P) is struck. V is a vacuum system and H a substrate heater (after Elliott 1984).
1.3.4 Glow-discharge decomposition

This method is more complicated than the others mentioned above, and requires some knowledge of plasma chemistry. It has been recognised as a prominent technique for making a-Si:H films after the discovery by Spear and LeComber (1975) that high-quality material can be produced by this technique. In glow-discharge decomposition, a plasma in a gaseous derivative of the material to be deposited is used to decompose the gas. The reactant gas chosen depends on the prospective films; for example SiH$_4$ and GeH$_4$ are used for making a-Si films and a-Ge films respectively. Amorphous Si:H films can be doped either n-type or p-type by adding phosphine (PH$_3$) or diborane (B$_2$H$_6$) gases to the silane gas.

However this method also possesses disadvantages in that substrate temperature and the pressure of the reactant gases are very critical parameters. For a detailed review of the glow-dicharge process see Brodsky (1978).

1.3.5 Chemical vapour deposition

This technique is similar to glow-discharge decomposition in that the source material is in the form of a gas which is decomposed, in this case by thermal energy. Temperatures of order of 1000 K are commonly used. The process is often used for making polycrystalline materials, particularly silicon using SiH$_4$ as the gas. The method is also used for making high purity amorphous silica (SiO$_2$).
1.4 Classification of amorphous semiconductors

Generally speaking, most amorphous solids that can be prepared by cooling from the melt are insulators or wide-bandgap semiconductors in which the energy bandgap is greater than about 1 eV. For example, Se, As₂Se₃, similar chalcogenide compounds or multicomponent systems and the common borosilicate glasses are all included in the criteria. Exceptionally glassy metals, which also can be prepared from the melt by rapid cooling, are classified as conductors. Other materials such as Ge, Te, Si, B and InSb, which cannot be produced in the glassy state by melt-quenching, can be obtained in the amorphous form by deposition. The bandgaps of these materials are generally less than about 1 eV, but exceptionally oxide films are dielectrics.

At the present time, the most preferred scheme of classification is dividing amorphous semiconductors into groups which have the same short-range structural coordination. This scheme is based on the general rule (Ioffe and Regal 1960) that the first coordination number of the corresponding crystal is still preserved in many amorphous semiconductors. Actually if we consider several compositions which have no crystalline phase, the above rule seems to be meaningless, but it does suggest that, in the Ge-Se system for example, Ge-like structural units might be expected to be dominant at low concentration of Se, while at higher concentrations there may be a tendency to favour GeSe₂-like units. It means that at all compositions the natural coordination of each element is likely to be preserved. Some representative materials classified this scheme, based on coordination number, are presented in Table 1.1.

Another scheme of classification might be to group materials according to their amorphous structure; for example the group which is best described by continuous random networks or by close packing of atoms,
<table>
<thead>
<tr>
<th>Nearest-neighbour co-ordination</th>
<th>Type (column of periodic table)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>VI</td>
<td>Se, Te</td>
</tr>
<tr>
<td>3</td>
<td>V</td>
<td>As, Sb, P</td>
</tr>
<tr>
<td>3 and 4</td>
<td>IV</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>IV-IV</td>
<td>Ge, Si</td>
</tr>
<tr>
<td>4</td>
<td>III-V</td>
<td>(Ga, In) (P, As, Sb)</td>
</tr>
<tr>
<td>4</td>
<td>III-VI</td>
<td>(Ga, In) (S, Se, Te)</td>
</tr>
<tr>
<td>4</td>
<td>III-IV-V</td>
<td>(Cd, Zn) (Si, Ge, Sn)$_x$(As, P)$_2$</td>
</tr>
<tr>
<td>6</td>
<td>III</td>
<td>B</td>
</tr>
<tr>
<td>3-2</td>
<td>V-VI</td>
<td>(As, Sb, Bi)$_2$(S, Se, Te)$_3$</td>
</tr>
<tr>
<td>4-2</td>
<td>IV-VI</td>
<td>SiO$_2$, (Ge, Sn, Pb)(S, Se, Te)</td>
</tr>
</tbody>
</table>

**Table 1.1** Classification of amorphous semiconductors according to their nearest-neighbour coordinations (after Mott and Davis 1979).
etc. However, insufficient structural data exist to classify many materials properly by this scheme.

Fritzsche (1973) suggested another scheme, namely classification according to whether the uppermost valence band is made up of non-bonding (lone-pair) orbitals or not. Materials which contain a large amount of a two-fold coordinated chalcogenide element S, Se, Te, or O are examples of the former case. See § 3.3.

1.5 Chalcogenide glasses

Chalcogenide glasses are materials which contain chalcogens (S, Se, Te) as a major constituent. Mostly chalcogenide glasses are formed with elements from Groups III, IV, V and VI of the Periodic Table. Of the binary glasses, As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Te$_3$ have been most extensively studied and often regarded as prototypes of chalcogenide glasses. Mixed systems of binaries and ternary compounds have also been the subject of detailed investigations. For example, As$_{30}$Te$_{48}$Si$_{12}$Ge$_{10}$ has been studied in relation to electrical switching phenomena (Ovshinsky 1968).

The glass-forming regions of some ternary alloys are presented in Fig 1.3. Inside of the glass-forming boundary, amorphous samples can easily be obtained by the melt-quenching method, but samples with compositions outside of the boundary require deposition techniques, such as sputtering, in order to attain the amorphous form.

Generally speaking, chalcogenide glasses obey the so-called '8-N bonding rule' proposed by Mott (1969), in which the local coordination is equal to the valency N of the element concerned when N>4 and equal to N when N<4. Chalcogenides were extensively studied in the pioneering work of Kolomiets (1964).
Figure 1.3 Glass-forming regions in some ternary alloys: Ge-P-S (1), Ge-P-Se (2), Ge-P-Te (3), Si-As-Te (4), Si-P-Te (5) and Ge-As-Te (6) (after Borisova 1981).
It has been reported that chalcogenides containing several percent of elements such as Ni, W, Fe and Mo are highly conducting if prepared by the co-sputtering method (Ovshinsky 1977, Flasck et al 1977). In this thesis the effect of Zn addition to amorphous Ge-Se films is investigated.

Chalcogenide glasses generally exhibit high transmission in the infrared to much longer wavelengths than other types of glasses. This unique property together with their low melting characteristics and wide glass-forming compositions has motivated much of the early optical studies of these materials. Semiconductors with bandgaps in the near-infrared and visible region have also provided interest to several workers in this field. Recently photo-induced phenomena found in these material have motivated many research investigations (e.g. Owen et al 1985).
Chapter 2 Theoretical background

2.1 Effects of disorder
2.2 Localization
2.3 Band models for amorphous materials
2.4 Defects and their electronic structure
   2.4.2 Lattice relaxation at defects
   2.4.3 Correlation energies
2.5 Optical properties
   2.5.1 Definition of absorption coefficient
   2.5.2 Fundamental absorption edges
   2.5.3 Various markers for the optical bandgap
2.6 Electronic transport
   2.6.1 Extended-state conduction
   2.6.2 Band tail conduction
   2.6.3 Variable-range hopping conduction at the Fermi energy
2.7 Thermoelectric power
2.8 The Hall effect
2.1 Effects of disorder

In a perfect crystal, a mathematical approach to the behaviour of the electrons is relatively simple because the potential in which they move is periodic in space. The electrons can be described by the well-known Bloch wavefunction:

\[ \Psi_k(r) = \exp(ik \cdot r)u_k(r) \quad (2.1) \]

where \( \Psi_k(r) \) is an eigenfunction which describes electronic states with distinct energy and wavevector \( k \), \( u_k(r) \) has the periodicity of the crystal lattice:

\[ u_k(r+R_j) = u_k(r) \quad (2.2) \]

where \( R_j \) is lattice translation vector connecting lattice points. The lifetime of these Bloch states is limited by abrupt scattering caused by lattice vibrations or imperfections. Even in impure crystals, the mean free path of the electron, \( L \), is normally much greater than the lattice spacing, \( a \), (i.e. \( L \gg a \)).

The 'band structure' in \( k \)-space can be used for representing the allowed energies of the electrons. However, the free-electron energy, \( E(k) = \hbar^2 k^2 / 2m \), is distorted by the lattice potential which can be considered as arising from reflection of the electron wave by the lattice planes. This results in energy gaps at the edges of the 'Brillouin zone'. However in non-crystalline materials, the large topological disorder causes the electrons to have very short mean free path because of strong scattering. Therefore \( k \) cannot be considered as a good quantum number and the concept of \( k \)-space is no longer applicable for the states of the electrons in non-crystalline materials.
In other words, the Bloch state approach has to be abandoned and 'band structure' is a meaningless concept in amorphous materials.

However, the quantity that still remains valid as description of electron states in amorphous solids is the density of states. This can be written in the following form,

\[ g(E) = \frac{1}{V} \sum_n \delta(E - E_n) \]  \hspace{1cm} (2.3)

where \( g(E) \) is the density of the states per unit volume per unit energy interval and \( V \) is the volume of the system. The integrated density of states is the more often used quantity, which can be written in the form,

\[ N(E) = \int_{-\infty}^{E} g(E) \, dE \]  \hspace{1cm} (2.4)

Weaire and Thorpe (1971) first showed that if short-range interactions between electrons are dominant, the density of state is mainly determined by the short-range order. Details about the density of states will follow in a later section.

2.2 Localization

Sufficient disorder disturbs the periodic potential and enhances scattering of the electrons. This results in reducing the mean free path, \( L \). As the limiting condition \( L \approx a \) is approached, \( (a= \text{ interatomic distance}) \), the Bloch wavefunction lose their coherence and a fundamental change in the wavefunction, \( \psi \), occurs. Fig 2.1 shows this process of modulation of the wavefunction. The exponentially decaying envelope represents an electron that has become localized near a single atomic site. This was first recognised by Anderson (1958) and is known as Anderson localization.
Figure 2.1 Form of the wavefunction in the Anderson model: (a) when $L \sim a$; (b) when states are just non-localized ($E \geq E_c$); (c) when states are just localized ($E \leq E_c$); (d) strong localization (after Mott and Davis 1979).
quantitative criterion for localization will be described briefly. He uses the 
tight-binding approximation, so a crystalline array of potential wells forms 
a narrow band of levels as shown in Fig 2.2. Because the wells are far apart, 
we can assume that overlap between the atomic wavefunctions \( \phi(r) \) on 
adjacent wells is small. Then the Bloch wavefunction for an electron in 
the crystal is

\[
\psi_h(x, y, z) = \sum \exp(ik \cdot R_n) \phi(r-R_n) \tag{2.5}
\]

where the suffix \( n \) represents the \( n \)th well and \( R_n \) is its lattice site.

The bandwidth \( B \) in Fig 2.2 is given by \( B=2\pi I \), where \( z \) is the 
coordination number and \( I \) is the transfer integral, which is given by

\[
I = \int \phi^*(r-R_n) H \phi(r-R_{n+1}) \, d^3x \tag{2.6}
\]

where \( H \) is the Hamiltonian of the atomic wavefunction.

Now let us consider what happens to this band of energies when the 
potential energy function \( V \) is non-periodic. As is seen Fig 2.2. \( V_0 \) is the 
value which contributes to the deviation of \( V \) from its periodic value. If 
\( V_0 \) is small, the mean free path is large. For large \( V_0 \), the mean free path is 
reduced. By the Ioffe-Regel rule (Ioffe et al 1960), the shortest possible 
mean free path will arise in the case that the wavefunction loses phase 
memory in going from atom to atom. Then equation 2.5 is changed to 
have the form:

\[
\sum A_n \phi(r-R_n) \tag{2.7}
\]

where the amplitudes \( A_n \) have random phases and magnitudes (see Fig 
2.1a). If \( V_0/B \) is very large, the wavefunctions for each isolated well will
Figure 2.2 The Anderson model of the potential wells for (a) crystalline lattice and (b) an amorphous network. $V_0$ is the disorder potential and $N(E)$ the associated density of states (after Mott and Davis 1979).

Figure 2.3 Density of states in the Anderson model (after Mott and Davis 1979).
fall off exponentially with distance as in Fig 2.1c,d. Anderson concluded that if \( V_0/B \) is greater than a certain value, which is governed by coordination number \( z \), all the electron wavefunctions in the system decay with distance \( r \) from the neighbourhood of some well \( n \) as shown in Fig 2.1c. Hence instead of equation 2.7, the wavefunctions of the localized states have the following form:

\[
\sum A_n \phi(r-R_n) \exp(-\alpha r)
\]  

(2.8)

where \( A_n \) is the same coefficient as before. Anderson put forward the criterion for localization in his paper (Anderson 1958), namely the absence of diffusion at \( T=0 \). If an electron on a certain site in the band does not diffuse away after an infinite time interval, then the state is localized and has a finite probability of remaining at a distance \( r \). The probability is related to Eq 2.8. If there is a finite chance of diffusion at \( T=0 \), then the state is delocalized or extended. The energy separation between localized and non-localized states for the Anderson model is shown in Fig 2.3. In this there is no discontinuity in \( N(E) \) or its derivative at \( E_c \) (Thouless 1970). As the disorder increases, the energy values \( E_c \) and \( E_c' \) move towards each other and for a critical amount of disorder, all states in the bands become localized.

### 2.3 Band models for amorphous solids

The crystalline density of states shows steep features at the band edges. These become smeared out in materials with no long-range order. Furthermore, fluctuations in short-range order, such as bond-angle distortions, lead to 'tailing' of states into the gap at the band edges. Band tails are more prominent if chemical disorder, i.e. wrong bonds, exists.
Another main cause of band tailing can be the occurrence of short-range disorder in non-bonded atom distances. This is particularly important for chalcogen atoms in amorphous semiconductors, which have non-bonding lone-pair orbitals forming the top of the valence band. The interaction between lone-pair orbitals causes the energy states to be raised, producing tailing of states from the valence band edge into the gap.

Several models of the band structure of amorphous semiconductors have been proposed. The difference amongst them lies in the extent of the band tailing. Cohen, Fritzschke and Ovshinsky (1969) suggested a model in which band tailing is so pronounced that the valence and conduction band tails overlap in the middle (Fig 2.4). The energy difference \( E_c - E_v \) between the two mobility edges is known as the mobility gap which contains only localized states. However, amorphous solid semiconductors are transparent in the visible or infrared region so that the density of states must be low.

Davis and Mott (1970) suggested another model which is more applicable to amorphous semiconductors. In the Davis-Mott model, the band tailing is limited to a few tenths of an electron volt and the states are separated by \( E_c \) and \( E_v \) into localized and extended states. They showed that the electron mobility drops by several orders of magnitude producing a mobility edge at the transition from extended to localized states. The interval between the energies \( E_c \) and \( E_v \) is defined as a mobility gap, which is regarded as the counterpart of the band gap in crystalline semiconductors. Furthermore defects in the random network, such as dangling bonds or vacancies, etc., makes a narrow band in the middle of the band gap and the Fermi level \( E_F \) should be pinned by this. This defect level was later replaced by a donor and an acceptor band on either side of \( E_F \) (Fig 2.4). Supported by experimental evidence, the actual shape of the density of states of amorphous materials is suggested to be that there are
Figure 2.4 Various forms proposed for the density of states in amorphous semiconductors. Localized states are shown shaded. (a) the CFO model proposed by Cohen et al (1969); (b) a real gap in the density of states for an ideal amorphous semiconductors (Mott and Davis 1979); (c) the Davis and Mott model (Davis and Mott 1970); (d) the Mott model (Mott 1972).
various gap states which are split off from the tail states and are located at well-defined energies inside the gap.

2.4 Defects and their electronic structure

2.4.1 Defects in amorphous semiconductors

In a crystal any departure from the perfect crystalline lattice is a defect, which can be a point defect, such as a vacancy or interstitial, an extended defect, such as a dislocation, or an impurity. Since there is no perfect lattice in amorphous material, a different definition of a defect is required. By analogy with the crystal, a defect can be defined as a departure from the ideal amorphous network. A continuous random network can be regarded as this ideal amorphous network in which all the bonds are satisfied. In ideal a-GeSe$_2$ all the germanium atoms are four-fold coordinated and all the selenium atoms two-fold coordinated. Then a distinctly different bonding state from this ideal network will be regarded as a coordination defect. The three-fold coordinated germanium dangling bond in the ideal network is one example. However, in amorphous materials, small differences in local structure contained in the disorder of the ideal network cannot be meaningfully resolved. Thus amorphous materials have fewer separated classes of defects with their energy levels broadened by disorder. Fig 2.5 shows this behaviour.

2.4.2 Lattice relaxation at defects

The electronic properties of amorphous semiconductors are affected by defect states in the gap because their electron occupancy can be changed by doping or by trapping and excitation of carriers. Coupling between the
Figure 2.5 Comparison of general form of the defect gap state distribution in amorphous and crystalline semiconductors (after Street 1991).

Figure 2.6 Configurational coordinate diagram describing the capture and release of an electron from the conduction band into a defect state (after Street 1991).
bonding electrons and the gap state electrons influences the defect structure and its associated energy levels. Fig 2.6 describes the effect of lattice relaxation. Firstly, consider the trapping of an electron from the conduction band onto a defect level. The potential energy of the state in the conduction band consists of two terms, one is the energy, $E_c$, of the electron at the bottom of the conduction band, and the other is the additional energy of lattice vibrations. The simple harmonic oscillator approximation gives an energy,

$$E(q) = E_c + Aq^2$$  \hspace{1cm} (2.9)

where $q$ is a configurational coordinate, $A$ is the strength of the network vibrations, and the equilibrium state is at $q=0$. If an electron is captured by the defect, an energy $E_T$ is released, and the energy level of the defect state then lies at $E_T$ below the upper energy state. This gives an energy

$$E_{\text{defect}}(q) = E_c - E_T + Aq^2 - Bq$$  \hspace{1cm} (2.10)

where $B$ is the deformation potential introduced from this interaction. Solving equation 2.10 gives a new lower minimum value, $E_c-E_T-W$ (where, $W=B^2/4A$), at $q=B/2A$, rather than at $q=0$. Hence the electron-phonon coupling causes the network to relax to a new equilibrium configuration at a lower energy. Consequent upon this lattice relaxation, there exist different types of excitation between the lower and upper levels. The dominant defect electronic transitions are characterised by three energies, $E_T$, $E_T+W$, $E_T+2W$. Among them $E_T+W$ corresponds to thermal excitation, and the others to optical transitions.
2.4.3 Correlation energies

Each energy level of the defect in the band gap can be occupied by up to two electron by the Pauli exclusion principle. For a single defect, three possible charge states exist depending on the position of the Fermi level as shown in Fig 2.7. For example, when a dangling bond defect is occupied by an electron, the charge is neutral. If this dangling bond is occupied by none or by two electrons, the charge states become e+ or e' respectively. The electronic energy levels of the last two charged states are not the same, but are separated by the Coulomb energy

\[ U_c = \frac{e^2}{4\pi\varepsilon_0 r} \]  

(2.11)

where \( U_c \) is called the correlation energy and \( r \) is the effective separation between two electrons, roughly the localization length of the defect wavefunction. Another contribution to this correlation energy arises from the lattice relaxation at the defect. Hence the addition of the electron may lower the defect energy level by the amount \( W \) (see Fig 2.6). Therefore the total correlation energy should be

\[ U = \frac{e^2}{4\pi\varepsilon_0 r} - W \]  

(2.12)

If the second term of this equation is larger than the first term, the correlation energy will be negative. This concept of negative correlation energy was first introduced by Anderson (1975) and was proposed for defects in chalcogenide glasses by Street and Mott (1975).

If we denote the three different defect states as \( D^0, D^+, D^- \), where the signs denote the different charge states by introducing electrons. The transfer of charge between two neutral defects is described by the reaction
Figure 2.7 Illustration of one-electron and two-electron energy levels of a defect and four possible transitions to the conduction and valence bands. The charge state is indicated when the Fermi energy lies in the different energy ranges. The defect is assumed to be neutral when singly occupied, with a positive correlation energy, U (after Street 1991).

Figure 2.8 Ordering of the 1e and 2e energy levels for positive and negative correlation energy defects. The diagram indicates the charge state (D\(^0\), D\(^+\), D\(^-\)) when the Fermi energy is in the different energy regions. Note that there is never a large concentration of singly occupied negative U defects (after Street 1991).
The left-hand side of the reaction has the energy $2E_d$ by the energy definition in Fig 2.8, and the right-hand side of the equation involves the correlation energy $U$ because two electrons have to be put on one site. Hence if $U$ is positive, the left hand side is the lower energy state so that all the defects remain singly occupied. If the $U$ is negative, the opposite is the case and equal densities of $D^+$ and $D^-$ are created exothermically. This can explain why ESR signals (related to paramagnetism) cannot be observed in materials which have negative-$U$ defects.

The two types of defect can be compared briefly in the following way: For positive-$U$ defects singly occupied paramagnetic states lie at a lower energy than doubly occupied states. For the negative-$U$ defects, the opposite is the case, with doubly occupied diamagnetic states being favoured. In the latter case the Fermi energy is strongly pinned between the two energy levels.

2.5 Optical properties

2.5.1 Definition of absorption coefficient

Let us consider the effect of a monochromatic plane wave of angular frequency $\omega$ and wavevector $q$ travelling through an absorbing medium. The electric field $E$ will cause forced oscillations of the atoms. If the wavelength is much longer than the interatomic distances, the perturbing effect of the electromagnetic wave will be very small. The relation between the macroscopic electric field $E$ and the electric polarization $P$ is linear. Hence

$$2D^0 \leftrightarrow D^+ + D^- \quad (2.13)$$
\[ D = E + 4\pi P = \varepsilon E \]  \hspace{1cm} (2.14)

where \( \varepsilon \) is the complex dielectric constant, which represents the response of the medium to the electromagnetic field. If \( n \) is the complex refractive index, then

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 = n^2 = (n^2 - k^2) + 2i nk \]  \hspace{1cm} (2.15)

where \( n \) is the real part of the refractive index and \( k \) the extinction coefficient. The optical properties may also be expressed in terms of a complex optical conductivity in the following way.

\[ \sigma = \sigma_1 + i\sigma_2 ; \varepsilon_2 = 4\pi\sigma_1/\omega ; \varepsilon_1 = 1 + 4\pi\sigma_2/\omega \]  \hspace{1cm} (2.16)

The electric field in the absorbing medium can be described by the expression:

\[ E = E_0 \exp[-i(\omega t - qz)] \]  \hspace{1cm} (2.17)

where \( q \) is the complex propagation vector and \( |z| \) the distance travelled in the medium. This is the solution of Maxwell’s equations for the electromagnetic field, with magnetic permeability \( \mu = 1 \). If \( q^2 = \omega^2\varepsilon/c^2 \), this equation represents a plane wave travelling in the \( z \) direction with velocity \( c/n \), and attenuated as \( \exp[-\omega k z/c] = \exp[-2\pi k z/\lambda] \) :

\[ E_z = E_0 e \exp[-i(\omega t - nz/c)] \exp[-2\pi k z/\lambda] \]  \hspace{1cm} (2.18)
We shall speak of an absorption coefficient $\alpha$, defined by $\alpha = 4\pi k/\lambda$, which is related to the imaginary part of the dielectric constant $\varepsilon_2$ by $\alpha = \varepsilon_2 \omega / cn$. Since $\alpha$ is proportional to $\varepsilon_2 \omega$ when $n$ can be considered as constant, it is proportional to the fraction of energy absorbed by unit thickness.

**2.5.2 Fundamental absorption edge**

If a material is illuminated by an electromagnetic wave that has energy comparable to the bandgap of the material, a large absorption occurs. This absorption energy is related to the excitation of electrons from the valence band to the conduction band. The rapid rise in absorption is known as the fundamental absorption edge. In crystalline semiconductors, this is normally steep, but in amorphous semiconductors the edge is much broader. This is due to disorder-induced broadening of the conduction and valence bands. A typical example is shown in Fig 2.9. The absorption edge is divided into three regions for separate descriptions.

**Region I:** High absorption region

The optical parameter of most interest is the bandgap energy $E_0$. The precise location of the gap is somewhat vague because the band tail density of states decays continuously with energy. Tauc et al. (1966) introduced a simple model for the bandgap. It is assumed that $N(E)$ increases as a power law of energy, $(E-E_0c)^c$ from an extrapolated conduction band edge, $E_0c$, with a similar shape for the valence band. If the matrix elements are independent of energy, then the absorption near the gap is given from the joint density of states by
Figure 2.9  Typical shape of a fundamental absorption edge for amorphous materials. The three separate regions are discussed in the text.

Figure 2.10  Examples of absorption edges whose fundamental dependence on photon energy is given by Eq 2.20 (from Mott and Davis 1979).
where \( A \) is constant. When the band edges are both parabolic, this reduces to

\[
\hbar \omega \alpha(\hbar \omega) = A (\hbar \omega - E_0)^n \quad \text{with} \quad n = 2
\]

Experimentally it is found that the best value of \( n \) depends on the material. In chalcogenide glasses, \( n = 2 \) seems to give a best fit. Fig 2.10 shows some example of so-called Tauc plots. Extrapolating of this type of plot to \( \alpha = 0 \) gives a value for \( E_0 \), which is known as the Tauc gap. However, it is somewhat doubtful whether in reality \( E_0 \) represents a true value for the optical gap. Nevertheless, it is often used as a convenient marker for the purpose of monitoring the changes of gap with composition or temperature for example.

**Region II**: Exponential absorption region

Most amorphous semiconductors show a typical absorption behaviour in the region below the band gap energy which is exponential with photon energy.

\[
\alpha(\omega) = \alpha_0 \exp\left[-\Gamma(\frac{E_0}{\hbar \omega})\right]
\]

where \( \Gamma \) is a temperature-dependent constant, typically having values in the range 10-25 eV\(^{-1}\). This exponential energy-dependent region of the optical absorption is called the Urbach edge after its first observation in alkali halide crystals (Urbach 1953). In spite of several theories and models proposed to understand this behaviour, its origin is still uncertain. The
most successful model was given by Dow and Redfield (1970) who suggested that the exponential edge comes from an exciton transition which is broadened by disorder-induced internal electric fields. On this model the slope of the edge can be used as a monitor of the amount of disorder present in an amorphous material. Cody (1984) emphasized that the Urbach-edge slope parameter $\Gamma^{-1}$ depends on the total amount of disorder in the system, but thermal and static disorder contributions cannot be separated in this way. The Urbach slope is often taken to represent the tailing of the density of states at the band edges.

**Region III**: Low absorption region

This low absorption region is believed to be related to transitions between impurity or defect levels. The region (where $\alpha < 10^4 \text{ cm}^{-1}$) is most difficult to study because the absorption is too small to be measured by conventional transmission-reflection spectroscopy. Photo-thermal deflection spectroscopy (PDS) is often used for probing this tail region. This technique will be described in detail in a later section.

### 2.5.3 Various markers for the optical bandgap

As was mentioned above, the optical bandgap of an amorphous material is not as distinct as that in its crystalline counterpart because of band tailing in the density of states. Several markers of the optical bandgap have been used for amorphous materials. The one most commonly used is $E_a$, which is defined as the photon energy at an absorption coefficient of $10^4 \text{ cm}^{-1}$ (Freeman and Paul 1978). The Tauc gap, which was described in the former section, is also used as a good marker. In most amorphous material these two values agree well. Another marker $E_{03}$, which is...
defined as a photon energy at the absorption coefficient is $10^3 \text{ cm}^{-1}$, sometimes shows better agreement with the Tauc gap for some sputtered films or glasses. Penn (1962) introduced another important marker called the 'Penn gap', relating the value with the static dielectric constant. A detailed explanation on this theory is discussed in Phillips (1973). The Penn gap is a measure of the energy separation between the 'centres of gravity' of the valence and conduction bands.

2.6 Electrical transport

Here, we will describe the principal electrical conduction mechanisms based on the Mott-Davis model. Each mechanism is dominant in different temperature regions. Illustration of three main conduction mechanisms expected in an amorphous semiconductor is shown in Fig 2.11.

2.6.1 Extended-state conduction

At high temperatures, thermally excited electrons move in extended states beyond the mobility edges and provide the contribution to electrical conduction. The general conductivity expression for any semiconductor is given by

$$\sigma = -e \int N(E) \mu(E) kT \frac{\partial f(E)}{\partial E} dE$$  (2.22)

where $N(E)$ is the density of state at energy $E$, $\mu(E)$ is the mobility of an electron at energy $E$ and $f(E)$ is the Fermi-Dirac function which is defined by
Figure 2.11 Illustration of the three main conduction mechanisms expected in an amorphous semiconductor.
f(E) = \frac{1}{1 + \exp[(E - E_F) / kT]} \quad (2.23)

Assuming a constant density of states and mobility, and considering conduction only by electrons excited beyond E_c, Eq 2.22 becomes

\sigma = \sigma_0 \exp[-(E_c - E_p)/kT] \quad (2.24)

where \sigma_0 = eN(E_c)kT\mu_c and can be estimated to be of the order of 10 to 10^3 (\Omega cm)^{-1}.

By analogy, if conduction occurs by holes in the valence band, the corresponding formula is

\sigma = eN(E_v)kT\mu_h \exp[-(E_F - E_v)/kT] \quad (2.25)

### 2.6.2 Band-tail conduction

At lower temperatures, thermal excitation may not be sufficient to contribute carriers in extended states. If electrons in the localized band-tail (at energy state between E_A and E_c) obtain sufficient energy \omega_i from their interactions with phonons, the electrons can hop from one site to neighbour sites in the band-tail. This process contributes to band-tail conduction, which is sometimes called thermally assisted hopping. The conductivity can be represented by the following.

\sigma = \sigma_i \exp[-(E_A - E_F + \omega_i)/kT] \quad (2.26)
where the pre-exponential factor $\sigma_1$ is several decades smaller than $\sigma_0$ in Eq 2.24 because of smaller density of states and lower carrier mobility compared with extended-state conduction.

2.6.3 Variable-range hopping conduction at the Fermi energy

At even lower temperatures, the dominant part for conduction will be lie at the Fermi energy assuming there is a finite density of states there. Conduction will occur by thermally assisted hopping between localized states. For temperatures such that $k_B T$ is less than the bandwidth of these states, conduction will be by variable-range hopping in which the hopping distance increases as the temperature is lowered. Such a process was proposed by Mott (1969) who derived the expression:

$$
\sigma = \sigma_3 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right]
$$

(2.27)

where $\sigma_3$ and $T_0$ are constants. For a density of states independent of energy, $T_0$ is given by $T_0 = 2(3/2\pi)^{1/4} [\alpha^3 / (k_B N(E_F))]^{1/4}$, where $\alpha$ is the inverse of the decay length of the localized wavefunction and $N(E_F)$ is the density of states at the Fermi energy. The process is characterised by a $T^{-1/4}$ temperature dependence of the logarithm of the conductivity and a plot of $\log \sigma$ versus $T^{-1/4}$ can be used to estimate $T_0$ and hence the density of states at $E_F$.

2.7 Thermoelectric power

Thermoelectric power (or thermopower for short) is another transport property which is closely related to the conductivity, $\sigma$. It possesses a great deal of information about transport mechanisms in amorphous
semiconductors. The Seebeck coefficient, $S$, is the constant of proportionality between the voltage and the temperature gradient which causes it. It is related to the Peltier coefficient, $\Pi$, which is the constant of proportionality between the heat flux transported by the electrons and the current density, by the equation $S=\Pi/T$. For the case of band conduction of electrons in extended states beyond $E_c$, the thermopower is given by Mott and Davis (1979) as

$$S_{\text{ext}} = -(k_B/|e|) \left[ \Delta E/(k_B T) - \gamma/k_B + 1 \right] \quad (2.28)$$

Hence it is immediately apparent that the slopes of the curves $\ln \sigma$ versus $1/T$ and $S$ versus $1/T$ should be same in the case of extended-state conduction. If both holes and electrons contribute to the conductivity, the thermopower can be written as a weighted sum:

$$S = (S_e \sigma_e + S_h \sigma_h) / (\sigma_e + \sigma_h) \quad (2.29)$$

The sign of the thermopower is reversed if holes dominantly carry the current. Hence the thermopower is a reliable guide to the nature of the dominant charge type, whether $n$- or $p$-type. For instance, most chalcogenide glasses exhibit a positive thermopower, indicating $p$-type conduction. Measurements of the thermopower can also be used to obtain a value for $\gamma$, the temperature coefficient of $(E_c-E_F)$, from the intercept of $S$ versus $1/T$ or the slope of $\Pi$ versus $T$.

### 2.8 The Hall effect

Measurement of the Hall voltage has been used as a complement to conductivity measurement in transport studies of crystalline...
semiconductors. If unipolar conduction occurs, the Hall coefficient provides a reliable estimate of the carrier concentration $n$ and the carrier type:

$$R_H = \frac{1}{ne}$$

(2.30)

$R_H$ is positive for holes and negative for electrons. This equation is valid only if the mean free path is sufficiently long for Boltzmann transport theory to apply and hence it is not appropriate for amorphous semiconductors. Moreover, it is found that the sign of $R_H$ is always opposite to that of the thermopower in many amorphous semiconductors. This sign anomaly is not understood in spite of several attempts to do so (Nebel et al 1996). In practice, the Hall effect is therefore less useful than the thermopower as a measurement for complementing conductivity data.
Chapter 3 Ge$_x$Se$_{1-x}$ glasses and amorphous thin films: a brief review

3.1 Optical absorption

3.2 Structure
   3.2.1 The Phillips’ raft model
   3.2.2 Continuous random network model
   3.2.3 Structure-related works

3.3 Density of states

3.4 Photo-induced effects
3.1 Optical absorption

Tronc et al (1973) reported the results of optical-absorption-edge measurements on Ge$_x$Se$_{1-x}$ glasses for the composition range 0<x<0.4. The absorption coefficients of Ge$_x$Se$_{1-x}$ glasses deduced from uv-visible spectra were plotted versus incident photon energy and are shown in Fig 3.1. They made a few immediate conclusions from the measured values of absorption coefficients: (i) For a given photon energy, the optical-absorption coefficient varies, in a monotonic way, versus x, between two definite compounds; it decreases from pure selenium to GeSe$_2$ and increases from GeSe$_2$ up to x=0.4. (ii) For a given photon energy, the absorption coefficient is small for amorphous GeSe$_2$ compared to amorphous selenium. (iii) The absorption curves for amorphous and crystalline GeSe$_2$ differ much more than do the corresponding curves for amorphous selenium and its crystalline varieties.

Kotkata et al (1993) obtained the optical absorption edges of as-deposited evaporated a-Ge$_x$Se$_{1-x}$ films, with x=0, 0.2, 0.33, 0.43 and 0.5, from a combination of optical and PDS experiments (Fig 3.2). They analysed the results as a function of composition in terms of chemical ordering, strain-induced disorder and coordination defects, taking stoichiometric GeSe$_2$ compound as a reference. In contrast to bulk Se glass (which shows a fairly sharp exponential edge), no clear exponential edge region was observed for a-Se. This was interpreted in terms of a-Se films deposited from the vapour phase containing a much larger defect density than bulk glasses obtained by melt-quenching. They found that the low-energy absorption of a-Ge$_x$Se$_{1-x}$ films (x=0.2 and 0.33) was considerably smaller than that of a-Se, which indicated that the density of defects (introducing deep states in the gap of a-Se film) was drastically reduced by the incorporation of a sufficient proportion of Ge atoms. This result supports the formation of a chemically
Figure 3.1 Optical-absorption edges of Ge$_x$Se$_{1-x}$ glasses (after Tronc et al 1973).

Figure 3.2 Optical absorption coefficient spectra for a-Ge$_x$Se$_{1-x}$ films with $x=0, 20, 33, 43, 50$ and $100$ at. % (after Kotkata et al 1993).
ordered network consisting of GeSe$_{4/2}$ tetrahedral units connected by Se-Se bridges for $x<0.33$ (Feltz 1985), which should greatly reduce the number of under and over-coordinated Se defect sites.

3.2 Structure

3.2.1 Phillips' raft model

Phillips (1979) developed a general topological theory of glass formation, which led him and co-workers (Bridenbaugh et al 1979) to propose a molecular cluster model for the specific case of chalcogenide glasses. Here we briefly summarise the topological theory first, and then proceed to discuss his structural model. The theory starts from Kauzmann's (1948) interpretation of the glass transition, which proposes that a glass state is formed to avoid an entropy crisis when cooling conditions do not allow crystallisation to occur. Phillips proposed that the glass forming tendency was maximized when the number of constraints ($N_{co}$) experienced by each atom is equal to the number of degrees of freedom ($N_d$) available to it. The number of constraints per atom is related to the coordination number. A system for which the number of constraints outnumbers the number of degrees of freedom is over-constrained and cannot easily form a glass. Phillips considered the case of a binary alloy $A_xB_{1-x}$ with only short-range bonding interactions. The average coordination number $n$ is given by,

$$n = xN_{cn}(A) + (1-x)N_{cn}(B) \quad (3.1)$$

where $N_{cn}$ is the coordination number given by Mott's 8-N rule. For chalcogenide glasses, the local force field is almost completely determined
by covalent bond-stretching and bond-bending terms, so that the number of constraints \(N_{\text{co}}\) per atom can be written as

\[
N_{\text{co}}(n) = \frac{n}{2} + \frac{n(n - 1)}{2} = \frac{n^2}{2}, \quad n \leq N_d - 1
\]  

(3.2)

Note that Eq 3.2 is only true for \(n \leq N_d - 1\) (Döbler et al 1980). Otherwise, the number of constraints should be altered to (Thorpe 1983)

\[
N_{\text{co}}(n) = \frac{n}{2} + \frac{(N_d - 1)(2n - N_d)}{2}, \quad n \geq N_d - 1
\]  

(3.3)

The number of degrees of freedom per atom, for a system in three-dimensional space is \(N_d = 3\) and, from the above, glass formation is optimal if \(N_{\text{co}} = N_d\). For a Ge\(_x\)Se\(_{1-x}\) glass with \(N_d = 3\) and \(n \geq 2\), these conditions lead to yield a critical average coordination number \(n_c = 2.4\) by use of Eq 3.3 and a critical composition \(x_c = 0.2\) by use of Eq 3.1. For compositions with \(x \leq x_c\), the network is under-constrained and each atom can adopt the local environment found in related crystalline materials. For compositions with \(x > x_c\), the network becomes over-constrained, and Phillips considers that under these conditions, a fully three-dimensional network cannot be formed.

In support of this theory, Phillips cited the work of Azoulay et al (1975) who made qualitative measurements of 'glass-forming ability' as a function of composition in the Ge\(_x\)Se\(_{1-x}\) system, in terms of the minimum quench rates necessary to form a glass. A broad minimum was found at approximately the critical composition defined by Phillips, and the increase in minimum quench rates with increasing Ge content up to the GeSe\(_2\) composition was interpreted as being due to the over-constrained nature of the network.
Figure 3.3 The layer-crystal structure of β- (high temperature-) GeSe$_2$.
The larger circles are Se atoms (after Phillips 1981).

Figure 3.4 The medium-range structure in g-GeSe$_2$ by the outrigger-raft model proposed by Phillips. The larger circles are Se atoms (after Phillips 1981).
Phillips (1980,1981) proposed that in a Ge\textsubscript{y}Se\textsubscript{1-x} glass with x≥x\textsubscript{c}, the over-constrained nature of the network should be removed by the formation of molecular clusters, which are made up of layers in which atomic arrangements are similar to those found in the high-temperature (β) form of crystalline GeSe\textsubscript{2}. The structure of β-GeSe\textsubscript{2} was determined by Dittmar and Schäfer (1976), and has 48 atoms in a monoclinic unit cell, within which the atoms are arranged in two layers normal to the a\textsubscript{0}-axis, with a centre-to-centre interlayer separation of 5.93 Å. The atomic arrangements in one of these layers are shown in Fig 3.3. The structure of one of the inter-cluster layers proposed by Phillips is simply obtained by removing Ge atoms at the edge of the unit cell and replacing these by Se-Se bonds, as shown in Fig 3.4. Thus the long-range order in the b-direction is limited by the Se-Se terminations, although the method of termination of the layers in the a-direction is not specified. Bridenbaugh et al (1979) suggested, however, that in selenium-rich glasses, the 'rafts' of Fig 3.4 could polymerise with Se chains. Phillips (1980) also suggested that on a macroscopic scale, such glasses are made up of stacked rafts in the form of columns, which are interspersed with selenium-rich regions.

### 3.2.2 Continuous random network model

In chalcogenide glasses, interatomic forces are almost completely covalent in character, whereas in oxide and halide glasses ionic contributions are significantly larger. Therefore, chalcogenide glasses should provide a good example of a Continuous Random Network (CRN) structural model (Zachariasen 1932). In a CRN structure of a binary system such as Ge\textsubscript{y}Se\textsubscript{1-x}, the 8-N valence coordination rule is satisfied for both components and at all compositions; for instance in Ge\textsubscript{y}Se\textsubscript{1-x} every Ge atom would be 4-fold coordinated and every Se atom 2-fold coordinated at
any value of $x$. According to the degree of chemical order in bonding, the CRN model can be divided into two different types; one is a random bonded network model (RBN) and the other is a chemically ordered bond network model (OBN).

In the RBN model there is no chemical preference for one kind of bond over another, so that the distribution of bonds is purely statistical; in a-$\text{Ge}_x\text{Se}_{1-x}$, Ge-Ge, Ge-Se and Se-Se bonds are allowed at all compositions except $x=0$ and 1. Thus for a general 4:2 binary alloy ($A_xB_{1-x}$), the RBN model predicts the following relations for the numbers of different types of bond (Lucovsky et al 1977):

\begin{align}
N_{AA} &= 4(1-x)^2/(2-x) \\
N_{AB} &= 4x(1-x)/(2-x) \\
N_{BB} &= x^2/(2-x) \\
\end{align}

(3.4)

In the OBN model, it is assumed that the strongest heteropolar $A$-$B$ bonds are favoured; a completely chemically ordered phase occurs at the stoichiometric composition $x_c=N_a/(N_a+N_b)$ (where $N_a$ is the local coordination of $A$ atom; for example $N_{\text{Ge}}=4$). In contrast to the RBN model, only $A$-$A$ and $A$-$B$ bonds are allowed for $A$-rich compositions ($0<x<x_c$), and conversely only $B$-$B$ and $A$-$B$ bonds for $1>x>x_c$. Thus the bond statistics for the OBN model for a 4:2 binary $A_xB_{1-x}$ alloy are, for the $A$-rich region ($0<x<0.67$)

\begin{align}
N_{AA} &= 2-3x \\
N_{AB} &= 2x \\
N_{BB} &= 0 \\
\end{align}

(3.5)
Figure 3.5  Bond-counting statics for 4:2 networks (e.g. a-Ge$_x$Se$_{1-x}$) (after Lucovský et al 1979).
and for the B-rich region (1>x>0.67):

\[
\begin{align*}
N_{AA} &= 0 \\
N_{AB} &= 4(1-x) \\
N_{AA} &= 3x-2 \quad (3.6)
\end{align*}
\]

These bond-counting statistics are shown in Fig 3.5 (Lucovsky et al 1979). There is considerable evidence from vibrational spectra and other results that the OBN model is obeyed for the most part in most chalcogenide glasses, although some departures from chemical order can sometimes be detected (Elliott 1984).

3.2.3 Structure-related works

Several diffraction studies of Ge\textsubscript{x}Se\textsubscript{1-x} glasses and films have been reported in the literature, and in general, the results for the GeSe\textsubscript{2} composition have confirmed the close similarity of crystal and glass in terms of short-range order.

Fawcett et al (1972) reported electron diffraction data for a-Ge\textsubscript{x}Se\textsubscript{1-x} evaporated films in the composition range 0\leq x\leq 0.73. They compared their average coordination number data with those calculated for two structural models: one is a random covalent network model in which the average coordination of Ge and Se are four and two respectively and the other is a chain-crossing model (only valid when x<0.33) in which the Se chain structure is maintained but the four-fold tetrahedrally coordinated Ge atoms act as chain-crossing points. The results showed that the RBN model could be appropriate at Ge-rich compositions. Similar conclusions were drawn by Molnar and Dove (1974) in a higher resolution electron diffraction study. Malaurent et al. (1980) suggested a new structural model,
the so-called non-continuous chemically ordered random network structure, for Ge_xSe_{1-x} glasses in order to explain the first diffraction peak in their diffraction data. Network models containing 35-50 atoms for the x=0.22 composition were constructed, in which Ge atoms formed chain-crossing links. In the models, distortions of bond lengths and bond angles were not allowed, so that closed rings could not form and broken bonds were present. After several models were constructed in which various sequences of atoms were forbidden, it was found that the first diffraction peak could be expected on a model in which Ge-Ge bonds were forbidden but Ge-Se-Ge sequences were allowed.

Fuoss et al (1981), in a study of differential anomalous X-ray scattering, showed that Ge is four-fold and Se two-fold coordinated for a-GeSe_2. This is consistent with early extended X-ray absorption fine structure (EXAFS) study by Sayers et al (1974). Fuoss et al further reported that both the Ge and Se atoms are three-fold coordinated for amorphous GeSe.

Recently, Nukui et al (1987) reported an X-ray anomalous scattering study of two glass samples, Ge_{15}Se_{85} and Ge_{25}Se_{75}. The radial distribution functions (RDF) of two samples are shown in Fig 3.6. The areas under the first-neighbour peaks of the RDF in the former sample were found to be 3.9 atoms for Ge and 2.1 atoms for Se. The first-neighbour distances around Ge were found to be 2.36 Å and that around Se, 2.36 Å. In the latter sample, the Ge coordination was found to be 3.8 and the Se coordination 2.2. The first-neighbour distances around Ge and Se were found to be 2.39 Å and 2.37 Å, respectively. Hence the presented results suggest that the glasses of selenium-rich compositions should consist basically of four-fold coordination around Ge atoms and two-fold coordination around Se atoms.

Susman et al (1990) studied the structure of g-GeSe_2 by neutron scattering. They found close similarity of the short range order in
Figure 3.6  The radial distribution functions (RDFs) obtained from anomalous scattering for Ge\textsubscript{0.15}Se\textsubscript{0.85} and Ge\textsubscript{0.25}Se\textsubscript{0.75} glasses. The upper curves include the local atomic arrangements around Se atoms, while the lower curves include those around Ge atoms (after Nukui et al 1987).
crystalline and glassy GeSe₂, which is characterised by GeSe₄ tetrahedral structural units. In addition, their neutron scattering data provided direct evidence that edge-sharing tetrahedra are present in the glass in a similar proportion to that found in the crystal.

Ross and Bourgon (1969) determined the phase diagram for the GeₓSe₁₋ₓ system in the range x=0~0.67 and recently Borisova (1981) compiled a complete phase diagram from several sources (Fig 3.7). As seen in Fig 3.7, crystalline compounds occur at the two compositions, GeSe and GeSe₂, and GeSe₂ melts congruently at 740 °C at a local maximum of the liquidus. It was found that the glassy state in the GeSe₂-Se region is stable and that interaction of the components in the particular system, GeSe-GeSe₂, has a eutectic character; the composition of the eutectic corresponds to Se contents of 58-62 at.% and the melting point is ~580 °C. It was also found that the dissociation energies for the single bonds of Ge-Ge, Ge-Se and Se-Se are 46, 49 and 46 kcal/mole, respectively.

Measurements of the viscosity nearer the melting point in the composition range x=0~0.33 (Laugier et al 1977) suggest that at these temperatures the structure of the melt can be described by a chemically ordered chain-crossing model. Density and thermal expansion coefficient measurements lead to similar conclusions for glasses (Feltz et al 1977), since discontinuities in these properties at the Ge₂Se₃ composition would not be expected from a random covalent network but could be explained in terms of the onset of Ge-Ge-Ge sequences with increasing Ge content in a chemically ordered network.

Loehman et al (1972), in a scanning electron microscopy study, found no evidence for gross phase separation in melt-quenched GeSe₂ glass, while Noda and Arizumi (1976) found, in a similar study, that GeSe₂ films show a grain-like structure which can be removed by annealing at 300 °C, which they interpreted as being due to formation of a three-dimensional
Figure 3.7 Phase diagram of the Ge-Se system (after Borisova 1981).
continuous network. Additional evidence for a chemically ordered network is provided by the band structure calculations of Lannoo and Bensoussan (1977), who were able to predict optical absorption and bandgap variations as a function of x assuming this type of network structure. It is of interest to note that they also showed that the calculated band structure was dependent only on the short-range order parameters of the structural model.

Tronc et al (1973) carried out Raman scattering experiments on Ge_{x}Se_{1-x} glasses for the range 0≤x≤0.4. The experimental results obtained from the anti-Stokes spectra are shown in Fig 3.8. As seen in Fig 3.8, three Raman lines are located at about 195, 215 and 250 cm⁻¹. The line at 195 cm⁻¹, also appearing in crystalline GeSe₂, strongly increases with increasing Ge content; hence they interpreted the line as arising from the vibrational modes of the GeSe₄ tetrahedra. They also reported that the origin of the line at 215 cm⁻¹ was associated with the Ge-Se-Ge sequence, one of the allowed sequences of three atoms in their lattice model, and that the line at 250 cm⁻¹ found in Se-rich glasses could be attributed to Se-Se bonds since this was found to decrease to zero at the GeSe₂ composition.

Nemanich et al (1977) observed a similar splitting of lines at 202 cm⁻¹ and 219 cm⁻¹ (Fig 3.9). The former was again interpreted as a symmetric bond-stretching mode of the GeSe₄ tetrahedra, but the latter (found to decrease rapidly with x in the composition range 0<x<0.33) was interpreted as arising from 6-membered (i.e. Ge₆Se₆) rings. The origin of the so-called 'companion line' observed at 219 cm⁻¹ next to the main stretching mode of the GeSe₄ tetrahedra is controversial. The companion line is unusually narrow and is strongly polarized, and moreover shows an unusual compositional dependence of the intensity. Bridenbough et al (1979) suggested that the companion line should originate from the Se-Se bonds which terminate the molecular raft units postulated by Phillips (1981).
**Figure 3.8** Anti-Stokes Raman spectra of Ge$_x$Se$_{1-x}$ glasses (0≤x≤0.4) (after Tronc et al 1973).

**Figure 3.9** Raman (solid line) and depolarization (dashed line) spectra of a-Ge$_x$Se$_{1-x}$. Note the appearance of the 'companion' line at ≈ 220 cm$^{-1}$ with increasing Ge content (after Nemanich et al 1977).
the contrary, Sugai (1981) interpreted the companion line as arising from
the fourfold ring (Ge$_2$Se$_2$) which is the edge-shared unit in the Phillips'
raft model.

3.3 Density of States

A chemical viewpoint is useful to begin the analysis of the electronic
structure of amorphous solids. Here we start by illustrating the energy-
level diagrams of the two elemental components, germanium and
selenium, which eventually make a-Ge$_x$Se$_{1-x}$ compounds (Fig 3.10). Of the
32 electrons in a germanium atom, 28 occupy low-energy orbitals making
up the first three shells of states tightly bound to the Ge nucleus. These
'core electrons' normally do not take part in the chemical bonding. The
outer 4 electrons which occupy the two 4s states and two of the 4p states in
the atom, make four equivalent sp$^3$ hybrid orbitals which overlap with
neighbours to form two new orbitals, a bonding and an antibonding
orbital. In the solid, interactions between bonds broaden the bonding and
antibonding levels into two bands, namely the conduction and valence
bands. The band gap $E_g$ can be defined as the separation between the two
bands. Fig 3.10 (b) shows the energy-level diagram of solid selenium. A
selenium atom, having 34 electrons, has six outside of closed shells - two
4s and 4p electrons. The 4s electrons lie sufficiently deep in energy so that
they can be considered as part of the atomic core. Thus chemical action
takes place among the four 4p electrons. Two out of three orthogonal p-
function orbitals, each occupied by one electron, form the bonding state
and one of these orbitals is occupied by two paired electrons of opposite
spin. These electrons are referred to as nonbonding or lone-pair electrons,
which do not take part in the chemical bonding and also their energy is
nearly unaffected by bonding mechanisms. Because of these lone-pair
Figure 3.10  Bonding schematic for the electronic structure of (a) solid germanium and (b) selenium (after Zallen 1983).
electrons, the valence bands of chalcogenides normally form two separate bands.

From the above individual energy-level diagrams of germanium and selenium, Lannoo (1977) obtained the possible bond orbitals of a-Ge$_x$Se$_{1-x}$ by a molecular-orbital approximation (Lannoo 1973). The obtained molecular bond structure is shown with the calculated energy level in Fig 3.11, where $\tau$ represents the selenium lone-pair state and $A$, $B$ represent antibonding and bonding states respectively. The flat degenerate molecular levels presented in Fig 3.11 eventually widen into the bands when further interactions are included. This molecular energy-level diagram is closely related to the shape of the density of states (DOS) of the material. From the diagram we can expect that the DOS of the valence band should be made of several different groups originating from each bonding state.

Inspired by Lannoo's model, Louie (1982) calculated the density of states of c-GeSe$_2$ and g-GeSe$_2$ by a linear combination of Gaussian orbitals pseudopotential method (Louie 1980). The geometric structure of crystalline c-GeSe$_2$, the high-temperature form (Dittmar et al 1976), contains 48 atoms per unit cell and the crystal has a layer structure with two layers in a unit cell (see Fig 3.3). For calculating the DOS of g-GeSe$_2$, he employed the outrigger-raft model proposed by Phillips (1981). In this model the glass is made up of randomly oriented one dimensional-like rafts (ribbons) which are fragments of the high-temperature form of c-GeSe$_2$ (see Fig 3.4). The calculated densities of states for the two structures are presented in Fig 3.12. As expected from chemical consideration, valence-band states can be classified into groups with distinct bonding characteristic. We first discuss the crystalline result. The theoretical bandgap 3.0 eV agrees well with the experimental value of 2.7-2.8 eV (Aspnes et al 1981). The states with the highest binding energies in the region from -15 to -12 eV correspond to the Se 4s levels. Bonding between
Figure 3.11 Molecular levels and molecular orbitals in Ge₄Se₆₋ₓ (after Lanoo et al 1977).

Figure 3.12 Calculated density of states of c-GeSe₂ and the Phillips' raft model (after Louie 1982).
the Ge sp³ orbitals and the Se p orbitals gives rise to the Ge-Se bonding states at energies from -8 to -2 eV. The top of valence band A₁ should be formed by Se lone pairs and the bottom of the conduction bands from antibonding Ge-Se bond orbitals. As seen in Fig 3.12, the formation of Se-Se dimers in the raft structure changes significantly the electronic density of states from the crystalline distribution. Defect states arise near the valence band edges to make the fundamental bandgap smaller. The states near -11 eV are supposed to be made by bonding Se 4s dimer states. However the overall feature of the DOS still remains similar to crystalline DOS though it is somewhat weakened and broadened.

Fig 3.13 shows recent X-ray photoelectron spectroscopy data of crystalline, glass and amorphous GeSe₂ (Theye et al 1994). The overall feature of the valence-band spectra is in good agreement with Louie's calculated DOS. As expected from the calculated DOS, the subband C correspond to Se atomic-like s states and the subband B comes from combinations of bonding sp³ orbitals at Ge sites and p orbitals at Se sites. Two structures A₂ and A₃ in the upper subband are related to Ge-Se p bonding states and finally A₁ at the top of valence band corresponds to the Se lone pair states. As seen in Fig 3.13, three different kinds of GeSe₂ samples show nearly identical shapes of spectra. This implies that amorphous films or glass samples of stoichiometric GeSe₂ have nearly the same structure as the crystal. This result is also consistent with our optical bandgap data presented in Fig 6.2. We were unable to find any evidence of the predicted defect states, located near the valence band edge, which was presented in the calculated DOS of glass GeSe₂ (Fig 3.12) computed in terms of the raft-structure model. This result should be interpreted as slight evidence that the controversial outrigger-raft model cannot fully explain the structure of a-GeSe₂.
Figure 3.13 Comparison between the X-ray photoelectron valence-band spectra of as-deposited evaporated \( \text{a-GeSe}_2 \) (points a), \( \text{g-GeSe}_2 \) (points g) and \( \text{c-GeSe}_2 \) (points c) (after Theye 1994).

Figure 3.14 Comparison between the X-ray photoelectron valence-band spectra of two Ge-rich \( \text{a-Ge}_x \text{Se}_{100-x} \) compounds \((x=43\text{ and }50\text{ at.\%})\) and stoichiometric \( \text{a-GeSe}_2 \) \((x=33\text{ at.\%})\) (a.u., arbitrary units) (after Theye 1994).
As presented in § 6.1.1, our optical data on a-Ge\textsubscript{x}Se\textsubscript{1-x} films show the distinct feature that the optical bandgaps decrease as the Ge content increases in the films. It is therefore of interest to consider XPS data (Theye et al 1994) on Ge-rich a-Ge\textsubscript{x}Se\textsubscript{1-x} films and discuss this with reference to the a-GeSe\textsubscript{2} spectra. As seen in Fig 3.14, the top of the valence band, i.e. the lone-pair states, gradually decreases as the Ge concentration increase, which is entirely expected because the relative portions of Se should become smaller. The valence band edges do not show any distinct shifts as the Ge content increases. This result is also consistent with that our Urbach edge parameters on Ge-rich samples, which were found to be nearly constant in the Ge-rich region. Hence the large decrease of the optical bandgap of Ge-rich samples must be ascribed to a downward shift of the bottom of the conduction band. This follows if we recall that the bottom of the conduction band of a-GeSe\textsubscript{2} consists of antibonding Ge-Se orbitals (Louie 1982), which are likely to be affected by the introduction of excess Ge-Ge bonds.

3.4 Photo-induced effect

The various photo-induced phenomena have been observed in amorphous chalcogenide semiconductors, ranging from minor shifts in the optical absorption edge to a variety of physical and chemical changes (e.g. photo-polymerization, photo-crystallization, photo-enhanced dissolution of metals etc.) (see Tanaka 1981). These effects in chalcogenide glasses are of considerable technological importance, having applications in optical-imaging, hologram recording and optical mass memories (Shimizu et al 1975, Shirakawa et al 1975). However, the mechanisms of those effects mainly related with structural changes are not fully understood as yet.
Here we review some former researches on those effects found in and related with Ge\textsubscript{x}Se\textsubscript{1-x} glasses or amorphous thin films.

If chalcogenide semiconductors (containing Se or S) are illuminated by light of photon energy close to the optical bandgap, they normally exhibit photo-induced changes in local atomic structure, which are manifested mainly by small red-shifts in optical absorption edge (photo-darkening). Tanaka (1980) found the photo-induced reversible changes in amorphous Ge-Se compounds (particularly a-GeSe\textsubscript{2}). The term ‘reversible’ means that such changed structure revert back to the original state by annealing at the glass transition temperature. Since the photo-darkening was found to be sensitive to pressure, Tanaka suggested that van der Waals bonding may have a role in process (Tanaka 1983). Several mechanisms have been proposed for the reversible changes (Street 1977, Elliott 1986): intermolecular and intramolecular bond breaking and lattice distortion, or minor bond rearrangements involving the chalcogen atoms relaxing between the minima of double-well potentials. Recently, however, the role of oxygen in these effects has been highlighted. Tanaka et al (1984) observed that the magnitude of the photo-induced shift in absorption edge of GeS\textsubscript{2} film is strongly dependent on the ambient oxygen pressure, and found a Ge-O stretching mode at 800 cm\textsuperscript{-1}, after illumination in air, in the infrared absorption spectrum. Tichy et al (1986,1987) performed further experiments on normally deposited films of Ge\textsubscript{30}S\textsubscript{70} and confirmed the development of features in the IR spectra at ~ 800 cm\textsuperscript{-1} upon illumination in various atmospheres. They suggested that the introduced oxygen from air might replace the Ge in Ge-Ge bonds to make Ge-O bonds upon illumination.

Harshavardhan et al (1987) reported a large decrease in mass when 80°-deposited Ge\textsubscript{25}Se\textsubscript{75} films were illuminated in air. Their result on the fractional changes in mass and thickness, as a function of exposure time, is
Figure 3.15  Fractional mass and thickness decrease as a function of exposure time, for Ge$_{25}$Se$_{75}$ films, photoirradiated in air (after Harshavardhan et al 1987).

Figure 3.16  Evolution of infra-red difference spectra (after-before illumination in air) with doses (in units of 100 mW min cm$^2$) for an 80° film of a-GeSe$_2$. The inset shows the Ir. absorbance in the region of the main chalcogenide stretch frequency (after Spence et al 1989).
Figure 3.17 Optical-absorption changes [shift in $\lambda$ (T=10 %)] on illumination under different conditions for films of a-GeSe$_2$ deposited at various angles (after Spence et al 1989).

Figure 3.18 Plots of $(\alpha h\omega)^{1/2}$ versus $h\omega$ for films deposited at various angles before and after illumination for a-GeSe$_2$ (o, 5°, before illumination; •, after illumination; □, 80°, before illumination; ■, after illumination) (after Spence et al 1989).
shown in Fig 3.15. By X-ray photoemission spectroscopy and mass measurements, they suggested that the anomalous effects are a direct consequence of the loss of material from the film surface, as a result of photogenerated volatile high-vapour-pressure oxide fractions on the surface.

Spence et al (1989) further studied the nature of the photo-induced oxidation using films of amorphous GeSe$_2$ and GeSe$_3$ films deposited at various angles of incidence. As seen in Fig 3.16, the IR spectra show changes of features, after illumination, in two main regions; 700-1100 cm$^{-1}$, the region containing the Ge-O stretch frequencies and 200-450 cm$^{-1}$, the region containing the main chalcogenide stretch frequencies. The peak corresponding to the Ge-O stretch frequencies grows with increase of illumination time; meanwhile the peak corresponding to the Ge-Se stretch frequencies decreases slightly, which indicates an increase in the number of Ge-O bonds and a decrease in the number of Ge-Se bonds. These results are consistent with those of others (Tichy 1986, Tanaka et al 1984). Fig 3.17 shows the shifts of the wavelengths in uv-visible transmission spectra after illumination for a-GeSe$_2$ films deposited at various angles, and Fig 3.18 shows the changes of the well-known Tauc plots after illumination, showing the changes of the optical bandgaps (i.e. photobleaching or photodarkening effects) of a-GeSe$_2$ films (Spence et al 1989).
Chapter 4  Sample preparation techniques

4.1 Radio-frequency sputtering
4.2 Sputtering techniques
  4.2.1 Sputter deposition
  4.2.2 Sputter etching
  4.2.3 Bias sputtering
    4.2.3.1 Conventional
    4.2.3.2 Variable phase angle
    4.2.3.3 Substrate tuning
4.3 Leicester sputtering system
  4.3.1 The vacuum system
    4.3.1.1 The pumping system
    4.3.1.2 Other parts of the vacuum system
  4.3.2 The sputtering chamber
  4.3.3 The gas-flow control unit
  4.3.4 The r.f. power supply
4.4 The sputtering deposition rate
4.5 Sample preparation
  4.5.1 The target
  4.5.2 The substrate
  4.5.3 The film deposition procedure and conditions
4.6 Determination of film thickness
4.7 Determination of film composition
4.1 Radio-frequency sputtering

The principle of sputtering is to remove material from a target and to deposit it onto a substrate to form a coating. The component parts are contained within a vacuum chamber which is first evacuated to a low base pressure (say 10^{-6} Torr) prior to the introduction of argon. In d.c. sputtering, a potential difference is applied between the target and substrate and a plasma struck. Positive argon ions are driven to the target where they exchange energy with surface atoms which are then ejected into the plasma and on towards the substrate. If the target is an insulator, then d.c. charging of its surface leads to extinction of the plasma and no sputtering occurs. With radio-frequency sputtering, however, the target material can be either an electrical conductor or an insulator.

In r.f. sputtering, the voltage needs to be capacitively coupled to the target surface. This is done by including a capacitor in series with the electrical feed to the target when metal targets are used. An insulating target is normally bonded to a metal backing electrode which can be directly connected to an r.f. power supply as shown in Fig 4.1. Electrons are more mobile than positive ions, and therefore if an a.c. voltage is applied to the target, electrons are attracted to the front surface of the target during the positive half-cycle of the r.f. cycle, and positive ions during the negative-half cycle. Hence a resultant negative bias builds up on the target surface. Ions in the plasma are accelerated to the target by this bias potential (V_B) and bombard the target with an energy of the order of V_B electron volts. Several processes may occur following the ion impact (see Keller and Simons 1979). The ions penetrate the target and are brought to rest by colliding with the residual target atoms. Some target atoms may be emitted from the surface and travel through the plasma to the substrate, while some target atoms may be backscattered by the gas atoms. Among the
Figure 4.1 Schematic diagram of RF sputtering electrode arrangement and potential distribution.

Figure 4.2 Physical processes involved in sputtering.
atoms successively reaching the substrate, some atoms can be condensed to the substrate, but some highly energetic atoms may knock out the deposited material from the growing film to the plasma again (Fig 4.2). By applying a d.c. bias to the substrate electrode, the rate of the re-emission of target material from the substrates can be controlled to some degree. This application of a bias to the substrate electrode, known as bias sputtering, has been investigated by several workers (Tardy and Meaudre 1983).

4.2 Sputtering techniques

4.2.1 Sputter deposition

Two main types of sputter deposition are commonly used. One is sputter deposition onto a substrate which is grounded and in the other the substrate is not grounded. The latter technique can be performed with the whole work table electrically isolated from ground. The use of an electrically floating work table often results in a higher quality of film than obtained with a grounded substrate.

4.2.2 Sputter etching

The sputter etching process is used in situations where it is desired to remove some material from the substrates. This is a useful technique for cleaning a substrate prior to deposition. Sputter etching can also be used in place of wet chemical etching techniques in the processing of integrated circuits and similar devices to produce resistor and conductor patterns. Normal photolithography techniques are used to define a pattern in a photoresist prior to etching. Line definition of less than 1 µm is possible.
4.2.3 Bias sputtering

Bias sputtering is a process where the substrate which is receiving material from the target is simultaneously sputter etched. Normally the arrival rate of material from the target is greater than the etch rate at the substrate so that there is still net film growth. Careful control of arrival and removal rate of material permits the deposition of films with properties that are very close to those of the original bulk target material. One of the main effects of bias sputtering is to remove gas trapped in the deposition film. There are three main techniques of bias sputtering, which are conventional, variable phase angle and substrate tuning.

4.2.3.1 Conventional

With conventional bias sputtering, power from the r.f. power supply is split between the target electrode and the bias sputter electrode (the work table). A control facility is provided so that the ratio of target power to work table power can be varied. The phase angle between the voltage on the target and the voltage on the bias sputter electrode is normally fixed.

4.2.3.2 Variable phase angle

In conventional bias sputtering, the phase angle between the voltage of target electrode and the bias sputter electrode is normally fixed. The nature of the bias sputtering process is affected by the phase angle. For some applications, variation of this phase angle may be beneficial.
4.2.3.3 Substrate tuning

Substrate tuning is a technique for bias sputtering which does not require any r.f. power to be applied directly to the bias sputtering electrode. Instead of r.f. power, a variable inductor is connected between the floating work table and a grounded resonant circuit, which can be tuned to the operating frequency of the sputtering system. When it is so tuned, the induced voltage between the target and the work table will be at maximum. This voltage can be sufficient to cause weak sputter etching of the substrate.

4.3 Leicester sputtering system

All the films studied in the present work were prepared using a Nordiko NM-2000-T8-SE1 sputtering system, a schematic diagram of which is shown in Fig 4.3. Details of each component of the system will be described separately.

4.3.1 The vacuum system

The vacuum pumping arrangement associated with an r.f. sputtering system has to perform two main functions, which are to pump the chamber down to a sufficiently low pressure to remove unwanted gases to an acceptable level (typically between $10^{-6}$ and $10^{-5}$ Torr) and to maintain the vacuum chamber at a pressure of between $10^{-3}$ and $10^{-2}$ Torr during the sputtering process whilst the sputtering gas is being continually bled into the chamber. The pumping system mainly consists of a diffusion pump and a rotary pump.
Figure 4.3 Schematic diagram of the Leicester sputtering system.
4.3.1.1 The pumping system

The diffusion pump is the most widely used high vacuum pump in sputtering applications because of its proven reliability, simplicity and low cost. The pumping stack used in the Nordiko NM 2000-T8-SE1 consists of a 6 inch oil diffusion pump (Varian VHS-250 mm), a water-cooled chevron baffle, a quarter swing butterfly isolation valve and a liquid nitrogen trap. The nitrogen trap is usually placed between the high-vacuum isolation valve and the diffusion pump so that the trap is not exposed to air when the chamber is vented. The pumping speed of the diffusion pump is 1400 l s⁻¹ at maximum and 110 l s⁻¹ when the chamber opened. The pumping stack is connected to the chamber by typically a 200 mm length of 150 mm diameter pipe. The ultimate pressure in the chamber is typically 10⁻⁷ Torr.

A Leybold-Hereus D30A direct-drive rotary pump is used to maintain the backing pressure (i.e. the pressure at the outlet of the diffusion pump) at a level considerably below the critical backing pressure of the diffusion pump. If the critical backing pressure is exceeded, large amounts of oil vapour may diffuse up towards the chamber. For reducing this backstreaming of oil, a foreline trap in the line from the rotary pump to the diffusion pump is fitted on our installation.

4.3.1.2 Other parts of the vacuum system

To obtain the best possible vacuum (p < 1 x 10⁻⁷ Torr), liquid nitrogen is fed into a Meissner coil, which is made of copper tubing and is located around the substrate electrode. The Meissner coil trap reduces the amount of H₂O and OH left in the chamber.
An Edwards Penning 8 head is fitted to the chamber at an appropriate place so that the actual chamber pressure can be monitored during sputtering.

A VSW Vacuum Analyst (a quadruple mass spectrometer) can be used to examine the residual gases in the chamber before and after sputtering. Examining the gases during sputtering is not possible because the sputtering pressure is too high for the mass spectrometer to operate, and also the r.f. power interferes with the operation of the instrument.

4.3.2 The sputtering chamber

The chamber of the Nordiko NM-2000-T8-SE1 sputtering system, 24" diameter and 15.8" high, is made of stainless steel and has a front opening door. The chamber can be raised up to 16" by an electrically driven hoist for the convenience to access the chamber interior. The chamber contains a multi-electrode turret, a substrate shutter, a substrate electrode and accessories which are needed to fix a target and a substrate holder to the corresponding electrodes. The multi-electrode turret is composed of three electrodes, which are for an evaporation source, conventional sputtering and high-rate magnetron sputtering. Each electrode is surrounded by a stainless steel earth shield and isolated by PTFE insulation. The appropriate electrode can be selected by rotating the turret. During this work, the 8" diameter conventional sputtering electrode fitted with a 4" diameter polycrystalline Ge target and a stainless steel shield of the same diameter were used. The target was attached with silver-loaded epoxy on to an oxygen-free copper backing plate and screw which screwed into the sputtering electrode. The substrate electrode was 8" in diameter and its distance from the target could be adjusted from 1 to 5 cm. Throughout this work a distance of 5 cm was used. The substrate was held onto an 8"
diameter copper platen by a contact mask and the platen was then locked in position on the substrate electrode. A heating element was situated in the substrate electrode, and thin deformable copper gaskets were inserted between the platen and heater for better thermal contact. Control of the temperature was achieved by a Eurotherm temperature controller with a chromel-alumel thermocouple. The thermocouple was located into a hole drilled in the side of the substrate platen. With this arrangement, temperatures up to 400 °C could be achieved. Inbetween the target and substrate, a rotary shutter was located. Prior to film deposition the shutter could be moved into position to block the substrate in order to etch the substrate surface for cleaning purpose.

4.3.3 The gas-flow control unit

The sputtering gases (zero-grade 99.999% pure argon and hydrogen) flow into the chamber through stainless-steel pipes and a Vacuum General 78-7 flow-ratio and pressure control system. The absolute chamber pressure was measured by a Vacuum General CM capacitive manometer. The analogue signal from this gauge is fed to the control unit which operates piezoelectric valves to maintain the correct pressure and ratio of the gases. Since the control system was designed to handle two lines of gas supplies simultaneously, an extra gas-mixing vessel is needed for handling more than three types of gases.

4.3.4 The r.f. power supply

The r.f. power for sputtering is supplied by a crystal-controlled r.f. generator, which has a maximum power of 1.25 kW and fixed frequency of 13.56 MHz. The output impedance is designed to be 50 Ω so that a
matching conventional flexible cable is used for feeding the power from the generator to the electrode. The r.f. power is supplied to both the target electrode and substrate electrode simultaneously by a power divider so that the bias-sputtering can be performed. Two matching units are located outside of the chamber. Each matching unit has a tuning control and a d.c. voltmeter so that optimum tuning can be achieved by controlling the reflected and forward power. Power ratios between the substrate and target electrodes can be adjusted flexibly from 1:1 to 25:1 when bias sputtering is performed. During this procedure the substrate electrode was grounded, so the power was applied to the target electrode only.

4.4 The sputtering deposition rate

The deposition rate of a conventional r.f. sputtering system is often considered to be of prime importance. Although high deposition rate appears to be desirable in order to reduce the total sputtering time for the production of thin film, it sometimes causes unsatisfactory film properties. Therefore the optimum condition of sputtering rate should be considered in relation to other parameters such as the etch rate, r.f. power, target size and target-to-substrate separation.

In general the erosion rate of the target material will increase as the amount of r.f. power applied to the target electrode is increased. A typical curve of erosion rate versus r.f. power is shown in Fig 4.4. Since the curve shown in Fig 4.4 is essentially a straight line, the slope of the curve can be a useful comparative measure of erosion rates. The slope can be expressed in terms of erosion rate per unit of input power per unit area of target (e.g. Å min⁻¹/Wcm⁻²). Thus:

\[ E = \alpha P \] (4.1)
Figure 4.4 Etch (erosion) rate of silica versus r.f. power (Nordiko 1980).

Figure 4.5 'G' factor versus target diameter for various separation (Nordiko 1980).
where \( E \) is the erosion rate, \( \alpha \) is a constant and \( P \) is the power density at the target surface. If we consider that material eroded from the target will be emitted in all directions, only the material emitted perpendicular to the normal surface of the target can reach the substrate. By the well-known cosine law, the amount of material emitted in any direction at any angle \( \theta \) to the normal surface, is proportional to \( \cos \theta \). Hence the rate of arrival of material at the substrate can be represented as \( GE \) where \( G \) is a dimensionless geometrical factor which can be calculated from the expression:

\[
G = [1 + (h/R)^2]^{-1} \tag{4.2}
\]

where \( h \) is the target to substrate separation and \( R \) is the radius of the target. \( G \) is the ratio of the rate of deposition at the substrate to the rate of erosion at the target. For example, \( G \) is plotted as a function of target diameter for various values of separation in Fig 4.5.

In most vacuum deposition process not all the material that arrives at the substrate remains, but is re-emitted from the surface. The re-emission coefficient \( \rho \) is the ratio of the amount of material leaving the substrate to the amount arriving. Hence the amount of material re-emitted from the substrate is \( \rho GE \), and the net deposition rate \( D \) is

\[
D = GE (1 - \rho) \tag{4.3}
\]

Using Eq 4.1 and 4.2, this gives

\[
D = \alpha P(1 - \rho)[1 + (h/R)^2]^{-1} \tag{4.4}
\]
Thus we obtain the relationship between the deposition rate, input power, target size and target to electrode separation. In an experiment, if some parameters (e.g. target-to-electrode separation h, target size R) are kept constant, the other parameters can be easily used in this relationship.

4.5 Sample preparation

4.5.1 The target

For making a-Ge\textsubscript{x}Se\textsubscript{1-x} films, a standard 4" diameter polycrystalline Ge target was used with 3.5 mm diameter selenium pellets. The film composition was varied by changing the numbers of selenium pellets on the Ge target. The selenium pellets were carefully distributed onto the Ge target uniformly to produce a homogeneous film composition. Fig 4.6 shows the variation of selenium portions with the numbers of selenium pellets and Fig 4.7 shows the dependence of film deposition rate on the film composition.

In the case of Zn-modified films, records of the target compositions for a-Ge\textsubscript{x}Se\textsubscript{1-x} films were used for controlling the Ge and Se portions of the films. The prospective ratio of germanium over selenium was fixed by referring to the records and the zinc foils were distributed over this target. Actually, the targets for making the Zn-modified Ge-Se films had two layers over the Ge target, which were the zinc foil layer and the selenium pellet layer. For this reason, controlling the film composition was not so easy that many trials could not be avoided for making the desired compositions of the films.
Figure 4.6 Film composition versus number of Se pellets on the Ge target for a-Ge$_x$Se$_{1-x}$ films.

Figure 4.7 Film deposition rate versus film composition for a-Ge$_x$Se$_{1-x}$ films.
4.5.2 The substrate

A substrate holder contained a set of several substrates for each sputtering. The substrates used depended on which measurements were to be made. Corning 7059 glass slides, which are highly resistive, alkali-free and optically flat, were used for the d.c. conductivity measurements and uv-visible spectroscopy. Polished c-Si wafers were used for IR-spectroscopy measurements and aluminium foils for EDAX. Mylar was used for EXAFS measurements, fused silica for PDS measurements and ordinary microscope slides for thickness determinations. A set of films was deposited on all these substrates simultaneously so that all films were expected to have same composition.

All substrates, except the mylar were carefully cleaned prior to loading onto the substrate holder. The substrates were prepared using the following steps:

1) Cleaned in tepol, which is a commercially available de-greaser.
2) Cleaned in acetone and rinsed in distilled water.
3) Cleaned in methanol and rinsed in distilled water.
4) Ultrasonically cleaned in pure methanol and rinsed in distilled water.
5) Completely dried with a hair dryer.

4.5.3 The film deposition procedure and conditions.

The substrate holder, which contained the set of substrates, was attached to the substrate electrode and the target was prepared and fitted. Then the chamber was closed and pumped down overnight. Normally the liquid-nitrogen trap was refilled every 9 hours. The next day the Meissner
coil was filled with liquid nitrogen to trap the water vapour remaining in the chamber. When the pressure inside the chamber reached about $2 \times 10^{-7}$ Torr, the sputtering procedure was started. Firstly the r.f power was supplied to the chamber, and then the sputtering gases admitted to the gas control unit. When the required gas-flow rate was established, the plasma was struck by an electric-power gun. If the plasma was difficult to strike, the sputtering gas (Ar) was arranged to flow at about 100 scc/min for a few seconds. Then the matching unit was tuned to reduce the reflected power to a minimum (<1 Watt). After closing the substrate shutter, the substrate was pre-sputtered over half an hour to remove impurities and the shutter was then opened for film deposition. Depending on the required film thickness, the sputtering time was adjusted. Sometimes before and after deposition, the mass spectrometer was used for monitoring the residual gases in the chamber. A typical spectra of the residual gases in the chamber is shown in Fig 4.8. Typical film deposition conditions were as follows:

- RF-power : 240 Watts
- Reflected power : < 1 Watt
- D.c. bias voltage : 710 Volts
- Substrate temperature : room temperature
- Gas-flow rate : Ar - 30 scc/min (unhydrogenated film)
  - Ar - 27 scc/min, H$_2$ - 3 scc/min (hydrogenated film)
- Chamber pressure : 3-6 mTorr

### 4.6 Determination of film thickness

The thickness of the sputtered films was determined by two methods. The first was a direct mechanical method, Telystep, which used a stylus to scan across a sharp groove produced in the central region of the film by a
Figure 4.8  Typical spectra of the residual gases in the chamber before (--) and after (---) filling the Meisner coil with liquid nitrogen.
sharp tool. The other, an optical method proposed by Cisneros et al (1983), provided the means of determining both the thickness and the real part of the refractive index of the films. The principle of the method is an analysis of the interference fringes present in the reflection spectra of the film. The method will be described in detail in Chapter 5.

4.7 Determination of film composition

The composition of the sputtered film was determined using a scanning electron microprobe facility situated at the Medical Engineering Department in Leicester university. The technique uses an electron beam focussed on to the sample surface and an analysis of the characteristic X-rays emitted from the surface. Details of its method will be presented in Chapter 5.
Chapter 5 Experimental Techniques

5.1 EXAFS spectroscopy
   5.1.1 Introduction
   5.1.2 Basic principles
   5.1.3 Theory
   5.1.4 Experimental details
   5.1.5 Data analysis

5.2 Infra-red spectroscopy

5.3 Scanning electron microscopy with EDAX

5.4 Optical measurements
   5.4.1 Reflection-Transmission spectroscopy
   5.4.2 Refractive index and film thickness
   5.4.3 High absorption coefficients
   5.4.4 Photothermal Deflection Spectroscopy
      5.4.4.1 Introduction
      5.4.4.2 Theory
      5.4.4.3 Experimental setup
      5.4.4.4 Measurement and signal analysis

5.5 D.c electrical conductivity measurements
5.1 EXAFS spectroscopy

5.1.1 Introduction

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is a unique probing technique for analysing the short-range structure of a solid. The technique involves measurement of the X-ray absorption coefficient $\mu$ as a function of incident photon energy $E$. If the X-ray photon has a higher energy than the binding energy of a core electron, when it is absorbed by an atom in the material the core electron is excited to a continuum state. By this process $\mu$ as a function of photon energy displays absorption edges, which are known as K-edges if the core electron comes from the K shell (i.e. $n=1$) and L-edges if it comes from the L shell ($n=2$). The excited photoelectron travels outward as a spherical wave. If there are no neighbouring atoms, $\mu$ will decrease smoothly just after the absorption edge. However, if the outgoing wave meets neighbouring atoms, it will be backscattered and the backscattered waves will interfere with the original outgoing wave either constructively or destructively. The interferences make the X-ray absorption signal oscillatory (see Fig 5.1). The oscillatory part of the X-ray absorption coefficient just after the absorption edge is called the 'Extended X-ray Absorption Fine Structure', i.e. EXAFS. A typical shape of the EXAFS is shown in Fig 5.2. Since the origin of the EXAFS is the interferences between the core electron wave and the backscattered waves from neighbouring atoms, it contains information concerning the interatomic relations between the core atom and the surrounding medium. Hence, by analysing EXAFS, the nearest bond-length and the number of neighbouring atoms from a probing atom can be obtained.

The theory of EXAFS was first derived from the original work of Kronig (1932) and developed in the phenomenological plane wave
Figure 5.1 Schematic diagram showing that the outgoing photoelectron (solid lines) and the backscattered waves (dashed lines) interfere to give EXAFS.

Figure 5.2 A typical shape of the EXAFS in Ge K-edge X-ray absorption spectrum of a-Ge$_x$Se$_{1-x}$. 

In the present work, EXAFS experiments have been carried out using the synchrotron radiation source at the CLRC Daresbury Laboratory in England and the data were analysed by computer programs available in the laboratory.

5.1.2 Basic principles

X-rays passing through a medium attenuate via three principal processes: scattering, photoelectric absorption and pair production. In EXAFS experiments, the energy range is from 1 keV to 40 keV and photoelectric absorption dominates. If a single X-ray photon is absorbed by an atom, an electron is excited to a higher energy level and the following equation applies.

\[ E_f = h\omega - E_b \]  

(5.1)

where \( h\omega \) is the energy of X-ray photon, \( E_b \) is the binding energy of the electron in its initial state and \( E_f \) is the kinetic energy of the electron after emission from the atom. The final-state energy \( E_f \) is also related to the wavevector \( k_f \) of the final-state electron by

\[ E_f = E_0 + \frac{h^2k_f^2}{2m} \]  

(5.2)

where \( E_0 \) is the energy of a free electron with zero momentum. It is called the threshold energy which is the effective mean potential experienced by an excited electron in the medium.
The X-ray absorption coefficient for a sample can be written as

$$\mu(k) = \mu_0(k)[1 + \chi(k)] \quad (5.3)$$

where $k$, the photoelectron wavevector, may be expressed in terms of the photon energy by use of equations 5.1 and 5.2. $\mu_0(k)$ is the absorption coefficient of the isolated atom, which is the smoothly varying background absorption when the EXAFS is ignored. Hence the EXAFS function, $\chi(k)$, can be defined as

$$\chi(k) = [\mu(k) - \mu_0(k)] / \mu_0(k) \quad (5.4)$$

5.1.3 Theory

The theory of EXAFS is essentially an electron scattering problem so that all of the wavefunctions can be expanded in terms of angular momentum eigenfunctions. Since the initial state has a well-defined angular momentum, the X-ray absorption due to excitation from a given initial state of an isolated atom can be expressed as (Gurman et al 1984)

$$\mu_0 = \sum_{m_0} \sum_m |< l_0 m_0 | e_r | l m > e^{2i\delta_i} |^2 \quad (5.5)$$

where $l_0$ and $m_0$ are the angular momentum quantum numbers of the initial state and $l$, $m$ are those of the final state wavefunction. The possible range of these is limited by the selection rules: for a K edge, for example, $l=1$ is the only state which contributes to the absorption. $\delta_i$ is the phaseshift due to the central atom potential.
The back scattered wavefunction may also be written in the form of an angular momentum sum. Hence the total final state wavefunction may be written as

\[ |f> = \sum_{lm} [I + Z]_{lm',lm}|lm> \quad (5.6) \]

where the unit matrix \( I \) represents the outgoing wave and the matrix \( Z \) the scattered wave. With equations 5.5 and 5.6, the EXAFS function \( \chi(k) \) defined in Eq 5.4 can be written as a linear function of the matrix \( Z \):

\[ \chi(k) = -\sum_{lm} <l_0|e^r|lm> \sum_{lm'} \text{Re}[Z_{lm',lm} e^{i(\delta_l + \delta_{lm'})}] <l'm'|e^r|l_0m_0> \quad (5.7) \]

Thus all the effects of the scattering atoms are contained in the matrix \( Z \) and consequently the EXAFS function is known once \( Z \) is known. An expression for \( Z \) is given in the theory of Lee and Pendry (1975).

The basic formula used to describe EXAFS can be obtained by approximating the above multiple scattering description, Eq 5.7, into a single scattering form (see Gurman 1984). The result is

\[ \chi(k) = A(k) \sum_{j} N_j/kR_j^2 |f_j(k)| \exp(-2\sigma_j k^2) \exp(2R_j/\lambda) \sin(2kR_j + 2\delta(k) + \Psi_j(k)) \quad (5.8) \]

where \( k \) related to the momentum of the photoelectron \( p \), by the relation, \( k = 2\pi/\lambda = p/h \). \( A(k) \) is a correction factor due to many-body effects, \( N_j \) is the number of scattering atoms in a shell \( j \) at a distance \( R_j \) from the absorbing atom and \( f_j(k,\pi) \) represents the electron scattering strength. Both \( N_j \) and \( f_j(k,\pi) \) are the main factors which contribute to the magnitude of the
oscillation amplitude. The amplitude of the oscillations is attenuated by the Debye-Waller term $\exp(-2\sigma^2/k^2)$, where $\sigma^2$ is the mean square deviation from the interatomic distance $R_j$. In amorphous solids $\sigma^2$ comes from either thermal or structural disorder. Further attenuation in the amplitude of oscillations occurs because of the term $\exp(2R_j/\lambda)$ which originates from inelastic losses in the scattering process. By these inelastic scattering processes the photoelectron may lose its coherence. The EXAFS signal, i.e. the oscillatory part of the X-ray absorption, is mainly due to the last sine term $\sin(2kR_j+2\delta(k)+\Psi_j(k))$, in which $2kR_j$ accounts for the phase shift of a free electron of wavevector $k$ as it travels the distance $2R_j$. The additional phase shifts $2\delta(k)$ and $\Psi_j(k)$ are introduced because the photoelectron wave experiences the atomic potential of the absorbing atom twice (when going out and coming back) and also the atomic potential of the scattering atom once during the trip.

5.1.4 Experimental details

Synchrotron radiation is normally used for EXAFS experiments because of its high intensity which is essential to obtain high signal to noise (S/N) ratios. The EXAFS signal is typically only a few percent of the total X-ray absorption, and hence for accurate measurements a high (S/N) ratio, normally greater than 100, is required. A synchrotron radiation source also has other merits such as a precisely pulsed structure and a high collimation of the beam which are important for various types of X-ray experiments.

The synchrotron radiation source at the CLRC Laboratory in Daresbury is shown schematically in Fig 5.3. It consists of an electron storage ring, NINA, which can carry an electron beam at energies up to 2 GeV and maintain currents of about 200 mA for several hours. The ring, with a
Figure 5.3 Layout of the synchrotron radiation source and beamlines in the CLRC Laboratory in Daresbury.
mean radius of 15.28 m, consists of 16 dipole magnets which continuously bend the beam along a circular path (see Fig 5.4). The bent beam emits strong continuum of radiation ranging from the infrared to the far X-ray region. This radiation is distributed to stations tangently situated around the ring. A total of 29 stations around the ring have their own experimental facilities and use different beam characteristics suitable for the particular purpose. One of the stations, 7.1, was used for probing the Ge, Se and Zn K-edges of the a-Ge_{x}Se_{1-x} and a-Ge_{x}Se_{y}Zn_{z} samples. All experiments were carried out in the transmission mode. The schematic arrangement for the experiments is shown in Fig.5.5.

The incident X-ray beam was monochromatized using a Si (111) double-crystal monochromator. Depending on the angle between the two crystals, a beam of any wavelength, i.e. photon energy, can be selected. Before and after passing through the monochromator, the size of the beam was defined horizontally and vertically by two slits. Both the monochromator and slits were kept in evacuated chambers. The samples were deposited onto mylar substrates which were folded several times to obtain the optimal thickness (a few tens of μm) and inserted into a sample holder situated between two ionization chamber detectors. The ionization chambers, filled with Ar gas, measured the incident X-ray beam intensity I_{0} and the transmitted beam intensity I_{t} respectively. Hence the absorption coefficient μ could be easily determined from the following simple relationship:

\[ I_{t} = I_{0} \exp(-\mu x) \]  

(5.9)

where x represents the thickness of the sample. The sample was scanned by the X-ray beam from the lowest to the highest photon energy depending on the region of interest. This was accomplished by connecting the
Figure 5.4 Schematic diagram of the electron storage ring, NINA.

Figure 5.5 Schematic diagram of the experimental setup in EXAFS station 7.1.
driving-motor of the monochromator to the computer data acquisition system. The beam intensity was also monitored and recorded by the computer during each scan.

5.1.5 Data analysis

The raw EXAFS data were recorded in the central computer of the Daresbury Laboratory and analysed using the computer programs available at the laboratory. Each transmission spectrum was first energy calibrated by the program, EXCALIB. This program also enables the summing of several spectra and the editing of glitches and discontinuities. Then the calibrated data was normalized by the program, EXBACK. The background of the EXAFS signal was subtracted as follows: the pre-edge data was fitted by a first-order polynomial and the post-edge data was fitted by third-order polynomial to make a smoothly varying background absorption $\mu_0$. The background were then subtracted to leave the EXAFS function $\chi(E)$ (see Fig 5.6). The function $\chi(E)$ was converted to the k-space function $\chi(k)$ and multiplied by some power (of the order of 1 to 3) to yield a normalized function $\chi(k)$ of the typical Gaussian shape. The accuracy of the subtraction was checked by a Fourier transform of the normalized function $\chi(k)$.

As the last step, the normalized data from EXBACK was processed by the program, EXCURVE92, which finally enabled extraction of the structural information from the data. This program is based on the fast curved wave theory which simplifies the scattering events as a single scattering. The experimental values were fitted to the calculated theoretical values by means of non-linear least-square fitting. In the process of fitting, several parameters were involved. Most of the parameters were kept fixed except for four main ones. The correlated pair $R_j$ (the nearest bond length) and $E_0$ (the absorption edge energy) are related parameters which control
Figure 5.6  Subtractions of (1) pre- and (2) post-edge backgrounds to yield the EXAFS function $\chi(E)$.  

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.6}
\caption{Subtractions of (1) pre- and (2) post-edge backgrounds to yield the EXAFS function $\chi(E)$.}
\end{figure}
the phase of the function $\chi(k)$, and the pair $N_j$ (the number of neighbours in j shell) and $A_1$ (Debye-Waller factor) controls the amplitude of the function $\chi(k)$. The parameters were continuously refined by iteration processes until the best fit between the experimental and theoretical curves was obtained. After consideration of possible different atom types as neighbours, i.e. changing the parameter ($T_j$), the curve giving the minimum fit index, $FI$, and disorder factor $R$ was chosen as the final result. The fit index, $FI$, is defined by

$$FI = \frac{1}{100N_p}\sum\left| \chi_i(\text{theo.}) - \chi_i(\text{exp.}) \right|^2$$

(5.10)

where $N_p$ is the number of data points in the spectrum and $n$ is the weighting factor which was mentioned in the process of EXBACK. The uncertainties in the parameters could be checked by a contour map which was also offered by EXCURVE92. The confidence region of a set of parameters was marked on this contour map (see Fig 5.7). A theory using the statistical test by this contour map is clearly described in Joyner et al (1987). After using the three computer programs mentioned above, the set of structural information of the sample, i.e. the nearest bond-length, the nearest bond-type, the number of the nearest neighbours and the mean-square deviation of the bond-length, was finally obtained.

5.2 Infra-red spectroscopy

Infra-red spectroscopy is another widely-used technique to probe the nature of chemical bonding in solids. The infra-red transmission spectrum normally shows absorption bands which can be interpreted in terms of vibrations of atoms and groups of atoms in solids. Generally speaking, dipole moments associated with asymmetrical molecular structures couple
Figure 5.7 A contour map of fit index for the correlated parameters, $N_1$ and $A_1$. The inside of the thick line indicates 95% confidence region.
to the oscillating electric field of the infra-red radiation and cause absorption at their normal vibrational frequency. Absorption bands in the shorter wavelength region (2-10 \( \mu \)m) result mainly from stretching and bending vibrations of individual bonds or diatomic structural units. Bands in the longer wavelength region (7-15 \( \mu \)m) are generally caused by more complex vibrations of polyatomic units and any molecules as a whole.

Classical electrodynamics specifies that in order for a molecule to absorb radiation it must (1) possess a vibrational or rotational frequency the same as that of the electromagnetic radiation, and (2) be associated with a change in the magnitude or direction of the dipole moment. Vibrations which satisfy these two conditions in the infra-red are called infra-red active. Vibrations which do not cause a change of dipole moment, for example certain vibrations of symmetrical bonds do not show absorption bands in the IR spectra and are called infra-red inactive. The latter modes can be probed by Raman scattering spectroscopy.

In crystals, conservation of momentum confines infrared absorption processes to phonons with wavevector \( k \) close to zero (i.e. the centre of Brillouin zone) so that the spectra shows quite sharp lines. However, in amorphous material the inherent disorder causes the \( k \)-selection rule to break down, enabling other phonons to be excited. Hence IR spectra of amorphous solids have broadened peaks compared to those of crystalline materials.

IR spectroscopy is useful for probing the short-range structure of amorphous solid when they have structural units which are capable of being vibrationally excited independent of the surrounding amorphous matrix (Sen and Thorpe 1977). In other cases, the vibrations are not confined to a small local region and can only properly be described in terms of network dynamics, in which all the atoms present contribute to the modes.
IR spectroscopy provides a useful method for estimating the hydrogen content in a sample (Lucovsky 1979). According to the work of Brodsky (1977), an estimate of the hydrogen content of a film \( N \) is given by

\[
N = \frac{c n \omega_0 m}{2 \pi \epsilon_0} \int \alpha(\omega) d\omega / \omega
\]  

(5.11)

where \( c \) is the speed of light, \( n \) the refractive index, \( \omega_0 \) is the frequency of the absorption band, \( \epsilon^* \) is the effective charge of the bonding unit including hydrogen in the surrounding matrix, and \( m \) the reduced mass. The integral term is the area under the hydrogen-related absorption band.

In the present study, the amorphous Ge\(_x\)Se\(_{1-x}\) and Ge\(_x\)Se\(_y\)Zn\(_z\) thin film samples for IR spectroscopy were deposited on polished crystalline Si substrates. IR transmission and reflection spectra in the wavenumber range 4000-200 cm\(^{-1}\) (\( \lambda = 2.5-50 \) \( \mu \)m) were measured by a Model 580B double-beam Perkin-Elmer infra-red spectrophotometer. In the transmission measurements, an uncoated c-Si substrate was placed in the path of the reference beam for the purpose of eliminating the effect of the substrate itself. A Perkin Elmer specular reflectance accessory was attached to the spectrophotometer for the reflection measurements. For removing extra absorption bands caused by unwanted water vapour and carbon dioxide, a Model CD3 air dryer connected to the sample compartment was operated for several hours before the measurements.

[Note to reader: It should be mentioned that results using this technique are not reported in this thesis.]
5.3 Scanning electron microscopy with EDAX

A Scanning Electron Microscope (SEM) is an advanced type of microscope, which allows surface topographical imaging at very high magnifications, well beyond those achievable by optical microscopes. The SEM is often combined with an Energy Dispersive X-ray Analyser (EDAX), which can provide information on the nature of constituent elements and their concentration. Fig 5.8 shows a schematic diagram of a combined SEM-EDAX apparatus. An electron beam generated from a heated tungsten cathode is focused on the sample surface by several electrostatic lenses and scanned point by a raster scanning controller. Secondary electrons produced by the striking electron beam create the image which reproduces the surface topography of the samples. The EDAX unit detects the different X-rays emitted from the collisions between the incoming electron beam and each components present in the samples. Fig 5.9 shows a typical spectrum obtained by EDAX. By analysing the spectrum profile, i.e. the ratio of the X-ray intensities, the nature and quantities of each component present can be determined. Detailed procedures on the analysis can be found elsewhere (e.g. Goldstein 1981).

For the present work, an ISI DS 130 model Scanning Electron Microscope with an EDAX, situated in the Medical Science Department, was used. The samples were deposited onto pure aluminium foil substrates. Normally the electron beam was focused over an initially chosen sample area (<1μm²) for a local compositional analysis and the same analysis for different regions of the sample were carried out repeatedly. During the scan, the results were logged and transferred to the linked computer. A histogram, showing the elemental concentrations, can be made as the sample was scanned by the electron beam.
Figure 5.8 Schematic diagram of a combined SEM-EDAX.

Figure 5.9 Energy dispersive X-ray spectrum of an a-Ge$_x$Se$_{1-x}$ film. Characteristic lines are superimposed on the continuum radiation.
5.4 Optical measurements

5.4.1 Reflection-Transmission spectroscopy

The reflectivity $R$ and transmission $T$ of the films in the UV-Visible region (200nm-2500nm) were measured at room temperature using a double-beam Perkin-Elmer 330 spectrophotometer. A Perkin-Elmer reflection accessory was used for the reflection measurements and a standard mirror (with 100 % reflectivity) was employed as a reference. Typical spectra for an amorphous Ge$_x$Se$_{1-x}$ film are given in Fig 5.10 where the interference fringes result from the multiple reflections within the film (see Fig 5.11).

Generally speaking, the optical constants $n$ and $k$ can be obtained from the $R$ and $T$ values through solving well-known Fresnel equations (Hecht 1987). However, unfortunately the effect of the substrate makes these equations extremely complicated so that they cannot be easily solved analytically. Other methods of solving these numerical solution, such as a graphical method (Turner 1950) or computer search routines (Berning 1960), have been proposed but they often lead to multiple solutions. Cisneros et al (1983) proposed a different approach to solve the problem using interference fringes in the reflectance spectra. By this method the refractive index of the films and their thicknesses can be easily obtained. The details of the method will be outlined in the next section.

5.4.2 Refractive index and film thickness

As shown in Fig 5.10, typical R-T spectra show oscillatory variations with wavelength owing to multiple reflections in the films. The refractive
Figure 5.10 Typical reflection $R$ and transmission $T$ spectra for a-Ge$_x$Se$_{1-x}$ film.

Figure 5.11 Schematic diagram of multiple-reflection events when the light penetrates a thin film sample.
index at different wavelengths can be determined from the wavelengths at which maxima and minima of reflection occur. The conditions for occurrence of maximum and minimum values of the reflectance are (Hall 1955)

\[ 4n\lambda = m\lambda_m \left[ 1 + \left( \frac{\delta_{af} - \delta_{fs}}{\pi mn} \right) \right] \]  

(5.12)

where \( n \) is the refractive index of the film, \( h \) is the geometrical thickness, \( m \) is a fringe order and \( \lambda_m \) is the wavelength corresponding to an extremum of order \( m \). Odd values of \( m \) give maxima in \( R \) and even values minima in \( R \). \( \delta_{af} \) and \( \delta_{fs} \) are phase angles corresponding to reflections at the air-film and film-substrate interfaces respectively. In the case of a transparent or nearly transparent film and substrate (i.e. little or no absorption), the phase angles \( \delta_{af} \) and \( \delta_{fs} \) can be neglected. Thus Eq 5.12 can be simplified to

\[ 4n\lambda = m\lambda_m \]  

(5.13)

where, \( nh = d_m \) is called the optical thickness. By this relationship, we can calculate the real geometrical thickness \( h \) if we can obtain \( m \) and \( n \). Assuming that variations of optical thickness from one extremum to the nearest neighbour are very small, from Eq 5.13 we can write

\[ d_{m-1} = d_m = d_{m+1} \]  

(5.14a)

or

\[ (m-1)\lambda_{m-1} = m\lambda_m = (m+1)\lambda_{m+1} \]  

(5.14b)

Consequently, the order \( m \) can be obtained from the following expressions.
As we assumed that the film is transparent (i.e. no absorption), R+T value can be regarded as unity. Thus the reflectivity at the extrema of the interference fringes is given by (Cisneros et al 1983)

\[ R_{\text{even}} = \frac{(1-n_3^2)}{(1+n_3^2)} \]  \hspace{1cm} (5.16a)

\[ R_{\text{odd}} = \left( \frac{n_3^3 n^2}{n_3 + n^2} \right)^2 \]  \hspace{1cm} (5.16b)

where 'even' and 'odd' refer to successive values of m and \( n_3 \) is the refractive index of the substrate. In the case of transparent films, odd integers correspond to maxima when \( R_{\text{max}} > R_{\text{sub}} \) and to minima when \( R_{\text{min}} < R_{\text{sub}} \), since \( R_{\text{even}} = R_{\text{sub}} \). In this optical work, Corning 7059 glass slides (\( n_3 = 1.53 \)) were used as substrates, hence \( R_{\text{even}} \) is calculated to be 0.044. Typically, spectra of all samples showed that both \( R_{\text{max}} \) and \( R_{\text{min}} \) values were greater than 0.044. Hence \( R_{\text{odd}} \) was supposed to correspond to maxima, which gives

\[ R_{\text{max}} = \left( \frac{n_3^3 n^2}{n_3 + n^2} \right)^2 \]  \hspace{1cm} (5.17)

Solving the quadratic equation for \( n \) after taking the positive root of \( R_{\text{max}} \) gives the two solutions:

\[ n' = \left[ \frac{n_3(1-R_{\text{max}}^{1/2})}{(1+R_{\text{max}}^{1/2})} \right]^{1/2} \]  \hspace{1cm} (5.18a)

and \[ n'' = \frac{n_3}{n'} \]  \hspace{1cm} (5.18b)
Applying these equations to real data for a-Ge_xSe_{1-x} films, n' was found to be smaller than unity (i.e. physically unacceptable), hence Eq 5.18b was employed to determine the refractive index of the films. The values of refractive index from Eq 5.18b were also used to obtain the geometrical thickness of the films using Eq 5.13.

### 5.4.3 High absorption coefficients

In transmission-reflection events when the light penetrates the film-substrate system, if the multiple reflections shown in Fig 5.11 are taken into account, the measured transmission can be expressed as

\[
T_{\text{meas}} = \frac{1 + R_2 R_3}{(1 - R_2 R_3)(1 - R_1)(1 - R_2)(1 - R_3)e^{-\alpha d}/(1 - R_1 R_2)e^{-2\alpha d}} \tag{5.19}
\]

where \( \alpha \) is the absorption coefficient of the film, \( d \) is the thickness of the film and \( R_1, R_2, R_3 \) are the reflection coefficients of the air-film, film-substrate and substrate-air interfaces respectively, which have the values:

\[
R_1 = \left[ \frac{n_{\text{film}} - n_{\text{air}}}{n_{\text{film}} + n_{\text{air}}} \right]^2 \tag{5.20a}
\]

\[
R_2 = \left[ \frac{n_{\text{sub}} - n_{\text{film}}}{n_{\text{sub}} + n_{\text{film}}} \right]^2 \tag{5.20b}
\]

\[
R_3 = \left[ \frac{n_{\text{air}} - n_{\text{sub}}}{n_{\text{air}} + n_{\text{sub}}} \right]^2 \tag{5.20c}
\]

Substituting the values \( n_{\text{air}} = 1 \), \( n_{\text{sub}} = 1.53 \) (Corning glass) into Eq 5.20c gives,

\[
R_3 = \frac{(1 - 1.53)/(1 + 1.53))^2 = 0.04 \tag{5.21}
\]
$R_3$ is so small value that it can be neglected, and also in the high photon energy region, both $R_1$ and $R_2$ can be regarded as the same measured value $R_{\text{meas}}$ because the film is highly absorbing so that only the reflections at the air-film interface become significant. Hence Eq 5.19 can be simplified to

$$T_{\text{meas}} = (1-R_{\text{meas}})^2 e^{-\alpha d}/(1-R_{\text{meas}}^2) e^{-2\alpha d}$$  (5.22)

Therefore, with two measured value, $T_{\text{meas}}$ and $R_{\text{meas}}$, if the film thickness $d$ is known, the absorption coefficient of the film $\alpha$ can be determined easily from Eq 5.22. However, in the low absorption region ($\alpha < 10^{-3} \text{ cm}^{-1}$), the equation is invalid because multiple reflections become significant. Sometimes, when the multiple reflections are neglected, the following simplified form is also used (Al-Shabarty 1974).

$$T_{\text{meas}} = (1-R_{\text{meas}}) e^{-\alpha d}$$  (5.23)

### 5.4.4 Photothermal deflection spectroscopy

#### 5.4.4.1 Introduction

The absorption coefficients obtained from the R-T measurements can give reliable optical absorption spectra only in the high absorption region (about $\alpha > 10^3 \text{ cm}^{-1}$). However, it is well known that low absorption region provides important information about band tailing near the band edges and defect states in the pseudo-gap. Hence, for determining the important low absorption coefficients of our thin-film samples, we employed the experimental technique of Photothermal Deflection Spectroscopy (PDS), which was first developed by Boccara et al (1980).
Before proceeding with the theoretical treatment of PDS, a brief physical description of technique is in order. Absorption of an optically exciting beam (pump beam) causes a corresponding change in the index of refraction of the optically heated region. The absorption also causes an index-of-refraction gradient in a thin layer adjacent to the sample surface. By probing the gradient of the varying index of refraction with a second beam (probe beam), one can relate its deflection to the optical absorption in the sample.

There exist two methods for performing PDS according to the above description: (1) collinear PDS where the gradient of the index of refraction is both created and probed within the sample, or (2) transverse PDS where the probing of the gradient of the index of refraction is accomplished in the thin layer adjacent to the sample. The collinear PDS can applied only to samples which are transparent to the probe beam. However, the second approach, transverse PDS, is suitable for any sample, opaque or transparent. Hence transverse PDS has been preferred by many researchers and we also employed this method. Fig 5.12 shows the schematic experimental setup for transverse and collinear PDS.

5.4.4.2 Theory

Even though the concept of beam deflection by thermally induced changes in the index of refraction has been known for a long time (Smith 1969), the complete theoretical foundations of the concept as a spectroscopy were established just a decade ago. We summarize the best theoretical treatment of PDS given by Jackson et al (1981) in this section. In the treatment, calculation of the expected beam deflection for PDS is divided into two parts. One first finds the temperature distribution in the sample.
Figure 5.12 Schematic diagram of experimental arrangement: (a) transverse PDS; (b) collinear PDS.

Figure 5.13 Geometry for collinear and transverse PDS.
and then solves for the optical beam propagation through an inhomogeneous medium.

I) Temperature distribution

Fig 5.13 shows the geometry of for collinear and transverse PDS. Regions 0 and 2 are optically nonabsorbing media. Region 1 is the absorbing medium and can be either a thin film, gas, liquid or solid. For simplicity, we assume that all three regions extend infinitely in the radial direction. This assumption does not significantly alter the applicability of the treatment, because focused laser beams are typically much smaller than the radial dimension of the sample, and the thermal diffusion length of most samples is less than typical sample dimensions for experimentally useful chopping frequencies. In the three regions, the temperature rise \( T_i \) satisfies the equations:

\[
\nabla^2 T_0 - \frac{1}{k_0} \frac{\partial T_0}{\partial t} = 0 \quad \text{Region 0} \quad (5.24 \text{ a})
\]

\[
\nabla^2 T_1 - \frac{1}{k_0} \frac{\partial T_1}{\partial t} = -\frac{Q(x, t)}{k_1} \quad \text{Region 1} \quad (5.24 \text{ b})
\]

\[
\nabla^2 T_2 - \frac{1}{k_2} \frac{\partial T_2}{\partial t} = 0 \quad \text{Region 2} \quad (5.24 \text{ c})
\]

subject to the following boundary conditions:

\[
T_0 \bigg|_{z=0} = T_1 \bigg|_{z=0}, \quad T_1 \bigg|_{z=\ell} = T_2 \bigg|_{z=\ell} \quad (5.25 \text{ a})
\]
where $K_i$ is the thermal conductivity, $k_i (= K_i/\rho_iC_i$ where $\rho_i$ is the density and $C_i$ is the specific heat) is the diffusivity, $T_i$ is the temperature rise of the ith medium above the ambient temperature, and $\ell$ is the thickness of the absorbing medium. $Q(r,t)$ is the heat deposited per unit volume oscillating at the frequency $\omega$ in the absorbing medium and is given by

$$Q(r,t) = \frac{1}{2} P \pi a \exp(-\alpha z) \exp(-2r^2/a^2) \exp(i\omega t) + \text{c.c.} \quad (5.26)$$

for a square-wave intensity beam, where $P$ is the pump beam power, $\alpha$ is the absorption coefficient, $a$ is the $1/e^2$ radius of the Gaussian pump beam and c.c. is the complex conjugate. It has been assumed above that over the interaction region between the pump and probe beams, the probe beam is focused to a smaller spot than that of the pump beam, and that the pump beam waist does not change over the confocal distance of the probe beam.

Equation 5.24 is solved by substituting the specified solutions of $T_0(r,t)$, $T_1(r,t)$ and $T_2(r,t)$ into it for each region. The constants of the solutions can be obtained by using the four boundary conditions. Hence the final temperature distribution can be obtained by combining the results. The detailed mathematical procedures are well explained in Jackson at al (1981). The important physical meaning of the final temperature distribution function is that the temperature can be represented by highly damped waves which decay over the thermal length $1/K_i$ and these waves experience both reflection and transmission when they propagate through a boundary.
II) Optical beam propagation

Here we calculate the effect of the temperature distribution on the probe beam. The temperature rise above the ambient temperature produces a spatially varying refractive index. Hence

\[ n(r,t) = n_0 + \Delta n(r,t) = n_0 + \frac{\partial n}{\partial T} \bigg|_{T_{\text{ambient}}} T(r,t) \quad (5.27) \]

where \((\partial n)/(\partial T)\) is typically \(10^{-4} \text{ } \text{C}^{-1}\) for liquids and \(10^{-5} \text{ } \text{C}^{-1}\) for solids. The propagation of the Gaussian probe beam through such an inhomogeneous medium is given by (Casperson 1973)

\[ \frac{d}{ds} \left( \frac{dr_0}{n_0} \frac{dr_0}{ds} \right) = V_{\perp n}(r,t) \quad (5.28) \]

where \(r_0\) is the perpendicular displacement of the beam from its original direction, \(n_0\) is the uniform index of refraction and \(V_{\perp n}(r,t)\) is the gradient of the index of refraction perpendicular to the beam path. Integration of Eq 5.28 over the path gives

\[ \frac{dr_0}{ds} \equiv \Phi = \frac{1}{n_0} \frac{\partial n}{\partial T} \text{path} V_{\perp} T(r,t) \, ds \quad (5.29) \]

where \(\Phi\) is the angular beam deviation from the beam path. Hence equation 5.29 gives a 3-D generalised form of \(\Phi\), but it is rather complicated. However, using diffraction theory, it has been shown that for modulation of the pump beam at low frequency, the amplitude of the probe beam deflection \(\Phi\) can be expressed as
where \( \frac{dn}{dT} \) is the temperature coefficient of the refractive index, \( P \) is the power of the pump beam, \( K \) is the thermal conductivity of the sample, \( r \) is the distance between the intensity maxima of the pump and probe beams, \( \alpha \) is the absorption coefficient, \( \ell \) is the sample thickness, and \( a \) is the \( 1/e^2 \) radius of the pump beam. Thus, for small \( \alpha \ell \leq 2 \), \( \Phi \) is proportional to \( \alpha \ell \) and \( P \). Furthermore, \( \Phi \) exhibits a maximum near \( r/a \leq 1 \). Hence if we assume that we only measure the maximum value of \( \Phi \) experimentally, equation 5.30 can be further reduced to

\[
\Phi = PA[1 - \exp(-\alpha\ell)] \tag{5.31}
\]

where \( A \) is the constant containing the thermal properties. Hence we can directly use the equation 5.31 to obtain the absorption coefficient \( \alpha \) of the films by measuring the probe beam deflection \( \Phi \) and pump beam power \( P \).

### 5.4.4.3 Experimental setup

PDS experiments were carried out using a setup designed for the transverse PDS method. A schematic diagram of the apparatus is presented in Fig 5.14. The setup consists of two main parts, the probe beam and pump beam arrangements, placed perpendicular to each other. For the pump beam, a 100 W quartz tungsten halogen bulb powered by a stabilised voltage supply is used as its source. Modulated by a mechanical chopper, the generated pump beam is focused by a 100 mm-focal-length mirror onto the slit of an Oriel 77250 grating monochromator. Then the beam passes through a filter, chosen to remove unwanted diffraction orders, and
Figure 5.14 Experimental setup of the transverse PDS system.
focused by two lenses (focal lengths are shown in Fig 5.14) onto the surface of the sample placed in a suprasil cuvette. The cuvette contains high purity carbon tetrachloride (CCl₄) as well as the sample.

The probe beam is generated by a 0.5 mW He-Ne laser, and focused by a 63 mm-focal-length lens to graze the sample surface where the pump beam is focused. The deflection of the probe beam is captured by a position detector and the output is measured by an EG & G PARC 5209 lock-in amplifier. The deflection signal is also monitored on a PM 3311 (U) Philips digital oscilloscope.

A detailed description of each component of the setup is as follows. The monochromator was able to cover the spectral range from 2.5 to 0.5 eV. Two interchangeable ruled gratings were used for covering the appropriate spectral range. The one which covered the visible region had a resolution of 15 nm and the other, which covered the infrared region, of 30 nm. For rejecting unwanted high-order diffractions, three different bandpass filters whose transmissions were higher than 95 %, were used for covering the specific spectral ranges; 450 nm ≤ λ₁ ≤ 800 nm, 800 ≤ λ₂ ≤ 1400 nm, and 1400 ≤ λ₃ ≤ 2400 nm.

Modulation of the pump beam was accomplished by a Bentham mechanical chopper. For optimising the signal to noise (S/N) ratio, the frequency had to be chosen carefully. Generally, low frequencies increase the magnitude of signal, but the stability of the signal is degraded because of noise originating from the detector or other mechanical vibrations, and vice versa for high frequencies. In our setup, the optimum frequency was found to be 7.2 Hz and this was used throughout the measurements.

For focusing the modulated and monochromatised pump beam onto the sample, two Crown glass lenses were used. The first, a 125 mm-focal-length plano-convex lens, collimated the beam and the second, a 24 mm-focal-length aspheric lens, then focused it tightly on the surface of the
sample. Precise focusing of the pump beam is essential to obtain a high intensity, which eventually enhances the S/N ratio. In this work, the best focused image size of the beam turned out to be 1 mm x 3 mm.

The samples used in the experiments were 0.3–2.5 μm thick hydrogenated and unhydrogenated a-Ge_xSe_1-x films deposited on 6-8 mm wide and 25 m long fused-silica substrates. The sample was inserted into a Hellma quartz cuvette and placed onto the back edge of an aluminium block placed at the bottom of the cuvette. The cuvette was filled with 99.95 % pure carbon tetrachloride (CCl_4), and covered by several layers of PVC cling film. It was then inserted and clamped into the brass holder mounted on an Ealing miniature stage which provided fine lateral and vertical positioning.

CCl_4 was chosen as the deflection medium for several reasons. This liquid has no absorption in the energy range of interest, 0.5-2.5 eV, and also has a large change of refractive index over the temperature change, ∂n/∂T. Moreover it does not affect the properties of the films (Amer 1984). It has the drawback that it can be a serious health hazard to heart and lungs so that careful handling was required.

The probe beam, a He-Ne laser (λ=632.8 nm), has a Gaussian intensity distribution with a 1/e^2 diameter, 2R_0, of 0.48 mm and a divergence angle, θ, of 1.7 mradians. A laser lens with a focal length of 63 mm was placed 50 mm (D_1) away from the laser source for focusing the beam on the sample. The focused spot size calculated by the following expressions (Oriel manual); R = 4λf/πR_in, where R_in = [(2R_0)^2 + θ^2D_1^2]^{1/2} had the radius of 55 μm. The beam offset z_q was confined by the spot size and other parameters, i.e the lens focal length f, the distance D_1, and the sample width s. Referring to the geometrical optic analysis of Frosio et al (1986), the minimum offset of our probe beam was calculated to have the value of 37 μm under the condition that the focal length f ≥ R_0(πs/2λ)^{1/2}. For the
present setup, a focal length value of 63 mm was employed according to this condition. The other parameters, the distance $D_1$, and $s$, were manipulated for the beam to have the minimum offset $z_0$.

A quadrant silicon photodiode used as a detector covered a total area of 7 mm$^2$ with four quadrants. Since the left two and the right two quadrants were electronically joined, the resultant two quadrants were operated to follow the horizontal movement of the probe beam. The voltages $V_1$ and $V_2$ produced across the two resultant quadrants under illumination, were processed by a home-built electronic circuit to give an output: $V_0 = 10(V_1 - V_2)/(V_1 + V_2)$. The value of $V_0$ was proportional to the probe beam deflection. The output from the detector was connected to a zero-centre Levell d.c. voltmeter and lock-in amplifier. The voltmeter checked the location of the deflected probe beam spot by showing the deviation value from the centre of the two resultant quadrants of the photodiode. The lock-in amplifier measured the deflection signal oscillating at the modulation frequency of the pump beam. Both the deflection signal of the probe beam and the modulated pump beam signal were monitored by the digital oscilloscope connected to the lock-in amplifier.

During the experiments, several sources of background noise affecting the stability of the signal were found and eliminated. Firstly, dust particles and impurities contained in the CCl$_4$ seriously impeded the stability of the signal because the small probe beam size, with a diameter of tens of microns, could be easily blocked by dust of similar size. In order to eliminate such particles, the cuvette was cleaned thoroughly through several steps, high purity CCl$_4$ was used, the samples was flushed with CCl$_4$ before mounting, and the cuvette was tightly sealed by cling film. Secondly, stray light, which originated from the pump beam source or from reflections of the pump and probe beam by the optical components, affected the signal. In order to cut off such light from the detector, an Oriel
He-Ne laser line filter was attached to the front of the photodiode detector. Thirdly, air currents resulting from the mechanical chopper were also found to affect the laser beam. Thus all optical paths were enclosed using black pipes and cloths. Finally, potential sources of noise, such as mechanical vibrations of the setup, were eliminated by placing all optical components on a heavy metal block which rested on a thick stone shelf for the purpose of absorbing vibrations.

5.4.4.4 Measurement and signal analysis

Before starting a measurement, a few prior steps had to be carried out. First of all, the cuvette and aluminium block were cleaned thoroughly with detergent and then ultrasonically cleaned with acetone and methanol. The sample was also carefully rinsed with CCl₄ before being mounted in the cuvette. Prior to clamping the cuvette into the sample holder assembly, the probe beam was adjusted to intersect the middle of the pump beam spot using the lens between the laser source and sample. Then the cuvette was placed in the sample holder assembly and the probe beam offset zₒ was minimized by moving the sample holder assembly laterally. The probe beam, after grazing the sample surface, was checked for distortion by inserting a piece of white paper in its path. Finally, the whole assembly, including the electronics, was left to settle down for a couple of hours.

Measurements were started from the lowest wavelength side, at about 450 nm, where the signal was in general the highest. The wavelength of the pump beam was varied by turning the dial of the monochromator manually little by little. The deflected probe beam signal was centralised between the two quadrants of the detector, monitored by the d.c. voltmeter, by changing the detector position laterally. The lock-in
amplifier, used for reading the magnitude of probe beam deflection, found a signal that was phase-coherent with the reference signal, initially in automatic mode, and later the phase adjustment was controlled manually to achieve better stability. The sensitivity of the amplifier signal was increased gradually as the signal strength became weaker. During most runs, the grating was changed twice and the filter three times. The signal varied typically from a few tens of mV down to about 10 μV.

Since the signal is dependent on the pump beam power, it must be normalized by the pump beam power for the purpose of calculating the absorption coefficient $\alpha$. Hence the relative pump beam power was measured at each wavelength at which the signal reading was made.

The experimental setups for the pump beam power measurements are shown in Fig. 5.15. Two different detectors, a silicon BPX 65 and a PbS cell, were used for the wavelength ranges 450-1000 nm and 1000-2500 nm, respectively. The pump beam was directed onto the detectors by means of a concave mirror and an objective lens. In the case of the BPX 65 detector, the small induced photocurrent from the unmodulated pump beam was amplified by a Keithley 427 current amplifier and then measured by a Levell multimeter. When the PbS detector was in use, the photocurrent, modulated by the pump beam frequency (600 Hz), passed into an electronic circuit containing a 50 V bias voltage and a 1 MΩ load resistor, and was then measured by the lock-in amplifier. The currents measured by both detectors were finally converted to the incident power using calibration curves for the detector responses as a function of incident photon wavelength.

Once the power of the pump beam at each wavelength was obtained, the signal was then normalized by these data. The power-normalized signal plotted versus incident photon energy typically shows interference fringes which resulted from multiple reflections of the pump beam within
Figure 5.15  Experimental arrangement for measurement of the pump beam power.
the film. The fringes becomes weaker as the photon energy increased and
the normalized signal finally saturated when the photon energy was high
enough for the film to be completely absorbing. From the saturation value,
the constant of the equation for the absorption coefficient $\alpha$ can be
determined and then relative absorption coefficient values can be
calculated at each incident photon energy. The PDS spectrum was then
smoothed by averaging the interference fringes on a logarithmic scale and
matched to the corresponding absorption spectrum deduced from R-T
measurement in the range of $10^3$-$10^4$ cm$^{-1}$. Hence the absorption edge was
extended down to about $10^1$ cm$^{-1}$ by a combination of these two spectra.

5.5 D.c electrical conductivity measurements

For measuring the d.c. electrical conductivity of the films, electrodes
were evaporated onto their surface. High-purity (99.99%) Al was used as
the electrode material and an Edwards 12E6/1514 evaporator was used.
Two electrodes, 12 mm long and 4 mm apart, were deposited. The film was
then clamped onto a copper holder in a cryostat (Fig 5.16), and leads of fine
gold wire were attached to the electrodes by a silver-loaded electrically
conducting paste. A thermocouple junction of copper-constantan was
attached to one side of the film also by silver paste and the reference
junction was inserted into an ice and water mixture. The cryostat was
placed inside a Delta Design Environmental Temperature Control Cabinet
which was capable of controlling the temperature from 150 to 520 K within
$\pm 0.5$ K accuracy. The cabinet was pumped down to below $10^{-6}$ Torr by an
Edwards E02 oil diffusion pump backed by an Edwards E2M5 rotary pump.
When the pressure of the cabinet reached below $10^{-6}$ Torr, the cabinet was
filled with a slight overpressure (about 2 psi) of helium. Heating of the
sample was accomplished by an internal heater in the cabinet and
Figure 5.16  Schematic diagram of the cryostat used in d.c. electrical conductivity measurements.
temperatures were reached by enclosing the cryostat with a flow of liquid-nitrogen vapour from a pressurized liquid-nitrogen cylinder. The temperature of the film was monitored using a digital millivoltmeter connected to the thermocouple. During the measurements, a constant voltage of 40 V was applied to the film from a stabilized power supply, and the induced current was read by a Keithley 616 electrometer. The measurements on each film were carried out twice, once while lowering the temperature from room temperature and the second while allowing the system to warm naturally from the lowest temperature. Finally the conductivity of film at each temperature was calculated by the following expression.

\[
\sigma = \frac{(L/W)t}{I/V} \quad (5.32)
\]

where \( I \) is the induced current, \( V \) the supplied voltage, \( L \) the separation between the electrodes, \( W \) the length of the electrodes and \( t \) the film thickness. For obtaining the temperature dependence of the conductivity, the following Arrhenius formula was assumed:

\[
\sigma = \sigma_0 \exp(-\frac{E_a}{kT}) \quad (5.33)
\]

where \( E_a \) is an activation energy obtained from the slopes of log \( \sigma \) versus \( 1/T \) plots.
Chapter 6  Results: Optical and electrical properties of a-Ge$_x$Se$_{1-x}$ and related alloy thin films

6.1 Optical properties of a-Ge$_x$Se$_{1-x}$ thin films
   6.1.1 Optical absorption edges
   6.1.2 Refractive index
   6.1.3 PDS data

6.2 Effect of hydrogenation

6.3 Ternary alloys of a-Ge$_x$Se$_y$Zn$_z$

6.4 Modelling the dielectric function
   6.4.1 Introduction
   6.4.2 Background theory
   6.4.3 Results
   6.4.4 Discussion
6.1 Optical properties of a-Ge$_x$Se$_{1-x}$ films

6.1.1 Optical absorption edges

The optical absorption edges of the sputtered a-Ge$_x$Se$_{1-x}$ films were obtained by careful analysis of transmission-reflection spectra.

Fig 6.1 shows the absorption coefficient plotted versus the incident photon energy. The results shows that the absorption edges shift to higher photon energies with decreasing germanium content in the samples. The customary measures of the optical bandgaps of amorphous semiconductors (Mott & Davis 1979), namely the Tauc gap $E_T$, and $E_{03}$ and $E_{04}$, have been determined from these edges. $E_T$ was obtained by fitting the high-absorption coefficient data to $\hbar \alpha = B(\hbar \omega - E_T)^2$, and $E_{03}$ and $E_{04}$ from the photon energies at which the absorption coefficients are $10^3$ and $10^4$ cm$^{-1}$ respectively.

In Fig 6.2, the variation with the germanium concentration of $E_{04}$ for our sputtered samples is compared with the data obtained by others on glasses (Tronc 1973) and on sputtered (de Neufville 1972) and evaporated films (Kotkata 1993). Allowing for expected differences in the behaviour of samples prepared in different ways, an overall picture emerges of a gap that varies in an upwardly concave manner from the end members, towards a maximum at the composition $x=0.33$ which corresponds to that of the stoichiometric composition GeSe$_2$. This type of behaviour is not entirely unexpected (Gurman 1992). In the forthcoming section of this chapter, § 6.4: Modelling the dielectric function, this result will be discussed again in terms of an ordered bond network model.

Fig 6.3 shows the Tauc curves of some representative films. These curves were plotted in anticipation of the high absorption coefficient data obeying $\hbar \alpha = B(\hbar \omega - E_T)^2$ and so $(\hbar \omega \alpha)^{1/2}$ is plotted as a function of
Figure 6.1 Absorption coefficient spectra deduced from R-T measurements for amorphous Ge<sub>x</sub>Se<sub>1-x</sub> thin films.
Figure 6.2 Optical gaps $E_{04}$ of a-Ge$_x$Se$_{1-x}$ versus germanium content $x$. •, sputtered films (present work); x sputtered films (de Neufville 1972); o, evaporated films (Kotkata 1993); ▲, glasses (Tronc 1973). (Note: the values for the glasses are $E_{03}$ and are therefore about 0.3 eV lower than the expected values of $E_{04}$.)
Figure 6.3  Representative Tauc curves of a-Ge$_x$Se$_{1-x}$ thin films. The numbers on the lines are germanium atomic percentage (%) of the films.
energy $\hbar \omega$. Fairly good linearity is found and the Tauc gap $E_T$ was determined as the photon energy at which the extrapolated straight lines intersect the abscissa of $\hbar \omega$. The results for $E_T$ (not shown) were found to be in general agreement with those for $E_0$.

The slopes $B$ of the straight lines of Fig 6.3 were calculated and the values of $B^{1/2}$ are plotted versus $x$ in Fig 6.4. The so-called Tauc constant $B$, is generally believed to reflect the density of states deeper in the bands (Mott & Davis 1979). The results from a study of evaporated films (Kotkata 1993) are co-plotted with our work. The variation of the $B^{1/2}$ with germanium composition falls almost linearly by a factor of three between $x=0.2$ and $0.9$, with data for sputtered and evaporated films being in fairly good correspondence. On some models for the Tauc absorption region (Mott & Davis 1979), $B$ is inversely related to the range of localized states at the band edges. Hence one can infer that the width of one or either of the band tails increases continuously as the Ge concentration increases.

Another parameter that can be extrapolated from the absorption edges is the slope $\gamma$ of the linear Urbach portions which are generally taken to represent the degree of tailing of either the conduction or valence bands. This parameter is plotted versus composition for the present data in Fig 6.5 along with results from studies by others on glasses and on evaporated films. In Fig 6.5, $\gamma$ - a measure of the steepness of the edge - falls as $x$ is increased for our sputtered films, with a shallow minimum occurring at about $x = 0.5$. For the composition range in which glasses can be fabricated, the same type of variation is found, although the absolute values are higher (Tronc 1973). At low $x$, the absorption edges of evaporated films (Kotkata 1993) appear to be broader than either glasses or sputtered films, with $\gamma$ passing through a minimum at $x = 0.33$. Eventually of course $\gamma$ must fall to that of the well-documented absorption edge of amorphous germanium, namely $\sim 5$ eV$^{-1}$. 

92
Figure 6.4  Tauc parameter $B^{1/2}$ of a-Ge$_x$Se$_{1-x}$ versus germanium content $x$.

- solid circles: sputtered films (present work);
- open circles: evaporated films (Kotkata 1993).
Figure 6.5 Urbach slopes $\gamma$ of a-Ge$_x$Se$_{1-x}$ versus germanium content $x$. •, sputtered films (present work); o, evaporated films (Kotkata 1993); ▲, glasses (Tronc 1973).
In § 6.1.3, experimental data for the absorption edges obtained by Photothermal Deflection Spectroscopy will be described. These results provide additional information on the Urbach slope parameter.

### 6.1.2 Refractive index

The real part of the refractive index $n$ was calculated by the method explained in § 5.4.2. The dispersion of $n$ for Ge$_x$Se$_{1-x}$ films with different compositions is presented in Fig 6.6. It is found that $n$ increases smoothly as the incident photon energy increases. The value $n(0)$, obtained by extrapolating the value $n$ to zero energy, increases with increasing Ge content in the samples.

In addition to the optical bandgap ($E_T$ or $E_0$), there are two other characteristic energies that can be derived from optical data. Wemple and Di Domenico (1971) and Wemple (1973) proposed that these can be derived from refractive index dispersion data by the following formula.

$$n^2 - 1 = E_d E_0 / (E_0^2 - h^2 \omega^2)$$

where $E_d$ is called the dispersion energy and $E_0$ the oscillator energy. The frequency dependence of the real part of the dielectric constant can be approximated by Eq 6.1 if interband transitions are regarded absorption by non-interacting oscillators having a single frequency. Values of $E_0$ and $E_d$ can be determined from the gradient and intercept of a plot of $(\hbar \omega)^2$ versus $(n^2-1)^{-1}$. The plot for our a-Ge$_x$Se$_{1-x}$ samples is shown in Fig 6.7 where $E=\hbar \omega$. Our data show good linearity for all compositions. Wemple and Di Domenico (1971) have reported similar behaviour for over fifty widely different ionic and covalent crystalline materials. From the linearity of the
Figure 6.6 Dispersion of the real part of the refractive index, n, for a-
Ge$_x$Se$_{1-x}$ thin films. The numbers on the curves are Ge % of the films.
Figure 6.7 $E^2$ versus $(n^2-1)^{-1}$: These plots can be used to determine the single-oscillator energy $E_0$ and the dispersion energy $E_d$. The numbers on the lines are germanium content $x$ for amorphous Ge$_x$Se$_{1-x}$ films.
curves, it would seem that Eq 6.1 describes the frequency dependence of the refractive index.

Wemple and Di Domenico (1971) found that the parameter \( E_d \), which is a measure of the strength of interband optical transitions, obeys the simple empirical relationship

\[
E_d = \beta N_C Z_a N_e
\]  \hspace{1cm} (6.2)

where \( N_C \) is the coordination number of the cation nearest neighbor to the anion, \( Z_a \) is the formal chemical valency of the anion, \( N_e \) is the effective number of valence electrons per anion and the constant \( \beta \) is essentially two-valued for a wide variety of solids and liquids, being 0.26±0.04 eV for ionic materials and 0.37±0.05 eV for covalent materials. Wemple (1973) further extended the validity of the simple empirical relationship, Eq 6.2, to amorphous solids. Noting that the presence of voids in amorphous solids may reduce the density, he found that \( E_d \) scaled with the ratio of the densities of the crystalline and amorphous materials. In his paper, \( E_d \) and \( E_0 \) for a-Ge are given as 35 eV and 2.3 eV, respectively and those of a-Se 18.6 eV and 3.9 eV, respectively.

The values of \( E_d \) and \( E_0 \) for a-Ge\(_{0.5}\)Se\(_{1.5}\) films obtained from Fig 6.7 are shown in Fig 6.8. It is seen that \( E_d \) monotonically increases with increasing Ge content in the samples. Referring to the \( E_d \) values for a-Ge and a-Se given by Wemple for evaporated films, the values for a-Ge\(_{0.5}\)Se\(_{1.5}\) alloys are expected to vary simply from 18.6 eV (the value for a-Se) to 35 eV (the value for a-Ge) with increasing Ge content in the samples. Our \( E_d \) values at low \( x \) are somewhat lower than expected but tend towards Wemple's value for a-Ge (\( x=1 \)). Density differences between evaporated and sputtered films may account for any lack of agreement. Similarly, according to the \( E_0 \) values calculated by Wemple, the \( E_0 \) of our a-Ge\(_{0.5}\)Se\(_{1.5}\) samples are expected
Figure 6.8  Single-oscillator energy $E_0$ and dispersion energy $E_d$ versus germanium content $x$ for a-Ge$_x$Se$_{1-x}$ films.
to fall from 3.9 eV to 2.3 eV with increasing Ge content in the samples. As seen in Fig 6.8, the $E_0$ of our samples show good agreement with the expected variation.

Our refractive index data can be interpreted using the following equation relating the refractive index at zero energy $n(0)$ to the Penn gap $E_g$ (Penn 1962)

$$n(0)^2 = 1 + (2/3)(\omega_p/E_g)^2 \quad (6.3)$$

where $\omega_p$ is the plasma frequency of the valence electrons and is proportional to the density of the material (Paul 1973). The Penn gap $E_g$ represents the average separation of the valence and conduction bands (i.e. greater than the optical bandgap).

As seen in Fig 6.6, $n(0)$ of our a-Ge$_x$Se$_{1-x}$ samples increases with increasing Ge content in the samples. From Eq 6.3, the increase of $n(0)$ may be interpreted to result from an increase of $\omega_p$ or a decrease of $E_g$ or both. Considering our optical bandgap data ($E_{0a}$, $E_T$, $E_0$), we expect the Penn gap $E_g$ to decrease with increasing Ge content in the samples.

If we consider the bond proportions in our samples, Ge-Ge bonds are more numerous in the Ge-rich samples. The volumes associated with Ge-Ge, Ge-Se and Se-Se bonds are known to be 11.2 Å$^3$, 10.4 Å$^3$ and 27.4 Å$^3$, respectively (see Table 6.2). Hence taking into account the bond volumes, we conclude that the Ge-rich samples should have a higher density and hence a larger plasma frequency compared to other samples.

Therefore, it seems that those two factors, the density of the films and the optical bandgap ($E_g$), might both play a role in the compositional dependence of $n(0)$ for our a-Ge$_x$Se$_{1-x}$ thin films.
6.1.3 PDS data

Fig 6.9 shows absorption edges of some chosen films deduced from both R-T and PDS measurements. By PDS measurements (see § 5.4.4), the absorption coefficients were extended reliably down to near $10^1 \text{ cm}^{-1}$. Unfortunately, some of the films were too thin (thickness < 0.5 µm) for this technique to be applied to the whole set of samples. Compared to the former absorption edges shown in Fig 6.1, the Urbach regions of the edges are somewhat different in these PDS measurements, which is expected since the R-T method is not reliable in the low-absorption region ($a<10^3 \text{ cm}^{-1}$).

The new Urbach slopes $\gamma$ are co-plotted with the former results in Fig 6.10. Those of 4 hydrogenated and 3 unhydrogenated a-Ge$_x$Se$_{1-x}$ films are presented in the figure. As seen, the slopes $\gamma$ of the unhydrogenated samples still show the downward trend as the germanium content increases in the samples. This seems to rule out the upward variation of $\gamma$ for $x > 0.3$ as found by Kotkata (1993).

The results for hydrogenated films ($X$ on Fig 6.10) are rather scattered. However for Ge-rich samples, the values of $\gamma$ are clearly higher than for the unhydrogenated films which means a steepening of the absorption edge. The effect of hydrogen in steepening the edge of a-Ge is well known (Lewis et al 1974). Just as for a-Si, hydrogen replaces weak bonds in the amorphous network, thereby reducing the extent of valence-band tailing.

6.2 Effect of hydrogenation

Compared to the beneficial effects of hydrogen incorporation in amorphous silicon and germanium, namely saturation of dangling bonds and a reduction in band tailing, we shall see that there appears to be weak
Figure 6.9 The optical absorption edges of some chosen films deduced from both R-T and PDS measurements.
Figure 6.10 Urbach slopes $\gamma$ in Fig 6.5 with the new values of $\gamma$, deduced from the altered absorption edges by the PDS measurements.
evidence for similar behaviour in our a-Ge\textsubscript{x}Se\textsubscript{1-x}:H films. It seems difficult to introduce hydrogen in concentrations of more than a few percent, as indicated by the absence, in our films at least, of infrared bands associated with hydrogen bonding. Unfortunately, our composition analysis using the SEM-EDAX has the drawback of not to be able to detect the absolute amounts of hydrogen in the films.

Fig 6.11 shows the optical absorption edges of our sputtered amorphous Ge\textsubscript{x}Se\textsubscript{1-x}:H samples. Comparing these edges to those of a-Ge\textsubscript{x}Se\textsubscript{1-x} samples in Fig 6.1, the edges of germanium-rich samples appear to be steepened slightly, showing that hydrogen incorporation has been achieved. For comparison, the optical bandgaps, $E_{04}$, of the a-Ge\textsubscript{x}Se\textsubscript{1-x}:H samples are presented in Fig 6.12 along with those of the unhydrogenated samples. The largest effects of hydrogen incorporation occur for the germanium-rich samples ($x > 0.7$), for which the optical gap increased by a few tenth of an electron volt. For the selenium-rich samples, there does not appear to be a consistently meaningful change in the slope of the edges and any changes of the bandgap are less clear-cut. In the case of germanium-rich samples ($x>0.7$), one expects a high concentration of dangling bonds and strained networks. It is well known that hydrogenation of amorphous germanium removes dangling bond defect levels from the gap and, by relieving strain, reduces the amount of bond tailing. It is the latter process that is responsible for sharpening the optical absorption edge and widening the gap. It is perfectly reasonable to expect similar behaviour in the germanium-rich alloys.

Other evidence for hydrogen incorporation can be found in the d.c. conductivity data shown in Fig 6.13. The d.c. electrical conductivities of the films were measured as a function of temperature from room temperature down to about 150 K. Results from hydrogenated and un-hydrogenated samples having the same composition are here selected from a larger set of
Figure 6.11 Optical absorption edges deduced from R-T measurements for hydrogenated $a$-Ge$_{x}$Se$_{1-x}$ thin films.
Figure 6.12 Optical bandgaps ($E_{04}$) versus germanium content $x$ of hydrogenated and unhydrogenated $a$-Ge$_x$Se$_{1-x}$ thin films.
Figure 6.13: Temperature dependencies of d.c. electrical conductivities for hydrogenated and unhydrogenated a-Ge$_{0.65}$Se$_{0.35}$ thin films.
data, for the purpose of comparison. The result shows that the d.c. conductivity at room temperature (294 K) falls by about 10%, and the calculated activation energy increases by about 0.06 eV after hydrogenation. If we take the activation energy as a measure of half the optical gap (assuming the Fermi level is pinned near the centre of the bandgap), these results provide further evidence of band widening by hydrogenation.

6.3 Ternary alloys of $\text{Ge}_x\text{Se}_y\text{Zn}_z$

The addition of zinc to GeSe films does not affect the optical absorption edges significantly, even in concentrations up to 27%. Fig 6.14 shows the absorption edges of some ternary films. The values of $E_{03}$ and $E_{04}$ were deduced from the absorption measurements. Here we tabulate results for four films having compositions close to Ge$_{50}$(Se$_y$Zn$_z$)$_{50}$, which illustrate the effect of zinc alloying when the germanium content is kept constant.

<table>
<thead>
<tr>
<th>$\text{Ge}_x\text{Se}_y\text{Zn}_z$</th>
<th>$E_{04}$</th>
<th>$E_{03}$</th>
<th>$E_a$</th>
<th>$2E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x%</td>
<td>y%</td>
<td>z%</td>
<td>eV</td>
<td>eV</td>
</tr>
<tr>
<td>49</td>
<td>51</td>
<td>00</td>
<td>1.28</td>
<td>0.95</td>
</tr>
<tr>
<td>54</td>
<td>27</td>
<td>19</td>
<td>1.23</td>
<td>0.99</td>
</tr>
<tr>
<td>53</td>
<td>24</td>
<td>23</td>
<td>1.21</td>
<td>1.02</td>
</tr>
<tr>
<td>50</td>
<td>23</td>
<td>27</td>
<td>1.27</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 6.1

Optical gaps ($E_{03}$ and $E_{04}$) and conductivity activation energies ($E_a$) in ternary alloys of $\text{Ge}_x\text{Se}_y\text{Zn}_z$. $2E_a$ is tabulated for comparison with the optical gaps.

It is seen that neither measure of the optical gaps ($E_{03}$ or $E_{04}$) is changed appreciably.

The d.c. electrical conductivities of the same films have been measured as a function of temperature from room temperature down to about 150 K. Plots of the logarithm of the conductivity versus reciprocal temperature
Figure 6.14 Optical absorption edges deduced from the R-T method for a-Ge$_x$Se$_y$Zn$_z$ thin films.
Figure 6.15  Temperature dependencies of d.c. electrical conductivities for a-Ge₄ₓSe₃₁ and two a-GeₓSeₓZnₓ thin films.
display linear (i.e. single-activated) behaviour, examples of which are presented in Fig 6.15. The activation energies \( E_a \) of the films were also calculated from the plots and are shown in Table 6.1. The values of \( 2E_a \) are also listed for comparison with the optical gaps. The similarity between \( 2E_a \) (1.32 eV) and \( E_{04} \) (1.28 eV) for the approximately stoichiometric a-GeSe film \( (z=0) \) suggests a Fermi level pinned near mid-gap which is a general phenomenon for amorphous chalcogenides (Mott & Davis 1979). Addition of zinc leads to a fall in \( E_a \) to ~ 0.41 eV and a tentative conclusion might be that the Fermi level has been shifted by about 0.25 eV. However, it should be mentioned that the value of the pre-exponential factor falls from \( \sim10^5 \) \( \Omega^{-1}\text{cm}^{-1} \) for a-GeSe to approximately \( 10^2 \) \( \Omega^{-1}\text{cm}^{-1} \) for the zinc-alloyed samples. This behaviour suggests a change in the conduction path and it is not possible to conclude that doping has occurred. For a further examination of this behaviour, it is needed to make thermopower measurements to establish the magnitude and direction of any shift in \( E_p \) and to ascertain if there is a change in carrier type, as occurs for example in Bi-doped glasses (Nagels 1981).

6.4 Modelling the Dielectric Function

[The author is grateful to Dr S J Gurman for considerable assistance with the analysis described in § 6.4]

6.4.1 Introduction

The dielectric function is defined by \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) where \( \varepsilon_1 \) and \( \varepsilon_2 \) are its real and imaginary parts. Corresponding to the dielectric function is the refractive index \( N=n+ik \), in which the real part \( n \) is the 'usual' refractive
index discussed in earlier sections and k is the extinction coefficient. Since 
\( \varepsilon = N^2 \), we can write

\[ \varepsilon_1 + i\varepsilon_2 = n^2 - k^2 + 2ink \]  \hspace{1cm} (6.4)

and, equating real and imaginary parts, we have

\[ \varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2nk \]  \hspace{1cm} (6.5)

The extinction coefficient k is related to the absorption coefficient by 
k=\( \alpha(\lambda/4\pi) \), where \( \lambda \) is the wavelength of light in a vacuum.

The four optical constants \( \varepsilon_1, \varepsilon_2, n \) and k are not independent parameters but are related through Kramers-Kronig relations (Elliott 1984). Their variation with photon energy contains information on electronic transitions and can be related to the density of electronic states.

A survey of the measured values of \( \varepsilon_1 \) and \( \varepsilon_2 \) for amorphous covalent alloys shows that they generally have very similar shapes when plotted as functions of photon energy. It follows that each may be described in terms of two basic parameters: an amplitude scale and an energy scale. Much work has been done on this scaling theory since its original statement by Philips (1968), and methods of calculating the scaling parameters, and hence the dielectric function, for homogeneous stoichiometric crystals have been given by von Vechten (1969) and Levine (1973).

Optical absorption is caused by the excitation of electrons across a bandgap, from a valence band (or bonding) state to a conduction band (anti-bonding) state. Thus for \( \varepsilon_2(E) \), the imaginary part of the dielectric function, the energy scaling parameter is related to a bandgap since the bandgap fixes the energy at which strong absorption sets in. The amplitude scaling parameter for \( \varepsilon_2(E) \) is related to the electron density.
The early work on scaling considered stoichiometric crystals, in which only one type of bond can occur. In order to extend it to amorphous materials of arbitrary composition, where several types of bond generally occur, we need to consider rather carefully the microscopic entities which give rise to the dielectric response of the material. The simplest model describes the dielectric function of the alloy as due to a combination of contributions from each bond present, each with a characteristic dielectric behaviour. We shall describe this as the independent bond model (IBM). The model gives good results for binary alloys (Gurman 1992) and even ternary alloys (Bayliss and Gurman 1994) and is the one we shall use here for Ge$_x$Se$_{1-x}$, amorphous thin films. It is oversimplified in that it neglects interaction between bonds. If these are significant we could describe the structure of the amorphous alloy in terms of larger structural units, such as a Ge-centred tetrahedron of bonds but this is not attempted here.

### 6.4.2 Background theory

The independent bond model

We assume that the dielectric function of an amorphous covalent alloys is based on the individual covalent bonds. The use of bond polarizabilities to build up the polarizability of a compound is well known in chemistry and it seems reasonable to apply a similar technique to amorphous covalent alloys. Thus, in Ge$_x$Se$_{1-x}$ we consider Ge-Ge, Ge-Se and Se-Se bonds in proportions which depend on the composition and which may be calculated (Gurman 1996) if the bond energies are known or obtained from EXAFS experiments. A Ge-Ge bond is assigned the dielectric function of amorphous germanium (amorphous to avoid the selection rules characteristic of crystals): the Ge-Se bond that of amorphous GeSe$_2$: 
and Se-Se bond that of amorphous selenium. The latter two could in fact be calculated from the first using scaling theory (Levine 1973) but we shall use experimental data in all cases.

We have to be careful about how the bond contributions add together. In molecules, we simply add the polarizabilities. This is sufficient because the bond density is low and so self-field effects are negligible. Such an approach has also been tried for amorphous covalent alloy (Shimakawa 1981) but it fails. The simple approach predicts a linear variation of \( \varepsilon_1(0) \) (the real part of the dielectric function extrapolated to zero energy) and \( E_g \) with composition. Whilst \( \varepsilon_1(0) \) is often roughly a linear function of composition, \( E_g \) rarely is. In fact the bandgap \( E_g \) of amorphous covalent alloys characteristically shows a cusp shape, peaking at a stoichiometric composition such as in GeSe₂.

A linear combination of bond susceptibilities or dielectric functions implies the existence of a uniform electric field throughout the sample and thus neglects the screening charge which is developed at the boundaries between components of different polarizabilities. Thus, for example, a highly polarizable inclusion in a dielectric matrix develops a surface charge when an external field is applied and this charge tends to exclude the field from the inclusion (Lenz's law). Hence the contributions from an inclusion with a large values of \( \varepsilon \) is less than that given by simple superposition of polarizabilities weighted by volume function. Nor is the simple Clausius-Mosotti expression likely to be accurate, although this is the standard approach used in chemistry. This is because the Clausius-Mosotti expression is not self-consistent and so is only valid when the polarizable medium occupies a volume that is a small fraction of the total volume of the sample.

The accurate calculation of the dielectric properties of a heterogeneous medium is a difficult problem which has been discussed in detail by
Grandqvist and Hunderi (1977). Here we use the effective medium approximation (EMA) of Bruggemann (1935). This considers a polarizable inclusion in an effective dielectric medium and treats it self-consistently. For a medium made up of several phases \( i \), the EMA expression for the mean complex dielectric function \( < \varepsilon > \) is

\[
\sum V_i (\varepsilon_i - < \varepsilon > ) / ( \varepsilon_i + 2 < \varepsilon > ) = 0
\]

(6.6)

where \( V_i \) is a volume function and \( \varepsilon_i \) is the complex dielectric function of phase \( i \). Shimakawa's (1981) treatment omits the denominator of Eq 6.6.

For our purposes the phases are the individual bonds, each with a dielectric function characteristic of a (stoichiometric) amorphous solid containing only that bond. Hence we write \( V_i \) in terms of a bond proportion \( v_{ij} \) and a volume per bond \( V_{ij} \).

\[
V_i \rightarrow v_{ij} V_{ij}
\]

(6.7)

The bond volume \( V_{ij} \) is obtained from the atomic density of the standard material. The bond proportions \( v_{ij} \) may be obtained from a general theory (Gurman 1996), a simple model (e.g. ordered or random bond networks) or from experiment. The possibility of small voids in the material can be taken into account by including a volume function with \( \varepsilon = 1 \) (Gurman 1992), but we do not consider this possibility here.

**Bond proportions**

The general theory of bonding in an amorphous binary covalent materials \( AB \) (Gurman 1996) gives the partial coordination number \( N_{ij} \),
the number of type j atoms bond to a type i atom, in terms of a bond energy difference $\Delta E$:

$$\frac{N_{AB}N_{BA}}{N_{AA}N_{BB}} = \exp\left(-\frac{2\Delta E}{kT}\right)$$

where $\Delta E = E_{AB} - \left(\frac{1}{2}\right)(E_{AA} + E_{BB})$ (6.8)

with $T$ a fictive temperature. $T$ is usually considered to be equal to the glass transition temperature (Gurman 1990), the temperature at which the structure becomes 'frozen in'. Equation 6.8 is found to describe the experimental data for amorphous covalent materials rather well. $\Delta E$ can be calculated from the electronegativities of the atoms (Pauling 1960). For the majority of amorphous covalent materials, $\Delta E$ is large (compared to $kT$) and negative so the right-hand side of equation 6.8 is large.

Two simple models are also used: the ordered bond network (OBN) and the random (RBN) bond network. These are limiting cases of equation 6.8. For the OBN we let $\Delta E \to -\infty$ and for the RBN we set $\Delta E = 0$. In both cases we can solve for the $N_{ij}$ very simply by use of equation 6.8 and the consistency equations.

$$N_A = N_{AA} + N_{AB}$$
$$N_B = N_{BA} + N_{BB}$$
$$c_AN_{AB} = c_BN_{BA}$$ (6.9)

in which $N_i$ is a total coordination and $c_i$ is an atomic concentration. The last of equation 6.9 states that the number of AB bonds is the same whether viewed from the A or from the B end.
The proportions of the several bonds present may be obtained from the partial coordinations. Denoting the proportion of ij bonds by $v_{ij}$ as in equation 6.7 we have

$$
v_{AA} = \frac{c_A N_{AA}}{N}
$$

$$
v_{AB} = \frac{2c_A N_{AB}}{N} = \frac{2c_B N_{BA}}{N}
$$

$$
v_{BB} = \frac{c_B N_{BB}}{N}
$$

$N = c_A N_A + c_B N_B$  \hspace{1cm} (6.10)

where $N$ is the total number of bonds of all types. For the OBN model, $\Delta E \to \infty$ implies that $N_{AA}$ or $N_{BB}$ is equal to zero. Use of equation 6.9 gives the composition range where one or the other is appropriate. Thus in this model we find:

\begin{enumerate}
\item[(OBN)]
$c_A N_A \leq c_B N_B$

$$
v_{AA} = 0 \quad v_{AB} = \frac{2c_A N_{AA}}{N} \quad v_{BB} = \frac{c_B [N_B - c_A N_A / c_B]}{N} \quad N = c_A N_A + c_B N_B
$$

\item[(RBN)]
$c_A N_A \geq c_B N_B$

$$
v_{AA} = c_A \left[ N_A - c_B N_B / c_A \right] / N \quad v_{AB} = \frac{2c_B N_B}{N} \quad v_{BB} = 0
$$
\end{enumerate}

(6.11)

For the RBN, $\Delta E = 0$. Solving equation 6.8 and 6.9 for the partial coordinations and then using equation 6.10 gives

\begin{enumerate}
\item[(RBN)]
$$
v_{AA} = c_A^2 N_A^2 / N^2 \quad v_{AB} = \frac{2c_A c_B N_A N_B}{N^2} \quad v_{BB} = \frac{c_B^2 N_B^2}{N^2}
$$
\end{enumerate}

(6.12)

6.4.3 Results

We have seen that Ge$_x$Se$_{1-x}$ samples may be made in the form of bulk glasses for $x \leq 0.4$ and as sputtered thin films over the whole composition range. Good structural and optical data are available for both forms.
Structural data on bulk glasses (Zhou et al 1991, Armand et al 1992) show that they are made up of a chemically-ordered network of four-fold coordinated germanium and two-fold coordinated selenium atoms. The bond lengths are independent of composition and take the usual covalent values with very little variation in bond lengths. The random structure of the glasses is therefore due to variation in bond angles, as is usual in covalent glasses. The local structure is accurately given by the OBN, which can therefore used to describe the bond proportions in the bulk glasses. Some information on the longer-range structure, suggesting a random arrangement of the larger structural units (such as Ge tetrahedra) is given by analysis of the infra-red data (Tronc et al 1973: Gurman 1996). The density of the glasses varies little with composition and is about 10% lower than that of the crystalline forms (Feltz et al 1983).

Thin film samples may be prepared over the whole composition range by means of RF sputtering (present work) or evaporation (Kotkata 1993). Our EXAFS data show on sputtered films that these also have a 4-2 coordinated network structure. The degree of chemical order is high but not complete, corresponding to a value $\Delta E/kT = -1$ in equation 6.8 (so that the right-hand side of equation 6.8 takes a value of about 7). The bond lengths are again the standard covalent lengths and there is little variation in these with composition.

The electronegativities (Phillips 1973) give a value for the bond energy difference $\Delta E = -0.36$ eV. For the bulk glasses $T_g = 300-600$ K, depending on composition (Feltz 1983). Hence for the bulk glasses $\Delta E / kT_g = -14 \to -7$, consistent with the observation of complete chemical order. The partial order observed in our sputtered films corresponds to the very high fictive temperature of about 4000 K.

Good optical data is available for bulk glass and thin film samples. For the bulk glasses $\varepsilon_1(0)$ has been measured by Lucovsky (1977) and the
absorption coefficient by Tronc et al (1973). For film samples we have data on the bandgap, in the form of $E_0$ (the energy where the absorption coefficient $\alpha = 10^4 \text{ cm}^{-1}$), for sputtered films (present work) and evaporated films (Kotkata et al 1993). The latter authors also give values of $\alpha$ and $\varepsilon_\infty$.

Amorphous $\text{Ge}_x\text{Se}_{1-x}$ materials can contain Ge-Ge, Ge-Se and Se-Se bonds and we need dielectric function for these. We use the experimental data for amorphous Ge (Donovan et al 1970), GeSe$_2$ (Murase 1982) and Se (Stuke 1970), the last two relating to bulk glasses. The variations in the measured values for a-Ge, and the previous analysis of $\text{Si}_{1-x}\text{N}_x$ (Gurman 1992) suggest that an experimental uncertainty of $\pm 5\%$ may be associated with these data. Also, in using experimental data we are implicitly assuming that the experimental samples contain no voids and, in the case of GeSe$_2$, are completely chemically ordered. We consider these points further below. The experimental data are shown in Fig 6.16.

**OBN**

We first consider the ordered bond model, appropriate to the bulk glasses and an approximation to the structure of the thin-film samples. In this only two types of bond exist at a given composition (Eq 6.11) and so the EMA expression, equation 6.6, is a quadratic in $<\varepsilon>$. We find that only one valid solution, with a positive value for the mean $\varepsilon_2$, exists at any composition.

In order to use equation 6.6 we need not only the bond proportions $v_{ij}$ but also the volume per bond (Eq 6.7). These may be obtained from the densities of the crystals and are given in Table 6.2. We use the crystal values since the bond lengths are known to be the same in crystalline and amorphous samples.
Figure 6.16 Standard dielectric functions: (a) dielectric function of a-Ge bulk glasses measured by Donovan (1970), (b) dielectric function of a-GeSe$_2$ (Murase 1982), (c) dielectric function of a-Se glasses (Stuke 1970).
Table 6.2

<table>
<thead>
<tr>
<th></th>
<th>Ge-Ge</th>
<th>Ge-Se</th>
<th>Se-Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length Å</td>
<td>2.44</td>
<td>2.38</td>
<td>2.31</td>
</tr>
<tr>
<td>Atomic vol. Å³</td>
<td>22.4</td>
<td>20.8</td>
<td>27.4</td>
</tr>
<tr>
<td>Bond vol. Å³</td>
<td>11.2</td>
<td>10.4</td>
<td>27.4</td>
</tr>
</tbody>
</table>

The bond volume is the atomic volume divided by two for Ge and GeSe₂ (four half bonds per unit) and by one for Se (two half bonds per unit).

With these bond volumes and the bond proportions given by equation 6.11 we can solve equation 6.6 for \( < \varepsilon > \), the mean dielectric function of the sample. From this we can obtain the absorption coefficient \( \alpha \) using

\[
\alpha = \left( \frac{1}{\text{c} \text{h}} \right) E \varepsilon_2/n
\]

(6.13)

where \( n = \sqrt{\frac{1}{2} \{ \varepsilon_1 + \sqrt{(\varepsilon_1^2 + \varepsilon_2^2)} \} \} \) is the refractive index and \( (1/\text{c} \text{h}) \) is a constant, where \( c \) is the velocity of light. With \( E \) in eV, \( \alpha = 10^4 \text{ cm}^{-1} \) corresponds to a value \( E \varepsilon_2/n \equiv 0.2 \). We use \( E_{04} \) as our estimate of the optical gap.

In Fig 6.17 we compare our modelled results with the experimental data for \( E_{04} \), the standard approximation for the optical bandgap. The sharp cusp in the modelled results at \( x = 0.33 \) (GeSe₂) is characteristic of the OBN results. The experimental data for bulk glasses (Tronc 1973) seems to shows a similar cusp and these are known to be fully ordered (Zhou 1991). The experimental data for our thin films suggest a more rounded peak on the data: this is probably due to the presence of some chemical disorder in these films. We consider this point further below. In general, the modelling reproduces the experimental data rather well, although it
Figure 6.17 Optical bandgaps ($E_{04}$) of a-Ge$_{x}$Se$_{1-x}$ versus Ge content $x$ in comparison with the modelled curve calculated in accordance with Ordered-Bonded-Network model (The data points are explained in the caption of Fig 6.2).
should be noted that the theoretical results are pinned to experimental data at $x=0.00, 0.33$ and $1.00$ by our use of experimental dielectric functions. However, we believe the reproduction of the shape of the $E_{04}$ curve is significant. It is clearly non-linear, contrary to the simple theories used by Shimakawa (1981) and Tronc et al (1973).

In Fig 6.18 we compare our modelled results for the low energy dielectric function $\varepsilon_1(0)$ with experiment. Again we see good agreement with experiment. $\varepsilon_1(0)$ is much less sensitive to bonding than is $E_{04}$. The same effects are seen in Si$_{1-x}$N$_x$ (Gurman 1992) and Si$_{1-x}$O$_x$ (Bayliss & Gurman 1994). We also note that $\varepsilon_1(0)$ is sensitive to the presence of voids, whereas $E_{04}$ is not (Gurman 1992). The agreement between theory and experiment suggests that the void proportion in evaporated films is low and comparable to that in the bulk glasses we use as standards for the dielectric functions.

In Fig 6.19 we compare values of the absorption coefficient $\alpha$. The modelling results can only be trusted for $\alpha > 10^3$ cm$^{-1}$ since, below this, $\varepsilon_2(E)$ is too small to be accurately taken from experiment. We note that the modelling results give a good description of the shape of $\alpha(E)$ in this range although there are some energy offsets (which give rise to differences in $E_{04}$ values as in Fig 6.17). It also appears that the modelling results give too broad a variation in $\alpha(E)$ at intermediate compositions (e.g. $x=0.2$). This may be due to the chemical disorder in the films or, more likely, since the experimental steepness appears in Tronc's (1973) data for bulk glasses, to a failure of the simple IBM to model correctly the rapid rise in $\varepsilon_2(E)$. If this is the case then a similar failure occurs in the more complex tetrahedral model (Gurman 1992).
Figure 6.18 Comparison of the OBN-modelled results (—) for the low energy dielectric function $\varepsilon_1(0)$ of a-Ge$_x$Se$_{1-x}$ with experimental data. x axis, Ge content; o, sputtered films (present work); x, glasses (Lucovsky 1977); Q, glasses (Feltz 1993); ♦, evaporated films (Kotkata 1993).
Figure 6.19 Comparison of the OBN-modelled results (—) for the absorption coefficient $\alpha$ (cm$^{-1}$) of a-Ge$_x$Se$_{1-x}$ (x=0.2, 0.33, 1) with experimental data. x axis, incident photon energy (eV); 0, sputtered films (present work); x, evaporated films (Kotkata 1993).
RBN

The presence of chemical disorder in an amorphous material would be expected to smooth out any sharp failures in the composition dependence of the optical properties, simply because it smooths out the composition variation of the bond proportions. We can easily handle partially-ordered or disordered materials in our theory, by calculating the bond proportions from equation 6.8 and 6.9 for a particular value of $\Delta E/kT$ and by including all these bond contributions in equation 6.6.

The results obtained for Ge$_x$Se$_{1-x}$ using $\Delta E/kT = 0$ (RBN); -1(best fit to structure) and $-\infty$ (OBN) are shown on Fig. 6.20 for $E_{04}$. We see that disorder does indeed smooth out the structure. For $E_{04}$, increasing disorder pushes the maximum towards higher Se content: this is expected since the Ge-Ge bond has the lowest bandgap and many bonds do exist for $x > 0.33$ if the order is not complete. All data appear to follow a smooth curve rather than showing a sharp cusp at $x = 0.33$. $\Delta E/kT = -1$ gives the best fit to our structural data.

The data for $\varepsilon_1(0)$ is much less clear cut. The theoretical rounding effect is rather small, and no rounding appears in the experimental data.

We have no experimental data on the dielectric function of amorphous Ge$_x$Se$_{1-x}$ except for the three reference compounds used (a-Ge, a-GeSe$_2$, a-Se). Scaling can be applied to the three bond contributions: the dielectric functions of both GeSe$_2$ (Ge-Se bond) and Se (Se-Se bond) can both be reasonably well represented by scaling the a-Ge (Ge-Ge bond) dielectric function using the theory developed by Phillips (1968) and Levine (1973) and further extended by Gurman (1992) and Bayliss (1991).
Figure 6.20  Comparison of optical gaps ($E_{04}$) of $a$-Ge$_x$Se$_{1-x}$ reproduced by several modelled results with experimental data. $x$ axis is germanium content. •, sputtered films (present work); the other data points are explained in the caption of Fig 6.2.
6.4.4 Discussion

We have described a self-consistent method for modelling the dielectric functions of amorphous covalent alloys. The method is based on the physical idea of a dielectric function which is a characteristic of a particular covalent bond. The dielectric function of the alloy is then obtained by self-consistently adding these contributions, weighted by the volume proportions of the different bonds present in the sample. The self-consistency requirement (the denominator of equation 6.6) is important since, without it, \( \varepsilon(E) \) is a linear function of bond proportions and hence, for chemically ordered systems, of composition. This model, used by Tronc (1973) and Shimakawa (1981) does not give good agreement with experiment.

The bond proportions can be obtained from theory (Gurman 1996) or from experiment. Most covalent amorphous materials show complete or nearly-complete AB ordering due to the large differences between covalent bond energies (Feltz 1993).

The structural data for amorphous sputtered thin films of Ge\(_x\)Se\(_{1-x}\) show that they are made up of a network of four-fold coordinated germanium and two-fold coordinated selenium atoms. The bond lengths take their usual covalent values and have very small mean square deviations. The degree of AB ordering is high but not complete, corresponding bond energy difference \( \Delta E/kT = -1 \). Bulk glass samples show complete order.

The modelled values of \( \varepsilon_04 \) show a sharp cusp at \( x = 0.33 \), the stoichiometric composition, if the chemical order is complete. This cusp is rapidly rounded off by the presence of chemical disorder.

Our modelled results give a fairly good description of the experimental data for \( \varepsilon_04 \) and \( \varepsilon_1(0) \), both as regards the absolute values (which are
pinned to experiment at $x=0.0, 0.33$ and 1.00 by our use of experimental dielectric functions) and the variation with composition. In particular the rounded shape, arising from partial chemical disorders, is apparent in the experimental data for $E_{04}$ for sputtered or evaporated films. The bulk glasses probably show a sharper variation although the data is sparse for $E_{04}$. Tronc's data for $E_{03}$ of Se-rich bulk glasses do show a good cusp-like behaviour. Our $E_{03}$ data is untrustworthy since it corresponds to very low values of $\varepsilon_3(E)(-0.1)$ where the experimental data is not clearly defined.

The shape of the absorption coefficient $\alpha(E)$ is reasonably well reproduced, for $\alpha > 10^3$ (corresponding to $\varepsilon_2(E) \sim 0.1$) although the model results fall off more rapidly at high $\alpha$. This is most likely due to experimental difficulties with highly absorbing samples: $\varepsilon_2(E)$ is unlikely to be in error by more than 10% - 50%.

There is, unfortunately, no experimental data for $\varepsilon(E)$ so we cannot compare the major, primary prediction of our model with experiment.
Chapter 7 Results: Structural properties of a-Ge$_x$Se$_{1-x}$ and related alloy thin films

7.1 EXAFS spectroscopy: a-Ge$_x$Se$_{1-x}$ films
7.2 EXAFS spectroscopy: a-Ge$_x$Se$_y$Zn$_z$ films
7.1 EXAFS spectroscopy: a-Ge\textsubscript{x}Se\textsubscript{1-x} films

EXAFS data from both the germanium and selenium K-edges in a-Ge\textsubscript{x}Se\textsubscript{1-x} thin-film samples (0.2 ≤ x ≤ 1) were obtained using the SRS beamline at station 7.1 in the CLRC Daresbury Laboratory. Measurements on the both K-edges were performed in transmission mode using 0.5-3.5 μm thick samples deposited on mylar substrates which did not absorb or attenuate the beam significantly in the energy range used.

X-ray absorption spectra for the Ge and Se K-edges of a-Ge\textsubscript{x}Se\textsubscript{1-x} films obtained from the experiments, were analysed using the computer programs described in § 5.1.5. The amplitude-damped EXAFS spectra, extracted from the absorption spectra, were then weighted by \( k^3 \) in order to compensate for amplitude reduction and Fourier-transformed to real space to yield radial distribution functions (RDFs). Some examples of the final EXAFS functions, \( \chi(k) \), and the RDFs for the Ge and Se K-edges of a-Ge\textsubscript{x}Se\textsubscript{1-x} films are presented in Fig 7.1-7.3. As seen in the figures, the samples show only one strong peak in the RDFs. This implies that our films preserve only short-range order primarily in the first shell of nearest neighbours and considerable structural disorder exists in higher shells.

When the k-space EXAFS spectra were Fourier-transformed to real space, the fitting range was selected from \( k=1 \) to 12.5 Å\(^{-1} \) for the Ge K-edge data and from \( k=2 \) to 11.5 Å\(^{-1} \) for the Se K-edge data in order to filter noise from the spectra and obtain better fittings of experimental curves with the theory. Throughout the analysis of each EXAFS spectrum by the EXCURV92 program, the amplitude factor AFAC (the parameter which corrects for amplitude reductions arising from events such as multiple excitations) and the VPI (the parameter which take into account inelastic losses and the core-hole lifetime) were fixed at 1.0 and -4.0, respectively for the Ge and Se K-edges. These values were obtained from an analysis of
Figure 7.1 The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge film at the Ge K edge.
Figure 7.2 (a) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{0.29}$Se$_{0.71}$ film at the Ge K edge.
Figure 7.2 (b) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{0.39}$Se$_{0.71}$ film at the Se K edge.
Figure 7.3 (a) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{0.66}$Se$_{0.34}$ film at the Ge K edge.
Figure 7.3 (b) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{0.66}$Se$_{0.34}$ film at the Se K edge.
results from a standard a-Ge sample. The parameter $E_0$ which adjusts for the position of the X-ray absorption edge, was chosen from the EXCALIB program and was allowed to vary freely in the fitting procedure. The scattering phaseshifts of each neighbour atom type were calculated and applied in the fitting process. The several parameters explained in § 5.1.5 were then continuously refined by iteration processes until the best fit between the experimental and theoretical curves was obtained. After using possible different atom types as nearest neighbours, the curve with parameters giving the minimum fit index, $F_I$, was chosen as the final result.

The lengths of the Ge-Ge, Ge-Se and Se-Se bonds determined from the analyses are presented in Fig 7.4. The values obtained from samples with different composition are plotted versus the Ge content. The Ge-Ge bond lengths were found to have an average of $2.46 \pm 0.03 \text{Å}$, with an indication of a slight increase in the values for the Se-rich samples (Ge<60%) from its average value. The average Ge-Ge bond length, $2.46 \text{Å}$, is slightly longer than the known crystalline value, $2.44 \text{Å}$. However, considering the experimental error, the agreement between the two values suggests that the nearest-neighbour bond lengths between Ge atoms are the same in crystalline and amorphous samples. The bond lengths of the Ge-Se and Se-Ge bonds, which were obtained from analyses of the Ge and Se K-edge data, respectively, were found to be both $2.38 \pm 0.03 \text{Å}$ and almost independent of composition. This value is the same as the known crystalline value, $2.38 \text{Å}$. The Se-Se bond lengths in samples with different compositions average to $2.32 \pm 0.03 \text{Å}$, again in good agreement with the known crystalline value, $2.31 \text{Å}$. The overall results are consistent with those obtained on bulk glasses (Zhou 1991) and suggest that the bond lengths are unaffected by the number or type of bonds surrounding each
**Figure 7.4** First-shell bond distances determined from the Ge and Se K-edge data versus Ge atomic percentage in a-Ge$_x$Se$_{1-x}$ samples.
atom. The amorphous nature of the samples does not therefore arise from variations of bond lengths between atoms.

The mean square deviation in nearest-neighbour distances (i.e. bond lengths), the Debye-Waller factors, $\sigma^2$, are shown in Fig 7.5. One of the fitting parameters, $A$, in the data analyses is related to this value, $\sigma^2$, by the equation $A=2\sigma^2$. The value of $\sigma^2$ is the half-width of the peak in the RDFs and is directly related to the amount of disorder in the bond lengths shown in Fig 7.4. Generally, in the case of amorphous material, the experimentally-determined Debye-Waller factor has contributions from both thermal and static disorder. If we assume that the crystalline state has only thermal disorder, the static disorder in the amorphous material can be easily determined by subtracting the value obtained from a crystalline standard. The Ge-Ge Debye-Waller factors in Fig 7.5 show little variation with Se content but are generally higher than that of the a-Ge sample ($40 \times 10^{-4}$Å²) and increase up to about $100 \times 10^{-4}$Å² in the sample with the largest Se content. This implies that though the values contain contributions from both thermal and static disorder, the disorder in bond lengths is increased with increasing selenium content in the a-Ge$_{x}$Se$_{1-x}$ films. This result is not entirely surprising. The a-Ge has an amorphous structure based on the tetrahedral bond, and the addition of two-fold coordinated selenium is expected to increase the disorder in the system. The Debye-Waller factors for Ge-Se and Se-Ge bonds are almost independent of the composition, having an average value of $37 \times 10^{-4}$Å². This implies that the disorder in these samples is similar over the whole composition range. Note that the values determined from both the Ge and Se K-edges are consistent with each other. Comparing the average value $37 \times 10^{-4}$Å² to that of a-Ge ($40 \times 10^{-4}$Å²), suggests that there is a fairly small static disorder in the lengths of Ge-Se and Se-Ge bonds. If we consider that the chemical bond energies decrease in the order of Ge-Se, Ge-Ge, Se-Se
Figure 7.5 Composition dependence of the mean square deviation in bond lengths obtained from the Ge and Se K-edge data for a-Ge$_x$Se$_{1-x}$ thin films.
it can be easily understood that Ge-Se bonds are mostly preferred and also have maximum chemical stability. Hence, compared to the lengths of other bonds, those of Ge-Se (Se-Ge) bonds should have less static disorder. As seen in Fig 7.5, the Debye-Waller factors for Se-Se bonds are distributed from $5 \times 10^{-4} \text{Å}^2$ to $25 \times 10^{-4} \text{Å}^2$ with varying germanium content ($20<\text{Ge}(%)<50$). The disorder in the Se-Se bond lengths appears to decrease with increasing Se content.

The lack of second-shell data is caused by the large disorder in the Debye-Waller factors in that shell. As seen in Fig 7.1-7.3, all the RDFs show only one distinct peak. However, the well-preserved short-range order of the first shell implies that the large disorder in the second shells is mainly related to a spread in the bond angles (Paesler 1983).

The degree of chemical order present in an amorphous material is highly significant for understanding the atomic structure of the material. It can be provided by EXAFS data in the form of partial nearest-neighbour coordination numbers. Values of the partial coordination numbers obtained from the Ge and Se K-edge experiments are presented in Figs 7.6 and 7.7, respectively. The data are plotted as a function of Ge concentration. The theoretical variations of the partial coordination numbers, calculated on the basis of two limiting structural models, the Random Bond Network model (RBN) and the Chemically Ordered Bond Network model (OBN), are co-plotted with the experimental results for comparison purposes.

In the RBN model it is assumed that each component atom (Ge or Se in our system) combines with any other atom independent of any chemical preference and purely statistically. This means that all types of bond have an opportunity of being formed at any composition, but their concentrations are weighted statistically by the number of each type of atom present. Thus in our $a$-Ge$_x$Se$_{1-x}$ films, Ge-Ge, Ge-Se and Se-Se first-
Figure 7.6  Partial coordination numbers obtained from the Ge K-edge data versus Ge atomic percentage in a-Ge$_x$Se$_{1-x}$ thin films. The solid and dotted lines are the OBN and RBN modelled results, respectively.
Figure 7.7 Partial coordination numbers obtained from the Se K-edge data versus Ge atomic percentage in a-Ge$_x$Se$_{1-x}$ thin films. The solid and dotted lines are the OBN and RBN modelled results, respectively.
neighbour bonds, appropriately weighted, are allowed at all compositions, except of course for the end members. In the OBN, on the other hand it is assumed that each component combines according to its chemical preference. In our system, the heteropolar bond, Ge-Se, is energetically preferred so that the number of these bonds are expected to be maximized at all compositions. A detailed discussion of the two models and the bond statistics based on them are presented in § 6.4.2.

Let us go back to the partial coordination-number data shown in the top box of Fig 7.6. Experimentally, the partial coordination number, $N_{\text{Ge-Ge}}$, i.e. the number of Ge atoms surrounding Ge, starts to appear from a Ge content of about 33% and increases with increasing Ge content up to a maximum of about 4. This result clearly shows that Ge-Ge bond are not made in the Se-rich region ($0 < \text{Ge(\%)} < 33$) as would be expected on the RBN model. Indeed the variation of the partial coordination number, $N_{\text{Ge-Ge}}$, with composition agrees well with the theoretical curve for the OBN model. In the bottom box of Fig 7.6, the variation of the partial coordination number, $N_{\text{Ge-Se}}$, is also in good agreement with that expected according to the OBN model. The number of Ge-Se bonds is maximized until a Ge content of 33%, at which point the stoichiometric composition GeSe$_2$ exists. Beyond this point Ge-Ge bonds are forced to replace Ge-Se bonds because insufficient Se atoms are present.

It should be noted that the total coordination number of Ge, i.e. the sum of the partial coordination numbers $N_{\text{Ge-Ge}}$ and $N_{\text{Ge-Se}}$, lies close to four within experimental error throughout the whole composition range (see Fig 7.8). These results amply demonstrate that each Ge atom has a coordination number of 4 (i.e. makes four covalent bonds with its neighbours, whether these be Ge or Se) independent of composition as predicted by Mott's 8-N rule (Mott and Davis 1979).
Figure 7.8 Composition dependence of total coordination numbers determined from the Ge and Se K-edge data for a-Ge\textsubscript{x}Se\textsubscript{1-x} films.
Fig 7.7 shows the partial coordination numbers of Se obtained from Se K-edge experiments. The variations of partial coordination numbers, \( N_{\text{Se-Se}} \) and \( N_{\text{Se-Ge}} \), again also agree well with the OBN modelled results. However, the values of \( N_{\text{Se-Ge}} \) in its Ge-rich region (Ge(%)>60) show some departure from the OBN modelled results and could be considered to follow better the variation expected for the RBN. Actually, a similar behaviour was found in the results on the partial coordination numbers, \( N_{\text{Ge-Ge}} \), in Fig 7.6. It is possible that some departure from strict chemical ordering occurs in Ge-rich samples. If chemical ordering is preserved, mechanical constraints will obviously increase, so that the bonding network may become more random. However the partial coordination number, \( N_{\text{Se-Se}} \), shows good agreement with the OBN modelled results and the total coordination number on selenium, i.e. the sum of \( N_{\text{Se-Ge}} \) and \( N_{\text{Se-Se}} \), is maintained at the value of around 2 within the experimental error over the whole composition range as shown in Fig 7.8. This figure clearly confirms that the coordination numbers of Ge and Se are maintained at the values of 4 and 2, respectively, independent of composition.

As a further test of chemical ordering in our a-Ge\(_x\)Se\(_{1-x}\) films, the bond distributions in our films were also calculated in terms of bonds per atom as suggested by Lucovsky (1977). The results are presented in Fig 7.9 and 7.10. The OBN and RBN modelled results are also co-plotted for direct comparison. As seen in the figures, all bond proportions agree better with the OBN modelled results than with the RBN ones, supporting the views that our films are chemically ordered at all compositions.

The variation of optical bandgaps presented in Fig 6.2 can be understood in terms of a chemically ordered bond network model. The slow variation in the optical gap on the Ge-rich side with \( x \) lying between 0.5 to 1 corresponds closely to the composition range in which Ge-Ge
Figure 7.9 Composition dependence of number of bonds per atom determined from the Ge K-edge data for a-Ge$_x$Se$_{1-x}$ films. The solid and dotted lines are the OBN and RBN modelled results, respectively.
Figure 7.10  Composition dependence of number of bonds per atom determined from the Se K-edge data for a-Ge$_x$Se$_{1-x}$ thin films. The solid and dotted lines are the OBN and RBN modelled results, respectively.
bonds predominate over others \((0.42 < x < 1)\). The rapid rise in the gap occurs in the region where Ge-Se bonds begin to exert their influence on the electronic band structure. Below \(x = 0.22\), Se-Se bonds dominate the structure and the optical gap falls slowly from its maximum value at the GeSe\(_2\) composition to that of amorphous Se. Through the study of modelling dielectric functions presented in § 6.4, we already showed that our optical gap data were well matched with the OBN modelled results.

Therefore, considering the overall results, we can safely conclude that our a-Ge\(_x\)Se\(_{1-x}\) films have a chemically ordered 4-2 covalent bond network structure throughout the whole composition range.

7.2 EXAFS spectroscopy : a-Ge\(_x\)Se\(_y\)Zn\(_z\) films

EXAFS measurements on 11 ternary alloys of a-Ge\(_x\)Se\(_y\)Zn\(_z\) films were also carried out using the SRS beamline at station 7.1 in the CLRC Daresbury Laboratory. Since the compositions of films have no regularity, we represent these as a-Ge\(_x\)Se\(_y\)Zn\(_z\) for convenience. In fact, the main aim of these measurements was to probe any structural differences that might result from Zn alloying a-Ge\(_x\)Se\(_{1-x}\) films.

Measurements on the Ge, Se and Zn K-edges were performed in the X-ray transmission mode using 0.38-1.37 \(\mu\)m thick samples deposited on mylar substrates. To obtain an effective sample thickness, the samples were folded several times.

The absorption spectra obtained from each of the measurements were then analysed by the same routine as that used for a-Ge\(_x\)Se\(_{1-x}\) samples. Examples of the final EXAFS functions, \(\chi(k)\) and radial distribution functions obtained by Fourier transformations of K-edge are shown in Fig 7.11-7.12. In all the RDFs, only one strong peak is present, suggesting that
Figure 7.11 (a) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform $\text{FT}$ for a-Ge$_{47}$Se$_{39}$Zn$_{14}$ film at the Ge K edge.
Figure 7.11 (b) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{47}$Se$_{39}$Zn$_{14}$ film at the Se K edge.
Figure 7.11 (c) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for $a$-Ge$_{47}$Se$_{39}$Zn$_{14}$ film at the Zn K edge.
Figure 7.12 (a) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{44}$Se$_{41}$Zn$_{15}$ film at the Ge K edge.
Figure 7.12 (b) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{41}$Se$_{41}$Zn$_{13$ film at the Se K edge.
Figure 7.12 (c) The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-Ge$_{44}$Se$_{41}$Zn$_{15}$ film at the Zn K edge.
preservation of short range order is confined to the first shell. This typical feature implies considerable disorder beyond the first shell.

The fitting ranges of k-space for the Fourier transforms were selected to be from $k=1$ to 13.5 for the Ge K-edge spectra, from $k=1$ to 12.5 for the Se K-edge spectra and from $k=1$ to 10.5 for the Zn K-edge spectra. Depending on the noise presented in the k-space EXAFS spectra, the fitting range of $k$ was adjusted for better RDF fitting. Throughout an analysis of each EXAFS spectrum, the amplitude factor, AFAC, and the parameter, VPL, were fixed at 1.0 and -4.0 respectively, for all three K-edges while the other parameters were allowed to vary freely in the fitting procedure.

The bond lengths between the component atoms were determined from the final RDFs and are presented in Fig 7.13. The values are plotted, for convenience, as a function of the Zn content in the samples. Hence values obtained from samples having the same Zn content but with otherwise different compositions are sometimes presented together at the same value of $x$. First of all, the lengths of the Ge-Ge, Ge-Se and Se-Se bonds are worth comparing to those found for the a-Ge$_x$Se$_{1-x}$ samples. The Ge-Ge bond lengths are $2.46\pm0.05\text{Å}$ independent of composition. These values are the same as those obtained for a-Ge$_x$Se$_{1-x}$ samples, which implies that Zn-alloying does not affect the lengths of the Ge-Ge bonds. As seen in Fig 7.13, the bond lengths of Ge-Se and Se-Ge were found to be $2.40\pm0.03\text{Å}$ independent of composition. Compared to the value, $2.39\pm0.03\text{Å}$, which were obtained for the a-Ge$_x$Se$_{1-x}$ samples, these also agree within experimental error. On the other hand, the lengths of the Se-Se bonds were found to be $2.37\pm0.03\text{Å}$, which is quite an increase from the value $2.32\pm0.03\text{Å}$ obtained for the a-Ge$_x$Se$_{1-x}$ samples.

Now let us look at the bond length data relating directly to bonds involving Zn atoms. Because of the relatively small amounts of the introduced Zn content ($<24\%$) and their chemical preference to make
Figure 7.13  First-shell bond distances obtained from the Ge, Se, and Zn K-edge data versus Zn atomic percentage in a-Ge$_x$Se$_y$Zn$_z$ films.
bonds with other elements, Zn-Zn bonds were not found in any of the RDFs. As seen in Fig 7.13, the Ge-Zn bond lengths have an average of 2.59±0.05Å essentially independent of composition, and the Zn-Se and Se-Zn bond lengths were both found to be 2.44±0.03Å, again with no obvious variations with composition. If we assume that all bonds are covalent, we can calculate the expected bond length from the radii of the individual atoms (Phillips 1973). From the well-known crystalline bond lengths of Ge-Ge, Se-Se, Zn-Zn (2.44, 2.31 and 2.66 Å, respectively), we can calculate the expected covalent radii of the Ge, Se and Zn atoms simply by dividing the above bond lengths by two, which gives the values 1.22, 1.16 and 1.33Å respectively. Hence, by adding the radii, the bond lengths of Ge-Zn and Zn-Se can be estimated to be 2.55 and 2.49Å respectively. Compared these 'ideal' covalent bond lengths with our experimental results (2.59Å and 2.44Å respectively), the agreement is fair. Of course the bonding in zinc is metallic, not covalent and so the radii of Zn in the compounds is expected to differ from that in the element.

The mean square deviations in the bond lengths, i.e. the Debye-Waller factors \( \sigma^2 \), are shown in Fig 7.14. The Ge-Ge Debye-Waller factors show the trend that the values slightly decrease from 70x10^{-4}Å² to 50x10^{-4}Å² with increasing Zn content in the samples. The average value, 60x10^{-4}Å², is higher than that of a-Ge (40x10^{-4}Å²), suggesting that, in the Zn-alloyed films, there is more static disorder in the Ge-Ge bond lengths than in a-Ge. The Ge-Se Debye-Waller factors are nearly constant, scattered around an average value of 50x10^{-4}Å², independent of composition. Comparing this to the average value obtained from a-Ge\(_x\)Se\(_{1-x}\) samples (37x10^{-4}Å²), suggests that the a-Ge\(_x\)Se\(_x\)Zn\(_z\) films have more static disorder in the Ge-Se bond lengths than a-Ge\(_x\)Se\(_{1-x}\) films. The Debye-Waller factors of the Se-Se bond lengths are distributed from 70x10^{-4}Å² to 5x10^{-4}Å² with increasing Zn content in the samples. In a-Ge\(_x\)Se\(_{1-x}\) samples the highest factor was
Figure 7.14 Composition dependence of the mean square deviation in bond lengths obtained from the Ge, Se and Zn K-edge data for a-GeₓSeᵧZn₉ films.
25\times 10^{-4} \text{Å}^2$; hence the distribution of the Debye-Waller factors also indicates an increase of disorder in the Se-Se bond lengths resulting from the Zn-alloying.

We now look at the Debye-Waller factors of the bond lengths containing Zn atoms. As seen in Fig 7.14, the Debye-Waller factors of the Ge-Zn bond lengths decrease from $55\times 10^{-4} \text{Å}^2$ to $5\times 10^{-4} \text{Å}^2$ with increasing Zn concentration. This implies that larger amounts of Zn content somewhat reduces the disorder in the Ge-Zn bond lengths. The Debye-Waller factors of the Zn-Se and Se-Zn bond lengths show nearly constant values independent of Zn concentration: $95\times 10^{-4} \text{Å}^2$ and $60\times 10^{-4} \text{Å}^2$ respectively. In views of the agreement found for the bond lengths between the Zn-Se and Se-Zn bonds, the above Debye-Waller factors seem to carry an unexpected discrepancy in their average values. However, if we consider the general fitting results of EXAFS spectra presented in Fig 7.11-7.12, we can notice that the Zn K-edge spectra generally show much larger discrepancies between the experimental data and the theoretical curves. Hence we suppose that the larger Debye-Waller factors of the Zn-Se bond lengths result from experimental or analytical errors in the Zn K-edge experiments.

So far we have examined the EXAFS results from the point of views of bond lengths and their degree of disorder as a function of composition. We now look into the local structure of the a-Ge$_x$Se$_y$Zn$_z$ films by means of data on the partial coordination numbers. The partial coordination numbers obtained from the Ge, Se and Zn K-edge experiments are presented in Table 7.1-7.3. In the tables, the analytical errors of the results are omitted for simplicity. Since our main interest is to investigate the degree of chemical order in the structure of our films, with the experimental partial coordination number, $N_o$, the calculated partial coordination numbers, based on two limiting structural models (OBN,
<table>
<thead>
<tr>
<th>Ge$_x$Se$_y$Zn$_z$</th>
<th>Bond type</th>
<th>Bond length (Å)</th>
<th>$N_e$</th>
<th>$N_{OBN}$</th>
<th>$N_{RBN}$</th>
<th>Debye-Waller (x10$^{-4}$ Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 53 5</td>
<td>Ge-Ge</td>
<td>2.446</td>
<td>3.9</td>
<td>2.0</td>
<td>2.3</td>
<td>70</td>
</tr>
<tr>
<td>38 56 6</td>
<td>Ge-Ge</td>
<td>2.445</td>
<td>3.7</td>
<td>1.7</td>
<td>2.1</td>
<td>75</td>
</tr>
<tr>
<td>58 32 10</td>
<td>Ge-Zn</td>
<td>2.559</td>
<td>1.4</td>
<td>0</td>
<td>0.5</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Ge-Ge</td>
<td>2.439</td>
<td>2.6</td>
<td>3.6</td>
<td>2.8</td>
<td>40</td>
</tr>
<tr>
<td>32 55 13</td>
<td>Ge-Se</td>
<td>2.368</td>
<td>3.7</td>
<td>1.8</td>
<td>1.5</td>
<td>60</td>
</tr>
<tr>
<td>49 39 13</td>
<td>Ge-Ge</td>
<td>2.446</td>
<td>3.9</td>
<td>3.5</td>
<td>2.4</td>
<td>65</td>
</tr>
<tr>
<td>47 39 14</td>
<td>Ge-Ge</td>
<td>2.459</td>
<td>3.9</td>
<td>3.5</td>
<td>2.3</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Ge-Zn</td>
<td>2.634</td>
<td>0.4</td>
<td>0</td>
<td>0.7</td>
<td>25</td>
</tr>
<tr>
<td>44 41 15</td>
<td>Ge-Ge</td>
<td>2.490</td>
<td>3.8</td>
<td>3.5</td>
<td>2.3</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Ge-Zn</td>
<td>2.436</td>
<td>1.0</td>
<td>0</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>54 27 19</td>
<td>Ge-Ge</td>
<td>2.458</td>
<td>4.3</td>
<td>3.6</td>
<td>2.5</td>
<td>60</td>
</tr>
<tr>
<td>40 40 20</td>
<td>Ge-Ge</td>
<td>2.451</td>
<td>4.0</td>
<td>4.0</td>
<td>2.0</td>
<td>65</td>
</tr>
<tr>
<td>53 24 23</td>
<td>Ge-Ge</td>
<td>2.455</td>
<td>4.2</td>
<td>3.2</td>
<td>2.4</td>
<td>60</td>
</tr>
<tr>
<td>37 39 24</td>
<td>Ge-Zn</td>
<td>2.635</td>
<td>0.4</td>
<td>0.5</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Ge-Ge</td>
<td>2.459</td>
<td>3.5</td>
<td>3.5</td>
<td>1.8</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 7.1 Results obtained from the Ge K-edge experiments for a-Ge$_x$Se$_y$Zn$_z$ films. The $N_e$ denotes the experimental value of partial coordination numbers, and the $N_{OBN}$ and $N_{RBN}$ are the modelled results.
<table>
<thead>
<tr>
<th>Ge₅Se₇Znₓ</th>
<th>Bond type</th>
<th>Bond length (Å)</th>
<th>Nₑ</th>
<th>N_OBSN</th>
<th>N_RBN</th>
<th>Debye-Waller (x10⁴ Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 53 5</td>
<td>Se-Se</td>
<td>2.381</td>
<td>2.2</td>
<td>0</td>
<td>0.7</td>
<td>70</td>
</tr>
<tr>
<td>38 56 6</td>
<td>Se-Se</td>
<td>2.382</td>
<td>2.5</td>
<td>0</td>
<td>0.8</td>
<td>75</td>
</tr>
<tr>
<td>58 32 10</td>
<td>Se-Zn</td>
<td>2.426</td>
<td>2.1</td>
<td>1.3</td>
<td>0.2</td>
<td>55</td>
</tr>
<tr>
<td>32 55 13</td>
<td>Se-Se</td>
<td>2.376</td>
<td>0.6</td>
<td>0</td>
<td>0.8</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Se-Zn</td>
<td>2.403</td>
<td>2.0</td>
<td>1.1</td>
<td>0.9</td>
<td>75</td>
</tr>
<tr>
<td>49 39 13</td>
<td>Se-Zn</td>
<td>2.415</td>
<td>0.2</td>
<td>1.3</td>
<td>0.3</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Se-Se</td>
<td>2.391</td>
<td>2.7</td>
<td>0</td>
<td>0.5</td>
<td>80</td>
</tr>
<tr>
<td>47 39 14</td>
<td>Se-Zn</td>
<td>2.444</td>
<td>1.9</td>
<td>1.3</td>
<td>0.4</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Se-Se</td>
<td>2.344</td>
<td>0.3</td>
<td>0</td>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>44 41 15</td>
<td>Se-Zn</td>
<td>2.428</td>
<td>2.2</td>
<td>1.5</td>
<td>0.4</td>
<td>50</td>
</tr>
<tr>
<td>54 27 19</td>
<td>Se-Zn</td>
<td>2.436</td>
<td>2.7</td>
<td>2.0</td>
<td>0.4</td>
<td>65</td>
</tr>
<tr>
<td>40 40 20</td>
<td>Se-Zn</td>
<td>2.424</td>
<td>2.5</td>
<td>2.0</td>
<td>0.5</td>
<td>60</td>
</tr>
<tr>
<td>53 24 23</td>
<td>Se-Zn</td>
<td>2.445</td>
<td>3.0</td>
<td>2.0</td>
<td>0.5</td>
<td>65</td>
</tr>
<tr>
<td>37 39 24</td>
<td>Se-Zn</td>
<td>2.447</td>
<td>2.6</td>
<td>2.0</td>
<td>0.6</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Se-Se</td>
<td>2.361</td>
<td>0.2</td>
<td>0</td>
<td>0.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 7.2 Results obtained from the Se K-edge experiments for a-
Ge₅Se₇Znₓ films. The Nₑ denotes the experimental value of partial
coordination numbers, and the N_OBSN and N_RBN are the modelled results.
<table>
<thead>
<tr>
<th>Ge$_x$Se$_y$Zn$_z$</th>
<th>Bond type</th>
<th>Bond length (Å)</th>
<th>N$_e$</th>
<th>N$_{OBN}$</th>
<th>N$_{RBN}$</th>
<th>Debye-Waller (x10$^4$ Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 53 5</td>
<td>Zn-Zn</td>
<td>2.472</td>
<td>3.2</td>
<td>0</td>
<td>0.3</td>
<td>80</td>
</tr>
<tr>
<td>38 56 6</td>
<td>Zn-Se</td>
<td>2.448</td>
<td>4.2</td>
<td>4.0</td>
<td>1.6</td>
<td>95</td>
</tr>
<tr>
<td>58 32 10</td>
<td>Zn-Se</td>
<td>2.437</td>
<td>4.4</td>
<td>4.0</td>
<td>0.8</td>
<td>105</td>
</tr>
<tr>
<td>32 55 13</td>
<td>Zn-Se</td>
<td>2.432</td>
<td>3.9</td>
<td>4.0</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>49 39 13</td>
<td>Zn-Se</td>
<td>2.432</td>
<td>3.3</td>
<td>4.0</td>
<td>1.0</td>
<td>80</td>
</tr>
<tr>
<td>47 39 14</td>
<td>Zn-Se</td>
<td>2.434</td>
<td>3.9</td>
<td>4.0</td>
<td>1.0</td>
<td>90</td>
</tr>
<tr>
<td>41 45 14</td>
<td>Zn-Se</td>
<td>2.441</td>
<td>3.8</td>
<td>4.0</td>
<td>1.2</td>
<td>110</td>
</tr>
<tr>
<td>44 41 15</td>
<td>Zn-Se</td>
<td>2.437</td>
<td>4.7</td>
<td>4.0</td>
<td>1.0</td>
<td>110</td>
</tr>
<tr>
<td>54 27 19</td>
<td>Zn-Se</td>
<td>2.434</td>
<td>4.2</td>
<td>2.8</td>
<td>0.6</td>
<td>100</td>
</tr>
<tr>
<td>53 24 23</td>
<td>Zn-Se</td>
<td>2.428</td>
<td>4.1</td>
<td>2.1</td>
<td>0.6</td>
<td>100</td>
</tr>
<tr>
<td>37 39 24</td>
<td>Zn-Se</td>
<td>2.437</td>
<td>4.3</td>
<td>3.3</td>
<td>1.0</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 7.3 Results obtained from the Zn K-edge experiments for a-Ge$_x$Se$_y$Zn$_z$ films. The N$_e$ denotes the experimental value of partial coordination numbers, and the N$_{OBN}$ and N$_{RBN}$ are the modelled results.
RBN), are also presented as $N_{OBN}$ and $N_{RBN}$. In calculating the partial coordination number, $N_{OBN}$, the chemical preference of bonding was decided on the basis of the bond energy and the electro-negativity. Then, from the result, first the number of Zn-Se bonds and next the number of Ge-Se bonds were maximized at all compositions in the calculation of $N_{OBN}$.

As seen in Table 7.1, the Ge K-edge data show that, at almost all compositions, the nearest neighbours of the probed Ge atoms are Ge or Zn atoms. Because of the relatively large difference in electro-negativity, most of Se atoms seem to bond with Zn atoms. The experimental partial coordination numbers do not agree exactly with any of the modelled results. However, comparatively speaking, the OBN modelled coordination numbers, $N_{OBN}$, correspond better to the experimental values, $N_x$, than do the RBN modelled results, $N_{RBN}$. The Se K-edge data in Table 7.2 also show that in the degree of agreement with the experimental values, the OBN modelled partial coordination numbers are much better than the RBN modelled ones. Examination of the nearest-neighbour types indicates that the probed Se atoms are mostly combined with Zn atoms, which confirms the existence of the chemical preference in making a bond. The Zn K-edge data in Table 7.3 also show results supporting the OBN model. The nearest neighbours of the probed Zn atoms are almost all Se atoms as we expect in the OBN model, and the experimental partial coordination numbers agree comparatively well with the calculated coordination numbers based on the OBN model.

The total coordination numbers of the Ge, Se and Zn atoms are shown in Fig 7.15. The data are plotted as a function of Zn content in the samples. The total coordination numbers of Ge atoms are comparatively well preserved at all compositions, having the average value of 4. The total coordination numbers of Zn atoms were also found to be 4, independent
Figure 7.15 Composition dependence of total coordination numbers obtained from the Ge, Se and Zn K-edge data for a-Ge$_x$Se$_y$Zn$_z$ films.
of composition. Those of Se atoms were found to be about 2.3, which is slightly higher than the expected value of 2. These results indicate that each Ge atom forms a covalent bond, having the coordination number 4 predicted by Mott's 8-N rule. However, the total coordination number, 4, of Zn atom is the unexpected result from the viewpoint of the Mott's 8-N rule, because a Zn atom has an electronic structure of [Ar]3d^{10}4s^{2} (Beiser 1987), which means that the outer shell of the Zn atom is filled. We speculate that the introduced Zn atoms adopt 4-fold coordination by the excitation of outer electrons. The slight increase of Se total coordination number from 2 could resulted from that the large differences in electronegativities between Se and Zn atoms which may cause the instant transfer of electrons from a Zn atom to a Se atom and an extra coordination to the covalent environment of Se atoms. The result that Zn is 4-fold coordinated up to Zn content of 24 % explains why the addition of this metal does not reduce the bandgap of the alloys. In the crystalline phase, ZnSe is a wide bandgap semiconductor (E_{g} ~ 2.8 eV) with the zincblende structure (Feltz 1993) and we speculate that the introduced Zn replaces Ge to make a mixed Ge-Se/Zn-Se semiconductor system. One would expect a reduction in the bandgap only if zinc adopted a higher metallic-like coordination rather than being tetrahedrally bonded as in the present system.

Considering the overall results, we come to the conclusion that, though the order is not complete, the a-Ge_{x}Se_{y}Zn_{z} films surely have chemical order in their structure, and each component combines by covalent bonds, having coordination numbers, 4 (Ge), 2 (Se), and 4 (Zn). Therefore, the structure of our a-Ge_{x}Se_{y}Zn_{z} films can be described as a partially chemically-ordered covalent bond network structure.
Chapter 8  Summary and suggestions for future work

8.1 Summary
8.2 Suggestions for future work
8.1 Summary

In this research study, the structure and properties of amorphous Ge\textsubscript{x}Se\textsubscript{1-x} and related alloys have been investigated by several experimental techniques. Hydrogenated and un-hydrogenated a-Ge\textsubscript{x}Se\textsubscript{1-x} samples were prepared in thin-film form by r.f. sputtering at room temperature employing an r.f. power of 240 W and an Ar pressure of 3-6 mTorr. The thicknesses of the samples varied from 0.5 to 3.4 μm and the composition range covered was 0.2<x<1. Zn-alloyed films, a-Ge\textsubscript{x}Se\textsubscript{y}Zn\textsubscript{z} were deposited under same conditions, with Zn concentrations up to 27 atomic %. The composition of the films was determined by SEM-EDAX.

Optical absorption edges of the a-Ge\textsubscript{x}Se\textsubscript{1-x} samples were deduced from transmission-reflection spectra and, for some samples, the data were extended to lower absorption coefficients by PDS measurements. The optical bandgaps, \(E_{04}\) were determined from the absorption edges and compared with data obtained by others on glasses and evaporated films. The optical bandgaps vary with composition from 0.85 eV to 2.4 eV and show a cusp-like maximum at the composition x=0.33 which corresponds to stoichiometric GeSe\textsubscript{2}.

From the absorption edges, two other parameters, the Tauc constant B and the Urbach slope \(\gamma\), useful for monitoring the band tailing in the density of states (DOS) were determined.

The real part of the refractive index \(n\) was calculated using the method of Cisneros et al (1983) by analysing fringes in the reflectivity data, and the dispersion of \(n\) for a-Ge\textsubscript{x}Se\textsubscript{1-x} films with different compositions presented. The value of \(n(0)\) increases with increasing Ge content in the samples. From the refractive index dispersion data, two other characteristic energies, \(E_d\) and \(E_0\), were derived using the formula proposed by Wemple
The derived values for a-Ge$_x$Se$_{1-x}$ films agreed well with expected values from Wemple's results.

The effects of hydrogenation on a-Ge$_x$Se$_{1-x}$ films were investigated by analysing optical absorption edges and d.c electrical conductivity data of a-Ge$_x$Se$_{1-x}$:H films. Significant changes of the optical bandgap occurred for Ge-rich samples ($x>0.7$) and an increase of the activation energy in the temperature dependence of the conductivity after hydrogenation provided evidence of band widening by hydrogenation.

The addition of Zn to GeSe films did not affect the optical absorption edges significantly, even in concentrations up to 27 %, and so the optical bandgap is not changed appreciably by Zn alloying. The temperature dependence of the d.c electrical conductivity showed that the activation energy for Zn-alloyed samples was less than half the optical gap, which tentatively suggests a shift of Fermi level with alloying.

The dielectric functions of a-Ge$_x$Se$_{1-x}$ alloys were modelled by combining contributions from the various types of bond present, each with a characteristic dielectric behaviour. From the dielectric functions of a-Ge$_x$Se$_{1-x}$ alloys, the absorption coefficients, the optical badgaps ($\varepsilon_0$) and $\varepsilon_1(0)$ were reproduced and compared with experimental data.

EXAFS measurements were performed on a-Ge$_x$Se$_{1-x}$ samples and data obtained from both the Ge and Se K-edges analysed. The lengths of Ge-Ge, Ge-Se and Se-Se bonds were found to be 2.46±0.03Å, 2.39±0.03Å and 2.32±0.03Å, respectively, independent of composition, and these bond lengths are nearly the same as those found in crystalline materials. The local structure of each component atom was obtained in the form of partial coordination numbers. The experimental values were compared with values calculated from two models, the OBN and the RBN. The results suggest that the a-Ge$_x$Se$_{1-x}$ films have a chemically ordered 4-2 covalent bond network structure throughout the whole composition range.
EXAFS measurements were also carried out on ternary alloys of a-Ge<sub>x</sub>Se<sub>y</sub>Zn<sub>2</sub> films. The addition of Zn did not affect the lengths of the Ge-Ge bonds but caused a slight increase in the Ge-Se and Se-Se bond lengths. The bond lengths of Ge-Zn and Zn-Se were found to be 2.59±0.05Å and 2.44±0.03Å, both independent of composition. The values agree well with the calculated ideal covalent bond lengths within the experimental error. The total coordination number of Zn atom was found to be four, with Zn atoms preferentially bonded to Se atoms. Comparison of the partial coordination numbers with modelled results, suggest that the structure has some degree of chemical order, though the order is not complete.

8.2 Suggestions for future work

1) From the behaviour of the activation energy in the d.c electrical conductivity data for Zn-alloyed a-Ge<sub>x</sub>Se<sub>1-x</sub> samples, the possibility of a shift in the Fermi level was implied. For a further examination of this behaviour, it is proposed that thermopower measurements are made to establish the magnitude and direction of any shift in E<sub>F</sub> and to ascertain if there is a change in carrier type.

2) PDS measurements on a-Ge<sub>x</sub>Se<sub>y</sub>Zn<sub>2</sub> samples would be useful to provide the composition dependence of Urbach edge slopes. Comparison of the values with those in a-Ge<sub>x</sub>Se<sub>1-x</sub> films will give a clear picture of any change in band tailing in the DOS due to Zn alloying.

3) Raman scattering experiments would be worth carrying out to obtain more information about the intermediate-range structure of the films.
4) The electronic density of states (DOS) of the samples could be probed by means of XPS (X-ray photoelectron spectroscopy) or UPS (ultra-violet photoemission spectroscopy), and ESR (electron spin resonance) could be usefully carried out to investigate defect states.

5) For an investigation of any photo-induced effects which might occur in a-Ge$_x$Se$_{1-x}$ films, R-T and PDS measurements for the samples before and after illumination by a light source (e.g. a Xe arc lamp) for several hours could be useful in examining any change in the optical properties of the films. EXAFS measurements before and after illumination could also be beneficial for examining any changes in the local structure of the films.
References


Jackson, W. B., Amer, N. M., Bocca, A. C. and Fournier, D., Applied optics, V20, No. 8, 1333.


135
Oriel Catalog (1990), Optics & Filters, (Oriel, Stratford-USA)