STRUCTURE AND ELECTRONIC PROPERTIES
OF
SPUTTERED AMORPHOUS GaP FILMS

by

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September 1994
To my parents
Abstract

Stoichiometric amorphous GaP films have been prepared by RF sputtering on to substrates held at temperatures from 20°C to 200 °C. Some room-temperature deposited samples were annealed at higher temperatures (200-400 °C) in vacuum. Structural, optical and electrical characterisation of these films was carried out by means of a variety of experimental techniques.

Electron microscopy experiments, using both transmission electron microscope (TEM) and scanning electron microscope together with energy dispersive X-ray analyser (SEM-EDAX) have revealed that, while on the macroscopic scale the samples are homogeneous, continuous and smooth, on the microscopic scale they contain structural inhomogeneities, namely voids, and a small degree of compositional non-uniformity.

Extended X-ray absorption fine structure (EXAFS) spectroscopy has provided information on the atomic structure of the films, in particular on the short-range order around both Ga and P atoms. It was found that the a-GaP network is four-fold coordinated and chemically ordered, i.e. wrong bonds, Ga-Ga and P-P bonds, do not exist. In addition the technique revealed very little disorder in the bond length but wide distributions in the bond angles, the latter being more pronounced around P atoms than around Ga atoms.

Information on the short-range atomic structure has been obtained from infrared (IR) spectroscopy through the identification of the vibrational modes of the bonds. The main finding of these measurements was that the a-GaP network is chemically ordered, which is consistent with the EXAFS work.

From a combination of conventional reflection-transmission (R-T) and the most recently developed photothermal deflection spectroscopy (PDS) techniques, the absorption coefficient in the range of $10^{-1} - 10^{5}$ cm$^{-1}$, the refractive index and values of the optical gap were determined. The results are explained in terms of the nature and distribution in energy of the density of states (DOS) in the forbidden gap. The DOS in the conduction band is also extracted from the X-ray absorption near edge structure (XANES) data, which is combined with the DOS-valence band information taken from the literature to obtain full details of the electronic structure of a-GaP.

D.c conductivity measurements at high- and low-temperatures showed a continuously varying activation energy. This was interpreted as a transport mechanism taking place in a band tail but in which the conduction path moves downwards in the tail as T is lowered.
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Abstract
Acknowledgements
Contents

Chapter 1: General Introduction 1
1.1 Introduction 2
1.2 Classification of amorphous materials 4
1.3 Tetrahedrally bonded amorphous semiconductors 5
  1.3.1 Structure 5
  1.3.2 Defects 9
  1.3.3 Density of states 10
  1.3.4 Electrical properties 13
  1.3.5 Optical properties 17
1.4 Amorphous GaP 21

Chapter 2: Sample Preparation 29
2.1 General methods of preparation 30
2.2 Radio-frequency (r.f.) sputtering 31
2.3 Leicester sputtering system 34
2.4 Films deposited and preparation conditions 36
Chapter 3: Experimental Techniques Used for Structural Determination

3.1 Electron microscopy
   3.1.1 Transmission electron microscope
   3.1.2 Scanning electron microscope with EDAX

3.2 EXAFS spectroscopy
   3.2.1 Introduction
   3.2.2 Theory
   3.2.3 Experimental details
   3.2.4 Data analysis
   3.2.5 Composition measurements
   3.2.6 XANES

3.3 Infrared spectroscopy

Chapter 4: Experimental Techniques Used for Optical and Electrical Properties

4.1 Optical measurements
   4.1.1 Reflection-Transmission method
       4.1.1.1 Refractive index and film thickness
       4.1.1.2 High absorption coefficients
   4.1.2 Photothermal deflection spectroscopy
       4.1.2.1 Introduction
       4.1.2.2 Principles
       4.1.2.3 Theory
       4.1.2.4 Experimental setup
       4.1.2.5 Low absorption coefficients

4.2 Conductivity measurements
Chapter 1: General Introduction

1.1 Introduction
1.2 Classification of amorphous materials
1.3 Tetrahedrally bonded amorphous semiconductors
   1.3.1 Structure
   1.3.2 Defects
   1.3.3 Density of states
   1.3.4 Electrical properties
   1.3.5 Optical properties
1.4 Amorphous GaP
1 General Introduction

1.1 Introduction

Although amorphous materials such as silicate glasses have been known and used for thousands of years, it was not until discoveries made in the 1960s and 1970s that scientific interest in them actually began. The first discoveries which came from the work of Ovshinsky [1] in 1968 were switching and memory effects in multicomponent chalcogenide glasses. These were followed by optical memory effects, imaging, photodoping and reversible photostructural changes, which opened up possibilities for technological applications. These phenomena also demonstrated that there was a large field of material science to be explored. The next major discovery was a new material, hydrogenated amorphous silicon (a-Si:H), produced by the glow-discharge decomposition of silane (SiH$_4$) by Chittick et al [2] at the S.T.L. Laboratories. This material possessed a very low density of localized states in the mobility gap and hence was able to be doped n and p type by adding small amounts of phosphine (PH$_3$) and diborane (B$_2$H$_6$) to the silane, respectively. Doping from the gas phase allowed its electronic properties to be controlled accurately over ten orders of magnitude. This was the breakthrough reported by Spear and LeComber [3] in 1975, and suggested new lines for both the study and application of the a-Si:H and its alloys. Subsequent fundamental studies of these materials revealed their unique properties, which contributed to the understanding of not only amorphous materials but also of crystals. Also the applications, most of which are already on the market today, include optical memory disks with extremely high information density, large-area electronic circuits on thin flexible substrates, faster and more durable photoreceptor drums for xerographic copying machines, X-ray lenses, optical scanners and inexpensive photovoltaic cells [4-
All these advances, consequently, have made the field of amorphous materials one of the most active and exciting areas of condensed matter physics.

Amorphous materials are distinguished from their crystalline counterparts by the lack of long-range periodic ordering of their constituent atoms. That is not to say that these materials are completely disordered on the atomic scale. Local chemistry i.e. the interatomic forces and bonds between atoms is still very similar to those in crystals and hence the nearest-neighbour bond length and coordination number of the crystalline state are normally preserved. However, at greater distances, a wide variations in the next-nearest interatomic separations, which arises from a distribution in bond angles about a preferred mean, and also broader distribution of so-called dihedral angles (Figure 1.1), which reflects the relative orientation of next-nearest-neighbour bonds, are found. It is these variations that result in the loss of long-range order in the network. Hence, amorphous materials can be defined as ones which possess short-range order extending only to a few interatomic spacing but no long-range order.

The absence of long-range order in amorphous materials has important consequences, one of which is the invalidity of the concepts like Bloch waves, Brillouin zones, selection rules, etc. Such concepts greatly simplify the mathematical treatments used for the description of different physical phenomena in crystals. To explain the properties of amorphous materials without their help is therefore a challenge for theoreticians working in this field. Similarly, the experimentalist is also challenged, because many classical experiments either cannot be carried out or lose their simple interpretation in the disordered state. Moreover, most spectroscopic techniques yield broadened and featureless spectra and lack distinctive signatures that have assisted to clarify the electronic structure of crystals. Despite these difficulties, there has been a good progress in the understanding of these materials but
still many questions remain unsolved. While these are being tackled by many methods, at the same time a search for new materials, which have either novel properties or are cheaper in production, is also going on. The topic of this thesis may be included in the area of new materials. Amongst the variety of less studied materials, we concentrate on amorphous GaP, one of the amorphous III-V semiconductors, produced by radio-frequency sputtering, and investigate its fundamental structural, optical and electrical properties using a variety of experimental techniques.

This thesis consists of seven chapters. Chapter 1 presents a general introduction to amorphous materials, especially of tetrahedrally bonded amorphous semiconductors. The objectives of the present study are also explained in this chapter. Chapter 2 describes the sample preparation techniques. Chapter 3 and 4 deal with the experimental techniques used for structural characterization and determination of optical and electrical properties of a-GaP films, respectively. Their basic principles, theoretical and experimental aspects and data analysis are covered briefly. Results obtained, together with their interpretations, are presented in Chapters 5 and 6. Chapter 7 summarizes the work carried out and gives suggestions for future work.

1.2 Classification of Amorphous Materials

Just as in crystalline materials, amorphous materials range from metals to semiconductors and insulators. This range has expanded particularly after the invention of sophisticated thin-film deposition techniques such as sputtering and glow-discharge decomposition. The materials produced show great differences, but nevertheless can be grouped into five major categories as outlined in Table 1.1. They are metallic glasses, tetrahedrally bonded semiconductors, pnictides, chalcogenides and oxides-nitrides. This
Table 1.1: Classification of amorphous materials

<table>
<thead>
<tr>
<th>Category</th>
<th>Metals</th>
<th>Semiconductors or Insulators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examples</td>
<td>CuZr, CoP</td>
<td>Si, Ge, GaAs</td>
</tr>
<tr>
<td>Coordina. num.</td>
<td>12→9</td>
<td>4</td>
</tr>
<tr>
<td>Band gaps</td>
<td>0</td>
<td>&lt;2 eV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Metallic glasses</th>
<th>Tetrahed. semi.</th>
<th>Pnictides</th>
<th>Chalcogenides</th>
<th>Oxides, Nitrides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordina. num.</td>
<td>12→9</td>
<td>4</td>
<td>3</td>
<td>2, 3</td>
<td>4-2, 4-3</td>
</tr>
<tr>
<td>Band gaps</td>
<td>0</td>
<td>&lt;2 eV</td>
<td>0.2-2.3 eV</td>
<td>1-3 eV</td>
<td>&gt;5 eV</td>
</tr>
</tbody>
</table>
classification is based on the number of nearest-neighbour atoms (i.e the coordination number) and the nature of bonding between them, since these bonding characteristics are the main parameters that determines the structure and the structure in turn determines the physical properties of materials.

Each category in the Table 1.1 is interesting in its own right and forms different fields of study. Nevertheless, amongst all, the most popular materials are the tetrahedrally bonded semiconductors due to the intense current interest in a-Si:H produced by glow-discharge decomposition of silane. We, too, in this work are interested in the tetrahedrally bonded semiconductors because amorphous GaP is another member of this category. Hence, in the following sections a brief discussion concerning their structure, defects, density of states, electrical and optical properties will be given.

1.3 Tetrahedrally bonded amorphous semiconductors

1.3.1 Structure

Tetrahedrally bonded amorphous semiconductors is a large family consisting of a-IV elements, a-IV-IV, a-III-V and a-II-IV-V compounds. All these materials can be produced only in thin-film form by some form of vapour deposition (e.g. evaporation, sputtering, glow-discharge decomposition) or by electrolytic decomposition, except a-II-IV-V compounds which can also be prepared in bulk glassy form by means of quenching from the melt. Generally speaking, the materials produced by quenching from the melt have structures similar to that in the liquid: short-range correlations and high coordination numbers are typical, and these give rise to metallic properties. In contrast, the structure of amorphous semiconductors prepared in thin-film form (materials that we will focus on hereafter) resembles very
much that in their crystalline counterparts, particularly the short-range order; four-fold coordination and basically the same atomic tetrahedra are found in both cases. The disorder in these semiconductors originates from slight deviations in bond length (~1%) and substantial variations in bond angle (~±10°) from that of crystals, which result in radially and angularly distorted tetrahedra. Specification of the most important aspects of the short-range order, which include the number and type of immediate neighbours and their spatial arrangement about a given reference atom, does not fully determine the structure of amorphous semiconductors. The network connectivity or topology, which is related to the distribution of dihedral angles (Figure 1.1) and ring sizes, and which has important consequences for electronic states, must also be determined. In fact, all these types of disorder are not independent of one another. For instance, when all bond lengths, bond angles and dihedral angles are completely regular, only six-membered rings characteristic of the crystalline diamond lattice occur (Figure 1.2 (a)). If topological disorder is present in the network, then this is readily identified by the occurrence of rings with different numbers of atoms, as shown in Figure 1.2 (b). It is believed that the topological disorder is necessary for the stabilization of some amorphous materials.

Experimentally, the determination of the structure of the amorphous materials is usually carried out by X-ray or electron diffraction. From an analysis of the angular distribution of the scattered intensity, a radial distribution function (RDF) is derived. The RDF, owing to the experimental averaging over a large number of atoms, only contains information on the radial structure about the average atom. In order to obtain other details of the short-range order, such as the local angular correlations, the experimental RDF is fitted to the RDF determined from structural models built either by hand or on a computer. Unfortunately, such a fit may not be unique, although
Figure 1.1: Illustration of the dihedral angle $\phi$ between next-nearest-neighbour bonds

Figure 1.2: (a) Perfect crystalline order (b) Topological disorder
A proposed model does become more credible if its RDF explains the peaks and fine structure in an experimental RDF.

The types of structural models proposed so far for the tetrahedrally bonded amorphous semiconductors can be grouped into two classes: microcrystalline and continuous random network. In the microcrystalline model, the solid is supposed to consist of randomly oriented small crystals separated by completely random regions. The broad diffraction rings typical of amorphous structure suggest that the crystal sizes must be of the order of 10 to 15 Å. This model is easy to visualize but encounters difficulty when one attempts to describe how these crystals are to be connected so as to maintain both incoherent diffraction between themselves and to keep the number of broken bonds minimal. For crystallite sizes of 10-15 Å, about half of the atoms must reside on the crystalline boundaries. Unless there is some mechanism to satisfy these bonds, the increase in energy would be intolerably high. In addition to this problem, the RDF calculated for microcrystalline models do not fit experimentally obtained RDFs that well.

In the continuous random network model, the solid is considered to consist of a network of atoms linked together by the same types of chemical bonds as in the corresponding crystal, but in a structure lacking long-range order. Such a network has no discontinuities, no high-angle boundaries between microcrystals and therefore avoids having a high proportion of broken bonds. However, in order to destroy the long-range order and at the same time to maximize the connectivity, variations in bond lengths, bond angles and dihedral angles are introduced, and these give rise to an increase in the energy of the network. Using balls and sticks, Polk [7] successfully constructed a continuous random network consisting of 440 atoms to simulate the structure of a-Si or a-Ge (Figure 1.3). In his model, each atom had four immediate neighbours arranged in a tetrahedral geometry. Bond length variations were kept small, of the order of ± 1% of their average value, but
Figure 1.3: The 440-atom continuous random network built by Polk to simulate the structure of a-Si or a-Ge
bond angle distortions of ± 20° were allowed. The random character of the network resulted in a flat distribution of dihedral angles. All of the atoms are contained on either five- or six-membered rings whose ratio was 1:4. The resulting network had a minimum strain and appeared capable of indefinite extension. Its density was determined to be 93±2 percent of the diamond cubic structure, in reasonable agreement with that of many amorphous samples. This model was, later on, extended to 519 atoms and refined on a computer by Polk and Boudreaux [8], Steinhardt, Alben and Wesaire [9], and Duffy, Boudreaux and Polk [10]. A different type of continuous random network, which contained only even-membered rings was built by Connell and Temkin [11]. Their 238-atom model was constructed following the same general procedure as Polk, and no difficulty was encountered in doing so. The network topology was significantly different from that of Polk and contained approximately four times more staggered configurations than eclipsed configurations [12]. Figure 1.4 compares the RDFs derived from the models of Polk-Boudreaux and of Connell-Temkin and the experimental data for a-Ge [13].

The structural models described above represent ideal continuous random networks in which connectivity is the prerequisite. According to Phillips [14], the optimal connectivity is achieved when the average coordination number is 2.45. In this case, the short-range order imposed by bond stretching and bending forces is just sufficient to exhaust the local degrees of freedom. Based on this idea, materials with lower coordination number than 2.45 are considered as insufficiently cross-linked and those having higher coordination number are considered as overconstrained. The tetrahedrally bonded amorphous semiconductors having four-fold coordination are therefore highly overconstrained, and they have to find ways to lower their huge strain energy. Indeed, one finds that these materials quite often contain strain-relieving voids, accompanied by a density deficit.
Figure 1.4: Comparison of the RDFs of the Polk-Boudreaux model (---), the Connell-Temkin model (•••) and an experimental curve (—) for α-Ge [13]
with respective to their crystals. Such microscopic inhomogeneities may scale from a few to several hundred Å, and can be in concentrations as much as 10-15%. The concentration, in fact, depends strongly on the deposition conditions: substrate temperature, deposition rate and hydrogen content are amongst the important parameters. Figure 1.5 demonstrates voids buried in the network grown at low and high substrate temperatures.

1.3.2 Defects

In addition to structural inhomogeneities such as voids, a real amorphous network may also contain defects which should be distinguished from the intrinsic disorder of the random network. In general, by analogy with the crystal, defects in amorphous materials are defined as departure from the ideal amorphous network in which all atoms have satisfied their bonding requirements. This approach leads to the idea of a coordination defect, in which an atom has either too many or too few bonds compared to the ideal bonding state. For tetrahedrally bonded amorphous semiconductors, overcoordinated defects involving too many bonds do not occur, but undercoordinated defects as exemplified by dangling bonds, divacancies, and also weak bonds, wrong bonds do occur. Figure 1.6 shows schematic representation of these defects.

The dangling bond is the simplest defect. It normally contains one electron and has therefore a net spin, which gives rise to an electron spin resonance (ESR) signal by which it is identified. The dangling bond is electrically neutral (D⁰) but can capture an electron and become negatively charged (D⁻) or lose its electron and become positively charged (D⁺). In either case, it does not produce an ESR signal.
Figure 1.5: Schematic representation of a void buried in a network grown at (a) low $T_s$ (b) high $T_s$. The open circles are Si(Ge); the filled circles are H.

Figure 1.6: Illustration of possible defects in tetrahedrally bonded amorphous semiconductors.
The divacancy is a stable defect in crystals. The six dangling bonds left by the removal of two adjacent atoms reconstruct to give two short and one long covalent bonds. This model was first proposed for amorphous semiconductors by Spear [15]. Adler [16] concluded from molecular orbital arguments that this defect has the lowest formation energy of any of the other coordination defects. However, since it has paired electrons and is diamagnetic, it cannot be detected by ESR experiments.

In the case of the weak-bond defect, the bonding requirement is fulfilled, but the bond length is increased, by say up to 20% of the crystalline value with a consequent weakening of the bond. Such defects occur mostly at the inner surfaces of voids, and are diamagnetic when neutral.

Wrong bonds, i.e. bonds between like atoms, are a defect type that is only significant for the case of compound materials. They are expected as a result of the topological disorder of the network. On the other hand, the partial ionic character of the bonding between like atoms should prevent their formation to some extent. Experimentally their existence, particularly in a-III-V compounds, has not so far been proved conclusively, and it remains a controversial subject.

1.3.3 Density of States

Knowledge of the energy distribution of the density of electronic states $N(E)$ is an essential prerequisite to a detailed understanding of transport and optical properties of a solid. This is as true for amorphous solid as for crystalline materials. Since the pioneering work of Bloch it is known that the density of electronic states of the crystal shows universal characteristics. For semiconductors, these are the sharp structure in the valence and conduction bands, and abrupt terminations at the valence band maximum $E_v$ and the
conduction band minimum $E_C$ (Figure 1.7). The sharp edges in the density of states produce a well-defined forbidden energy gap. Within the band the states are extended, which means that the wavefunctions occupy the entire volume. In the past, it was believed that these specific features of the band structure were direct consequences of the long-range order of the crystal. Hence for an amorphous solid having only short-range order, there was considerable doubt about the validity of the band structure concept. However, two common observations, namely the transparency of window glass and often small changes of resistivities on melting suggested otherwise. The reason why the band picture is still valid was first explained by Ioffe and Regel [17] who pointed out that it is the short-range order rather than the long-range order which is responsible for most of the important physical properties of the material. Since then, it has been proved both theoretically and experimentally that amorphous materials have densities of states similar to that in the corresponding crystal but the lack of long-range order results in some changes. These changes can be summarized as:

1. The sharp structures present in the crystalline band spectrum are smeared out, yielding a rather smooth and featureless spectrum for the corresponding amorphous material. The electron states in these bands are still extended in nature.

2. The band edges are broadened into the forbidden gap, giving rise to a region of band tail states. The nature of the electron wavefunction in these tail states is no longer extended, instead it is localized in space. This means that an electron placed in such a region cannot diffuse at zero temperature to other regions.

Several models were proposed for the band structure of amorphous semiconductors, which were all the same in the sense that they took into account the above features and used the concept of localized states. However, the difference amongst them lies in the extent of the band tailing. Figure 1.8
Figure 1.7: Schematic density of states diagram in region of band edges for a crystalline semiconductor

Figure 1.8: Schematic density of states diagrams in region of band edges for tetrahedrally bonded amorphous semiconductors (a) the Davis-Mott model (b) modified Davis-Mott model
(a) illustrates schematically the Davis-Mott model [18] which is more applicable to the tetrahedrally bonded amorphous semiconductors. According to Davis and Mott, the tails of localized states should be rather narrow and should extent a few tenths of an electron volt into the forbidden gap. In the model, $E_C$ and $E_V$ represent the energies which separate the ranges where the states are localized and extended. Mott suggested that at the transition from extended to localized states the electron mobility drops by several orders of magnitude producing a mobility edge. Hence, the interval between the energies $E_C$ and $E_V$ is defined as a mobility gap, and may be considered to take the place of the band gap in crystalline semiconductors. Davis and Mott furthermore proposed that a band of compensated levels which originates from defects in the random network e.g. dangling bonds, vacancies, etc. exist near the middle of the band gap and that the Fermi level $E_F$ lies in it. Mott later on replaced this band by a donor and an acceptor band situated approximately equidistant on either side of $E_F$ (Figure 1.8 (b)).

Experimental support for the proposed density of states model described above came first from field-effect measurements [19] (Figure 1.9). Curve 1 in the figure is a typical experimental density of states plot for an a-Si:H sample deposited by the glow-discharge technique on a substrate held at about 520 K, and gives clear evidence for the predicted electron tail and gap states. As indicated in the figure, the tail states lie just below $E_C$ and cover a small region while the gap states are distributed throughout the forbidden gap. The dotted curves show a likely division of the gap states into its two components. Distribution A, extending from the $E_C$ side into the gap contains acceptor-like states which are neutral when empty, so that below $E_F$ they will carry a negative charge denoted by $n^-$. Curve B contains states from the opposite side of the mobility gap which are neutral when full and therefore provide positively charged donor-like states above $E_F$, denoted by $p^+$. The
Figure 1.9: Density of states distributions deduced from field-effect measurements for a-Si
charges states described are identical to those envisaged in the modified Davis-Mott model.

Comparison of curve 1 with 2 in Figure 1.9 illustrates the basic significance of the preparation technique in determining the electronic properties of the material. Traditional methods for thin-film preparation such as thermal evaporation generally leads to a high density of gap states shown by curve 2. In contrast, the samples prepared by the decomposition of silane (SiH₄) in a radio-frequency glow-discharge plasma have much lower gap states (curve 1). The reason for this difference is now clear and attributed to the presence of H in the latter samples. H in these samples saturates dangling bond defects, leaving a small number of states in the gap associated with them.

1.3.4 Electrical Properties

Two different approaches have been developed for describing electrical properties of the amorphous semiconductors; the first is based on the distribution of the density of states and the second is motion of the small polaron [20]. Here, we will adopt the first approach and use the Davis-Mott model depicted in the preceding section since it accounts for other properties of these materials. On the basis of the Davis-Mott model, there can be four processes leading to conduction, each of which is dominant in different temperature regions (Figure 1.10). These are:

(a) Extended-state conduction:

At high temperatures, electrons are thermally excited to the extended states beyond E_C in the conduction band where they drift under the influence of the applied field, resulting in extended-state conduction. In order to derive
the formula describing this conductivity, we start from the general conductivity expression for any semiconductor

$$\sigma = e \int N(E)\mu(E)kT \frac{\partial f(E)}{\partial E} dE$$  \hspace{1cm} (1)

where

- $N(E)$ = density of states at energy $E$
- $\mu(E)$ = mobility of an electron at energy $E$
- $f(E)$ = Fermi-Dirac function:

$$f(E) = \frac{1}{1 + \exp[(E - E_p)/kT]}$$  \hspace{1cm} (2)

Using the relationship

$$\frac{\partial f(E)}{\partial E} = -f(E)[1 - f(E)]/kT$$  \hspace{1cm} (3)

$\sigma$ can be written as

$$\sigma = e \int N(E)\mu(E)f(E)[1 - f(E)]dE$$  \hspace{1cm} (4)

According to the Davis-Mott model, the Fermi level $E_F$ is situated near the middle of the gap and thus sufficiently far from $E_C$, the energy which separates the extended from the localized states, so that Boltzmann statistics can be used to describe the occupancy of states:

$$f(E) = \exp[-(E - E_F)/kT]$$  \hspace{1cm} (5)

Assuming a constant density of states and mobility, substituting eq. (8) into eq. (7) and integrating, one finds for the conductivity

$$\sigma = \sigma_0 \exp[-(E_C - E_F)/kT]$$  \hspace{1cm} (6)
Figure 1.10: Schematic illustration of the temperature dependence of conductivity. The activation energies associated with the processes described in the text are indicated.
Here $\sigma_0 = eN(E_C)kT\mu_c$ and generally lie in the range between 10 and $10^3$ $\Omega^{-1} \text{cm}^{-1}$.

Extended-state conduction can also take place via holes in the valence band. Then the corresponding formula is

$$\sigma = eN(E_V)kT\mu_h \exp\left[-\frac{(E_F - E_V)}{kT}\right]$$  \hspace{1cm} (7)

(b) Band-tail conduction:

At lower temperatures excitation can only occur to the localized states in the band tails (i.e. between $E_A$ and $E_C$). Electrons in these states can contribute to the conductivity only if they acquire sufficient energy $\omega_1$ from their interactions with phonons, to hop from a localized site to its nearest-neighbour site. This process is called thermally assisted hopping, and the conductivity generated can be easily calculated from equation (4), provided that the energy distribution of the density of localized states is known. If one assumes that density of states behaves as some power $s$ of $E$,

$$N(E) = \frac{N(E_C)}{(\Delta E)^s} (E - E_A)^s$$  \hspace{1cm} (8)

with $\Delta E = E_C - E_A$, then the conductivity is given by

$$\sigma = \sigma_1 \exp\left[-\frac{(E_A - E_F + \omega_1)}{kT}\right]$$  \hspace{1cm} (9)

where

$$\sigma_1 = \left(\frac{\hbar}{6}\right)\nu_{ph}e^2R^2N(E_C)\left(\frac{kT}{\Delta E}\right)^s C$$  \hspace{1cm} (10)

$$C = sI\left(\frac{\Delta E}{kT}\right)^s \exp\left[-\frac{\Delta E}{kT}\left(1 + s\left(\frac{kT}{\Delta E}\right) + s(s-1)\left(\frac{kT}{\Delta E}\right)^2 + \ldots\right)\right]$$
$u_{ph}$ = phonon frequency typically of the order of $10^{13}$ s$^{-1}$

$R$ = the distance covered in one hop.

The pre-exponential factor $\sigma_1$ in eq. (9) is several decades smaller than $\sigma_0$ in eq. (6). This is partly because of lower effective density of states and also because of a lower mobility near $E_A$ compared with $E_C$.

(c) Hopping conduction at the Fermi energy

At still lower temperatures, carriers in the band of localized states around Fermi energy $E_F$ are the main contributors to the conductivity. They move between neighbouring states via thermally assisted hopping as described in (b). This conductivity is small and has a temperature dependence of the form

$$\sigma = \sigma_2 \exp\left[-\frac{\omega_2}{kT}\right]$$  (11)

where

$$\sigma_2 = \left(\frac{1}{6}\right)e^2 R^2 v_{ph} N(E_F) \exp(-2\alpha R)$$

$\omega_2$ = the average energy difference between the states

$\alpha$ = the inverse localization length

(d) Variable-range hopping conduction at the Fermi energy:

At very low temperatures, where $kT \ll \omega_2$, the rate of thermally assisted hopping to neighbouring states is very small and an electron prefers to tunnel beyond its nearest neighbours to more distant states in order to find a state of similar energy since there is a greater selection of possible energies there. This is called variable-range hopping, and was first proposed by Mott. Using an optimization procedure, Mott [21] derived the conductivity formula of the form

$$\sigma = \sigma_3 \exp\left(-\frac{A}{T^{1/4}}\right)$$  (12)

where

$$\sigma_3 = \left(\frac{1}{6}\right)e^2 R^2 v_{ph} N(E_F)$$
One can note from eq. (12) that unlike the conductivity mechanisms depicted in (a), (b) and (c), variable-range hopping conduction is characterized by a $T^{-1/4}$ temperature dependence. This behaviour has indeed been observed in tetrahedrally bonded elemental amorphous semiconductors, namely a-Si and a-Ge.

### 1.3.5 Optical Properties

Optical properties of a solid are of interest because of their importance not only in fundamental research but also in applications. They are characterized in terms of the complex dielectric function $\varepsilon_1(\omega) + i\varepsilon_2(\omega)$, or alternatively, the refractive index $n$ and the absorption coefficient $\alpha(\omega)$, which are related to one another by the following expression

$$\alpha(\omega) = 2\pi\varepsilon_2(\omega) / n\lambda$$

(13)

in which the imaginary part of the dielectric function $\varepsilon_2$ is also related to the optical transitions between the valence and conduction bands by

$$\varepsilon_2(\omega) = 4\pi^2\varepsilon^2 \frac{1}{\Omega} \sum_{C,V} [M_{CV}]^2 \delta(E_C - E_V - \hbar\omega)$$

(14)

Here $\Omega$ is the illuminated volume of the sample, $M$ is the dipole matrix element connecting valence and conduction band states, and the delta function expresses the conservation of energy. The sum is over all initial and
Enal states. The matrix elements in a crystalline semiconductor are non-zero only for states of the same crystal momentum $k$. Optical transitions between energy levels which conserve both energy and momentum are termed direct transitions. Indirect transitions to a state of different $k$ can occur through the absorption or emission of a phonon to conserve the total momentum. Such transitions are generally weak and only observed at energies where the direct transitions are forbidden.

In an amorphous semiconductor, owing to the lack of long-range order, momentum is not a good quantum number and the requirement of $k$-conservation is relaxed. Transitions then occur between any two states for which energy conservation applies. The matrix element therefore reduces to an average $M(\hbar\omega)$ over all pairs of states separated by energy $\hbar\omega$. This average value is still energy-dependent because the states that contribute to $M(\hbar\omega)$ change with energy. In this case, equation (4) becomes

$$\varepsilon_2(\omega) = 4\pi^2 e^2 a^3 M^2(\hbar\omega) \int N_V(E) N_C(E + \hbar\omega) dE \quad (15)$$

where $a$ is the interatomic spacing and the integral is the joint density of states. The shape of the $\varepsilon_2(\omega)$ spectrum is the product of the energy dependence of this integral and the matrix element.

Figure 1.11 presents the $\varepsilon_2(\omega)$ spectra for a-Si and c-Si, deduced from Kramers-Kronig analysis of the ultraviolet reflectivity data [22]. From their comparison, one can firstly note that the sharp structures i.e. the van Hove singularities in the crystal spectrum, are smeared out completely but nevertheless the overall shape is retained. This is due to the similarity of the short-range order and density of band states in the two phases. Secondly, the value of $\varepsilon_2(\omega)$ is about an order of magnitude larger for a-Si than for c-Si below 3 eV, which is a direct consequence of the breakdown of the $k$-selection rules that is strictly obeyed in the crystal. It is this feature that makes a-Si
Figure 1.11: The imaginary part of the dielectric function \( \varepsilon_2 \) for a-Si and c-Si

Figure 1.12: Typical absorption spectrum of a-Si:H with sub-regions A, B, C
more favourable than c-Si for solar-cell applications because, while a very thin film (~1 µm) of a-Si suffices to absorb most of the solar-spectrum light, a much thicker (>50 µm) of c-Si is required for the same purpose. In addition to the need for substantially less material in the a-Si case, the low fabrication cost and the ability to deposit large-area samples are further advantages of a-Si for this application.

Figure 1.12 shows the optical absorption edge of a-Si:H, in which three sub-regions, namely a power-law region A, the Urbach region B and a tail region C, typical of amorphous semiconductors are indicated. Each of these regions involves different optical processes which will now be discussed briefly.

In the power-law region, the absorption is ascribed to transitions between the extended states just beyond the mobility edges in the valence and conduction bands. Normally the density of states in this region is assumed to be represented by power laws

\[ N_V(E) \propto E^p \]
\[ N_C(E) \propto (E - E_0)^q \]  \hspace{1cm} (16)

where energies are measured from the valence band mobility edge, and \( E_0 \) marks the mobility edge in the conduction band (i.e. which is taken to be a measure of the optical gap). Inserting eqs. (16) into eq. (15) and assuming that the matrix elements are independent of energy,

\[ \alpha = \kappa_2(\omega) = \text{const.}(\hbar \omega - E_0)^p q^{q+1} \]  \hspace{1cm} (17)

is obtained. If the form of the densities of states at both band edges are parabolic, i.e. \( p=q=1/2 \), then the photon energy dependence of the absorption becomes
Using this relation, the optical gap $E_0$ is readily extracted. However, because of the contribution of the band-tail extended-states transitions in the absorption given above, there is a considerable doubt whether in reality $E_0$ does represent a true value of the optical gap. Nevertheless, it is a useful marker in monitoring changes of the absorption edges with, for example, temperature or pressure.

In the Urbach region, the absorption has an exponential energy dependence
\[ \alpha(h\omega) = \alpha_0 \exp(h\omega / E_U) \]  
(19)

where $E_U$ is the Urbach slope and $\alpha_0$ is a constant. This behaviour has been found in all amorphous semiconductors, so that it is accepted as universal feature of these materials. However, the physical origin of this feature has not yet been clarified, although various mechanisms have been proposed. Of these, the most plausible one was an exciton transition broadened by random internal electric fields that arise from static spatial fluctuations in potential, density variations, charged defect centres or from longitudinal optical phonons [23]. Unfortunately, experimentally, it is not easy to check the correctness of this theory. The current belief for tetrahedrally bonded elemental amorphous semiconductors is that the absorption shape is simply given by the joint density of states and hence reflects the disorder broadening of the bands. For instance for a-Si:H, the valence band tail has an exponential slope of about 45 meV. It is broader than the conduction band tail and so dominates the joint density of states, and is indeed close to the slope of the Urbach edge.

In the tail region, the absorption is weak and very structure and composition sensitive. Hence, it is attributed to transitions between localized
gap states arising from defects in the material. According to Jackson and Amer [24], for the case of a-Si:H, the relation between the defect density $N_D$ and the tail absorption $\alpha$ is given by

$$N_D = \frac{c n m_e}{2 \pi^2 \hbar^2} \left[ \frac{(1 + 2n^2)^2}{9n^2 e^2 f_{oj}} \right]^{E_{\text{max}}} \int_0^{E_{\text{max}}} \alpha(E) dE$$

$$N_D = 7.9 \times 10^{15} \int_0^{E_{\text{max}}} \alpha(E) dE$$

where $c$ is the velocity of light, $n$ is the refractive index, $m_e$ is the electron mass and $E_{\text{max}}$ is the energy at which the tail begins. The constant of proportionality is obtained by assuming unity oscillator strength $f_{oj}$ and a factor of 2 local-field correction. From the tail absorption, other defect-related information such as correlation energy $U$ [25], and the position and width of the defect band [26] can also be extracted.

1.4 Amorphous GaP

There are nine binary III-V compounds resulting from the combination of group III (In, Ga, Al) and group V (Sb, As, P) atoms. The crystalline forms of these compounds have been studied extensively because of their scientific and technological importance. As for their amorphous counterparts, relatively speaking, they have not been given as much attention as either the crystalline III-Vs or other elemental amorphous semiconductors, namely a-Si and a-Ge. As a result of this, many fundamental problems associated with them still remain unsolved.
So far, in the study of amorphous III-V materials, most of the emphasis went into prototype GaAs. In the present study, however, we have chosen GaP because it is the most remarkable III-V with respect to its properties as we shall show shortly using some published reports.

Stuke and Zimmerer [27] have carried out detailed optical work on flash-evaporated a-III-V semiconductors, in which $\varepsilon_1$ and $\varepsilon_2$ spectra for each compound were calculated from the reflectivity curves using Kramers-Kronig analysis. The $\varepsilon_2$ spectrum obtained for a-GaP is shown in Figure 1.13 where the crystal data is from [28]. Comparison of these two spectra calls for the same general comments made for a-Si and c-Si in section 1.3.5: the three maxima in the crystal spectrum are smeared out completely and only a broad maximum is retained; furthermore the amorphous spectrum is shifted as a whole to lower energy. In the case of a-GaP, this shift was found to be the strongest amongst all other a-III-V compounds. Stuke and Zimmerer [27] also checked the fulfilment of the sum rule [29], for which the effective number of valence electrons, $n_{\text{eff}}$, contributing to absorption in the investigated range of energy was calculated from

$$n_{\text{eff}} = \frac{2}{\pi \hbar^2 N_{\text{at}}} \left( \frac{m e^2}{\pi \epsilon_0} \right) \int_0^E E \varepsilon_2(E) dE$$

where $N_{\text{at}}$ is the number of atoms per cm$^3$, $m$ is the free electron mass and $e$ is the elementary charge. The result of such calculations for amorphous GaSb, GaAs and GaP are shown in Figure 1.14. The spectral dependence of $n_{\text{eff}}$ for the corresponding crystalline materials taken from [28] are also shown in the figure. For a-GaSb and a-GaAs, at high energy, $n_{\text{eff}}$ reaches values which are close to the values of the corresponding crystalline materials. Thus for these materials the sum rule is fulfilled by the $\varepsilon_2$ spectra, just as in the crystalline
Figure 1.13: The $\varepsilon_2$ spectra of amorphous and crystalline GaP

Figure 1.14: The spectral dependence of the effective number of valence electrons $n_{\text{eff}}$ for (1) a-GaSb (2) c-GaSb (3) a-GaAs (4) c-GaAs (5) c-GaP (6) a-GaP
state. However, for a-GaP, the $n_{\text{eff}}$ value at 12 eV is lower than that of the crystalline state and this deficit is the largest compared to other a-III-Vs.

Connell and Paul [30] have studied the absorption edges, optical energy gaps, refractive indices and pressure coefficients of amorphous Si, Ge and III-V compounds, and have looked for any relation between these quantities and those of the corresponding crystals. Table 1.2 summarizes their findings. As can be seen from the table, the refractive indices of amorphous materials generally lie within about 5% of their crystalline counterparts whereas the energy gaps are very different from the crystalline band gaps. The latter is particularly striking in the case of GaP which reveals the largest discrepancy (0.42 eV amorphous, 2.22 eV crystalline).

**Table 1.2: Optical and structural parameters of amorphous and crystalline (in parentheses) materials**

<table>
<thead>
<tr>
<th></th>
<th>$n$</th>
<th>$E_0$ (eV)</th>
<th>$\frac{1}{n} \frac{dn}{dP}$ ($10^{-3}$/kbar)</th>
<th>$\frac{dE_0}{dP}$ (meV/kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.5±0.1</td>
<td>1.4</td>
<td>-0.05</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>(3.42)</td>
<td>(1.1)</td>
<td>(-0.3)</td>
<td>(-1.5)</td>
</tr>
<tr>
<td>Ge</td>
<td>4.05±0.1</td>
<td>1.0</td>
<td>-0.8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>(4.01)</td>
<td>(0.67)</td>
<td>(-1.0)</td>
<td>(5.0)</td>
</tr>
<tr>
<td>GaP</td>
<td>3.8±0.2</td>
<td>0.42</td>
<td>-0.25</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>(3.37)</td>
<td>(2.22)</td>
<td>(-0.3)</td>
<td>(-1.1)</td>
</tr>
<tr>
<td>GaAs</td>
<td>3.6±0.2</td>
<td>0.61</td>
<td>-0.7</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>(3.40)</td>
<td>(1.35)</td>
<td>(-0.7)</td>
<td>(11.3)</td>
</tr>
</tbody>
</table>

The influence of the annealing temperature on the absorption edges of flash-evaporated a-Ge, a-GaAs and a-GaP was investigated by Theye [31,32] and Gheorghiu and Theye [33,34]. It was found that a-GaP differs from the other two materials in two ways: first its absorption edge is considerably broader and exhibits more important tailing towards low energies, and
Figure 1.15: $\hbar \omega \sqrt{e_2}$ versus photon energy in the absorption edge region for (a) a-GaAs films annealed at 300 K (+) and 515 K (•) (b) a-GaP films annealed at 300 K (+) and 570 K (•)
second this tail becomes even more extended after annealing (Figure 1.15) instead of being reduced.

Thus far, these observed striking optical properties of a-GaP were invariably attributed to short-range chemical disorder, that is, to the presence of like-atom bonds i.e. Ga-Ga and P-P bonds (wrong bonds) in its network in addition to Ga-P bonds which exist exclusively in the case of c-GaP [30,34]. This interpretation was based on the fact that the change in the nature of bonding produces pronounced effects on the properties of materials. The interpretation was also considered to be probable from a topological point of view. The first continuous random network model (CRN) proposed by Polk [7] contains a considerable number of odd-membered rings and hence necessitates a high proportion of wrong bonds if applied to the a-GaP network. In contrast, the CRN model introduced by Connell and Temkin [11], which consists of only even-membered rings, requires perfect chemical ordering. Electron diffraction experiments of Dixmier et al [35] have shown that a-GaP adopts the Connell-Temkin CRN. This conflict naturally has led to investigations aimed at direct identification and quantification of chemical disorder in a-GaP, for which in particular EXAFS was used since the very different scattering factors of Ga and P atoms allow for an easy separation of the contributions from the two types of first neighbours around each atom. Such experiments did indeed reveal the existence of wrong bonds, with a proportion of 25%, in flash-evaporated samples [36,37]. On the contrary, Raman scattering [38] and photoemission spectroscopy [39] indicated a high degree of chemical ordering in sputtered a-GaP samples.

The problem of chemical disorder is an important one since it gives rise to states in or around the optical gap region [40,41] and thereby dominates many electrical properties. From the application point of view, materials containing such disorder are unstable and hence cannot be used in devices. Therefore, in the present work, with the aim of resolving this
problem at least for r.f. sputtered samples, we have carried out a detailed structural study using EXAFS, IR spectroscopy, TEM and SEM-EDAX. While the former two techniques dealt with not only the chemical disorder but also the intrinsic disorder of the network, the latter two provided information on microscopic and macroscopic inhomogeneities present in the samples. The optical properties near the absorption edge of the samples were also investigated by combining the conventional R-T method and the most recently developed PDS technique. (The latter technique was installed during the course of this work by the author.) Furthermore, high- and low-temperature d.c. conductivity experiments were performed to determine the electrical properties of the samples. A particular effort was made to correlate the results obtained from these techniques as much as possible so that a complete picture of a-GaP can be drawn.

This work was part of a major III-V project carried out by the group of Thin Amorphous Films in the Department of Physics and Astronomy of this University. Apart from a-GaP [42,43], a-GaAs [44,45], a-GaAlAs [46], a-GaAsP [47] and a-InP [48,49,50] have also been investigated in detail as a function of composition and deposition conditions (substrate temperature, hydrogen etc). The author of this thesis has been involved with some of these investigations [45,49,50].

References [42,43,45,49] are attached to the end of the thesis.
References

[12] When the dihedral angle $\phi$ between next-nearest-neighbour bonds is 60°, the bonds are in the staggered configuration, and when $\phi$ is 0°, the bonds are in the eclipsed configuration.
Chapter 2: Sample Preparation

2.1 General methods of preparation
2.2 Radio-frequency (r.f.) sputtering
2.3 Leicester sputtering system
2.4 Films deposited and preparation conditions
2 Sample Preparation

2.1 General Methods of Preparation

There is a great variety of methods for preparing amorphous materials. The oldest established one is melt-quenching in which bulk material is produced by rapid cooling of the liquid to below the glass transition temperature. Here the cooling rate is the most critical factor and has to be sufficiently fast in order to prevent crystal nucleation and growth. Experimentally, a wide range of cooling rates \(10^{-5}-10^8\) Ks\(^{-1}\) with the use of different quenching techniques are accessible, and hence a variety of materials including most of the chalcogenides, diamond lattice-type semiconductors, typified by CdGeAs\(_2\), and transition-metal oxide glasses can be produced by this method. Other methods, such as chemical reactions and precipitation from solution and more recently developed gel desiccation, can also produce bulk materials, particularly for those systems which have very viscous melts near the melting point and hence pose considerable technical problems in the melt-quenching technique.

Amorphous materials may also be fabricated in the form of thin films by vapour-condensation techniques, for instance, thermal evaporation, d.c. and r.f. sputtering, glow-discharge decomposition and chemical vapour deposition. Of these, the simplest and most commonly used is thermal evaporation in which a source material is vaporized in a high vacuum either by resistance heating or by electron-beam bombardment and then condensed onto a substrate held at a fixed temperature. This method, however, has serious drawbacks which are the lack of control over purity and, in the case of the source material being a compound or an alloy, the composition of the resulting film. Deposition by sputtering is more complex but offers greater flexibility and control over
the deposition conditions. The sputtering process involves the bombardment of a target by energetic ions created in a low-pressure plasma, causing erosion of a material either atom by atom or in clusters of atoms, and subsequent deposition of a film on a substrate. The process can be induced by the application of either a high negative voltage to the target as in d.c. sputtering or, more commonly, a radio-frequency field as in r.f. sputtering. In glow-discharge decomposition, an r.f. field is also employed to create a plasma which, in this case, leads to chemical decomposition of a reactant gas that are generally hydrides. The glow-discharge decomposition has been in intensive use since the realization of the fact that the technique can readily produce device quality, both undoped and doped, amorphous materials (e.g. a-Si:H, a-Ge:H). As for chemical vapour deposition, it is analogous to the glow-discharge decomposition except that in the former sufficiently high temperatures (of the order of 1000 K) are used for the decomposition of the reactant gas. The advantage of this method is the absence of ion and X-ray damage to the films.

There are also various other methods that have been used to a lesser extent to prepare amorphous materials. Amongst these are electrolytic deposition, neutron or ion bombardment, shock-wave transformation and shear amorphization.

Good reviews of the preparation methods mentioned above can be found in Ref.[1-8].

2.2 Radio-frequency (r.f.) Sputtering

Sputtering, particularly using radio-frequency fields, has already established as a very versatile, useful technique for depositing a wide range of elemental and compound thin films. The technique is also
suitable for mass production required by industrial applications. In addition, it has further advantages in that the films produced are in general mechanically strong and also good control of deposition parameters is possible, thus permitting optimization of the electro-optical properties of the films.

Figure 2.1 illustrates the basic layout of the technique. The target, which is made of the material to be deposited, and the substrate attached to a heater are placed some distance apart in a chamber, which is initially evacuated by an oil diffusion or turbomolecular pump together with a mechanical pump. An r.f. field (at typically 13.6 MHz) is capacitatively coupled to the target. A sputtering gas (usually argon) and sometimes additional gases, for example hydrogen in the case of reactive sputtering, are introduced into the chamber at a pressure of $10^{-3}$-$10^{-2}$ Torr. Application of the r.f. field causes the striking of a plasma through the ionization of the gases. During each negative half-cycle of the field, the positive ions in the plasma are attracted to the target. Similarly, during each positive half-cycle, electrons are attracted to the target. Owing to the difference in mobility between electrons and ions, more electrons than ions arrive at the target surface, which results in the build-up of a negative bias voltage $V_b$ within a few r.f. cycles. The voltage on the target surface can then be described as an r.f. voltage with a superimposed negative d.c. bias. While the r.f. voltage mainly sustains the plasma in a steady state, the negative d.c. bias accelerates ions from the plasma towards the target, causing the bombardment of the target with an energy of the order of $V_b$ electron volts. Following the ion bombardment, a number of phenomena may occur simultaneously at the target (see Figure 2.2):

1. Some of the incident ions may be reflected, probably being neutralized by Auger electrons from the target.
Figure 2.1: The basic layout of the r.f. sputtering technique

Figure 2.2: Interaction of ions with a target
(2) The impact of the ion may cause the target to eject secondary electrons, which are accelerated away with an initial energy equal to the target voltage.

(3) The ions may be implanted into the target.

(4) The ion impact may damage and possibly disorder the surface of the target.

(5) The ion impact may set up a series of collisions between atoms of the target, which leads to the ejection of one of these atoms. This is the sputtering process.

(6) The target emits UV and X-ray radiation.

(7) A significant fraction of the energy of the bombarding ions is dissipated in the target in the form of heat.

According to the above events, electrons, ions and neutral species from the target are injected into the plasma with different energies. Prior to reaching to the substrate, some of them undergo inelastic collisions, resulting in thermalization due to processes such as ionization, excitation and dissociation, whereas the others travel through the plasma unaffected.

When a thermalized sputtered neutral or excited target atom arrives at the substrate, it condenses and diffuses around with a motion determined by its binding energy to the substrate until it finds a final low-energy site. During this process, it may re-evaporate or join with another atom to form a pair. This atomic pair has lower mobility and is therefore likely to be joined by other atoms, beginning the nucleation process of film growth. This process leads initially to isolated islands, which, as they grow in size, coalesce to form a continuous film. Meanwhile, the substrate and growing film are subjected to many types of bombardment due to the high-energy charged/neutral particles and also UV and X-ray radiation which come from the target and plasma. Most of these bombarding species are not incorporated in the film but they can dissipate their kinetic and
potential energy at the film surface which can influence the nucleation and growth process, and hence the structure and properties of the deposited layer. The bombardment effect can be controlled by an external bias intentionally applied to the substrate. The technique is then known as bias sputtering.

2.3 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 Figure 2.3.

The chamber, made of stainless steel, is 24” in diameter and 15.8” high, and has a front opening door. It can be raised by 16” using an electrically driven hoist to ease access to the chamber interior. The chamber contains a multi-electrode turret, a substrate electrode and accessories necessary for fitting the target and substrates to the corresponding electrodes. The multi-electrode turret consists of an evaporation source, a conventional sputtering electrode and a high-rate magnetron sputtering electrode. Each electrode is isolated by PTFE insulation and surrounded by a stainless steel earth shield. The required electrode is selected by rotating the turret. Throughout the work, the conventional 8” diameter sputtering electrode was employed. The earth shield of this electrode was mask down by a reduction shield with an aperture a little larger than 4” so as to accommodate a 4” target. The target was bonded onto an oxygen-free copper backing plate using silver epoxy cement and then screwed into the sputtering electrode.

The substrate electrode is also 8” in diameter. The substrates were clamped by a contact mask to a removable copper substrate platen which
Figure 2.3: Schematic diagram of the sputtering system.
was locked in position to the substrate electrode by means of a special key wrench. Heating of the electrode and hence the substrates was achieved using a heater element situated on top of the electrode. Stabilization of the temperature was obtained by a Eurotherm temperature controller and a chromel-alumel thermocouple. The thermocouple, which was electrically insulated using a quartz sleeve, was located into a hole drilled in the side of the substrate platen. In order to ensure good electrical and thermal contact, thin deformable copper gaskets were inserted between the platen and the electrode.

The distance between the target and the substrates could be varied from 1 to 10 cm. A target substrates separation of 5 cm was used. In between the target and substrate, a rotary shutter was positioned to allow sputter cleaning of the target prior to deposition.

The chamber was pumped by a Varian VHS-250 mm oil diffusion pump with a liquid-nitrogen cold trap. The diffusion pump was backed by a Leybold-Hereaus D30A direct-drive rotary pump. A water-cooled baffle below the trap and also a foreline trap between the two pumps were used to reduce the backstreaming of oil from the pumps into the chamber. This arrangement enabled the chamber to be pumped down to a pressure of about 6x10^{-7} Torr overnight. A VSM vacuum analyst quadrapole mass spectrometer, which monitors the residual gases in the chamber, revealed that the main contaminants at this pressure are water-vapour, nitrogen, oxygen and hydro-carbons. In order to reduce the level of these contaminants, a Meisner Coil (a coil of copper tubing) located around the substrate table was filled with liquid nitrogen. The cryogenically cooled surface of the coil caused condensation of the contaminants, particularly water-vapour, thus resulting in the ultimate chamber pressure being better than 2x10^{-7} Torr (see Figure 2.4).
Figure 2.4: Typical spectra of the residual gases in the chamber
— before — after filling the Meisner coil with liquid nitrogen
The sputtering gases, 99.999% pure argon and zero-grade hydrogen, were admitted into the chamber through stainless steel pipes, and their flow rates were controlled by a Vacuum General 78-7 flow-ratio and pressure control system. A Vacuum General CM capacitive manometer, which measures the absolute chamber pressure, fed the signal back to the piezoelectric valves in the control unit so that the correct pressure and ratio of the gases are maintained. The flow of the gases, however, could not be increased solely to reach the sputtering pressures of 10⁻³ to 10⁻² Torr, without reducing the speed of the pumping system. This was done by partially closing the pumping port in the chamber with a throttle plate.

The r.f. power was provided from a SG-1250 Model r.f. generator. The generator, in essence, is a piezoelectric crystal producing a small r.f. electric signal at a frequency of 6.78 MHz. The electronic circuit attached to the generator increases the frequency of the signal to give the desired output frequency of 13.56 MHz and amplifies the signal itself to attain the voltage and current output characteristics of the generator. The output impedance of the generator was adjusted at the factory as 50 Ω so that a conventional flexible 50 Ω co-axial cable could be used to transfer the power from the generator to the electrodes in the chamber. However, the impedance of the electrodes and the plasma is different from 50 Ω, thereby causing an impedance mismatch which leads to power being reflected back to the generator. To overcome this problem, a matching unit placed between the end of co-axial cable and the electrodes has been used.

2.4 Films Deposited and Preparation Conditions

The r.f. sputtered a-GaP films investigated in this study were produced from a 4" diameter and 3 mm thick stoichiometric
polycrystalline GaP target fabricated by a hot-pressing technique by Testbourne Ltd. During film production, an r.f. power of 250 W was applied only to the target, leaving the substrates floating, and the reflected power was reduced to <1 W by tuning the matching unit. The bias voltage generated at the target was then \( \sim 550 \) V. Argon gas was chosen as the sputtering gas; its flow rate was kept constant at 30 scc/min which resulted in a sputtering pressure of \( \sim 3-4 \) mTorr.

Various types of substrates were used simultaneously in order that the films can be studied by many different techniques. The substrates were: fused silica for optical reflectivity and transmission measurements (UV/visible/near-IR) and PDS (photothermal deflection spectroscopy), Corning 7059 glass (highly resistive) for electrical measurements, polished c-Si wafers for IR spectroscopy, mylar and Cu for EXAFS experiments, mica for TEM work, aluminium foil for EDAX analysis and a microscope slide for thickness determinations. All the substrates, except the mylar and mica, were degreased in detergent and then ultrasonically washed in acetone and methanol before being mounted. The temperature of the substrates were varied between room temperature and 200 °C.

The resulting films were 1-1.2 \( \mu m \) thick, corresponding to deposition rates of 30-40 \( \AA/min \), respectively. These films, hereafter, will be referred to as \( a\text{-GaP}(T_d) \) where \( T_d \) is the deposition temperature. Some of the films prepared at room temperature were subsequently annealed at higher temperatures (200-400 °C) in a separate vacuum cryostat (10\(^{-5} \) mTorr). The annealing duration was two hours. These films, hereafter, will be referred to as \( a\text{-GaP}(T_a) \) where \( T_a \) is the annealing temperature.

In addition to a series of films with different deposition and annealing temperatures, two other series of films have also been prepared during the course of this study. These are:
1. a-GaP(H) : Hydrogenated amorphous GaP films were sputtered reactively from the target in an argon-hydrogen gas mixture. The hydrogen content in the films were varied by altering the ratio of the H-flow rate to that of Ar from 0 to 45 scc/min whilst the total flow rate was fixed at 30 scc/min. During deposition, the substrate temperature was held at room temperature, and the other deposition parameters were maintained exactly the same as those of a-GaP(T<sub>3</sub>). The resulting films were 0.9-1.2 μm thick.

2. a-Ga<sub>1-x</sub>P<sub>x</sub> , 0.5≤x≤1 : P-rich amorphous GaP films were deposited by a method of r.f. co-sputtering for which small pieces of red phosphorus were uniformly placed on the target and P concentrations beyond stoichiometry were obtained by increasing the number of the P pieces. Deposition of these films, however, was found to be difficult; quite often a-Ga<sub>x</sub>P<sub>y</sub>O<sub>z</sub> films resulted. This was mainly because of the high susceptibility of P to oxidize. Therefore, special attention had to be paid to keep the residual oxygen level very low during deposition. This was achieved by having a chamber base pressure better than 2x10<sup>-7</sup> Torr, and by using very pure P pieces (99.999 %) which were stored in an argon atmosphere prior to use. The other deposition parameters were kept exactly the same as those used for a-GaP(T<sub>3</sub>), except that the substrate temperature was held at room temperature. The films had thicknesses of 1-2 μm.
References


Chapter 3: Experimental Techniques Used for Structural Determination

3.1 Electron microscopy
   3.1.1 Transmission electron microscope
   3.1.2 Scanning electron microscope with EDAX

3.2 EXAFS spectroscopy
   3.2.1 Introduction
   3.2.2 Theory
   3.2.3 Experimental details
   3.2.4 Data analysis
   3.2.5 Composition measurements
   3.2.6 XANES

3.3 Infrared spectroscopy
3 Experimental Techniques Used for Structural Determination

The structure of the sputtered amorphous GaP films deposited in the present study was investigated using techniques of electron microscopy (both with a TEM and a SEM to which an energy dispersive X-ray analyser (EDAX) is attached), EXAFS and IR spectroscopy. Each of these techniques is sensitive to different features of the structure; hence information ranging from the macroscopic appearance of the films and microscopic inhomogeneities in their network to local atomic arrangements were obtained. These results will be the subject of Chapter 5 while this Chapter describes briefly the basic principles and the experimental aspects of the above techniques as well as the methods used to extract of the structural information.

3.1 Electron Microscopy

Electron microscopy is a technique of making and interpreting highly magnified images and diffraction patterns produced by an electron beam. The process of making electron micrographs and the mechanism of image formation depend on the type of the electron microscope used.

3.1.1 Transmission Electron Microscope

TEM is one of the most important category of electron microscopes, in which an energetic electron beam is passed through a sample. The beam is generated by an electron gun and focussed onto the sample by a double condenser lens system. An electron-optical system, which typically consists of an objective lens, an intermediate lens and a projector lens, forms the image
on a fluorescent screen. The lenses used may be electrostatic, electromagnetic or a combination of the two. Appropriate apertures are placed near these lenses to improve the image quality. All the components of the microscope and the sample are enclosed in a vacuum provided by a pumping system.

In a TEM, the image can be formed by a variety of geometric optic configurations. The most commonly used are bright-field and dark-field modes (See Figure 3.1 (a), (b)). In the former, a small aperture inserted in the back focal plane of the objective lens intercepts the diffracted beam and only allow the transmitted beam to construct the image. In the latter, the objective aperture is displaced from the optic axis to intercept the transmitted beam and allow the diffracted beam to form the image. However, in this mode a poor-quality image is produced because of the additional spherical aberration and astigmatism present when the electron path is not close to the optic axis. In order to retain the resolution of the bright-field mode, the incident beam on the sample is tilted so that the diffracted beam travel along the optic axis. This technique is then known as centred dark field.

A TEM can also be operated to produce a momentum space image i.e. a diffraction pattern, from a sample. Figure 3.1 (c) indicates the essential features of this operation mode in which both the transmitted and diffracted beam are accepted by the objective aperture and used to obtain the diffraction pattern. The pattern is actually imaged at the back focal plane of the objective lens; however, it can be formed on the fluorescent screen like the real-space image by suitably adjusting the strengths of the intermediate lens. Recording of the images is then achieved by directly photographing the fluorescent screen.

In the present work, a Joel Jem 100 Cx model TEM which belongs to the Medical Sciences Department of the University of Leicester was used. Extremely thin free-standing films (~100 Å) were studied so that they can be viewed directly without requiring any surface replica methods. The films
Figure 3.1: TEM imaging modes: (a) bright-field (b) centred-dark-field (c) diffraction
were originally sputtered onto mica substrates. Deposition of such a thin films (for which the deposition duration is ~2 min) simultaneously with thicker films (for which the deposition duration can be over 5 hours) used for other measurements, was made possible by use of a small mechanical shutter, attached to the substrate platen, which selectively masked the relevant substrate without disturbing the deposition elsewhere. The films and mica substrate were placed into distilled water where small pieces of free films could be floated off. These pieces were then transferred onto standard copper microscope grids.

The TEM was firstly employed in the selected-area diffraction mode so that the amorphous nature of the films could be checked by the observation of diffuse rings. Then the mode was switched to the bright-field mode in order to investigate any structural inhomogeneities in the films. Although all the films appeared to be macroscopically homogeneous, continuous and smooth, the presence of microscopic inhomogeneities such as voids were sometimes revealed in this mode. They appear as a contrast in the images due to the local density fluctuations they produce. Further discussions on this topic and the images and diffraction patterns obtained will be presented in Chapter 5, section 5.1.

3.1.2 Scanning Electron Microscope with EDAX

SEM and EDAX are two separate instruments which provide observation and characterisation of the specimens, respectively. In reality, they are quite similar, and so can be combined to form a very powerful versatile instrument. Figure 3.2 shows a schematic diagram of such an instrument. A beam of electrons originates from a heated tungsten cathode. It is accelerated and focussed by electric and magnetic lenses to ~1μm diameter
at the sample surface. The electron beam is deflected by scanning coils so that the sample is scanned point by point in a raster pattern. Electrons striking the sample cause emission of secondary electrons, back-scattered electrons, Auger electrons, characteristic and continuum X-rays and photons of various energies.

The SEM part of the instrument collects the secondary electrons, amplifies the signal and then produces images on a television-type screen, revealing the surface topography of the samples. These images have lower resolution and magnification compared with those obtained in TEM but have the advantage of being three dimensional in appearance.

In the EDAX part of the instrument, the primary radiation of interest is the characteristic X-rays. They are detected and measured by an energy dispersive system in which a lithium-drifted silicon crystal detector, together with appropriate circuitry, is used to discriminate the X-ray energies. Figure 3.3 shows a typical spectrum obtained in this way in the present study. From the energy of the emitted characteristic X-rays, the component elements present in the sample are identified qualitatively. Quantitative determination of each element can be carried out using the ratio of the measured intensity of a characteristic X-ray from the element to that from a standard pure element. Prior to the determination, the ratio is corrected for background effects such as continuum X-rays and electronic noise, and for the so-called ZAF factor where $Z$ refers to the atomic number of the element emitting the X-ray, $A$ represents the absorption of the X-rays by the surrounding elements and $F$ refers to the fluorescence from the sample. Detailed explanations on both qualitative and quantitative elemental analysis can be found in references [4-7].

In the present work, an ISI DS 130 model scanning electron microscope including an energy dispersive X-ray analyser facility (situated in the Medical Sciences Building of the University of Leicester) was employed. Prior to the
Figure 3.2: Schematic drawing of the electron-optical system of a combined SEM-EDAX

Figure 3.3: Energy dispersive X-ray spectrum of an a-GaP film. Characteristic lines are superimposed on the continuum radiation
analysis, the operation conditions were optimized using a standard c-GaP sample. The a-GaP films (~1μm thick), deposited on conductive aluminium foil substrates to avoid both the electrostatic charging and heating of the samples, were then investigated. In the first stage of the investigation, the secondary and backscattered electron images showing the surface topology of the films were obtained. The electron beam was then focussed over a chosen sample area (~1μm²), and local compositional analysis with 2-3% accuracy was carried out. This was repeated for different regions of the sample. In the second stage of the investigation, the presence of microscopic compositional inhomogeneities such as phase separation were searched for. For this, the EDAX was set to detect one particular characteristic X-ray line (either from Ga or P) and the output was linked to a computer. As the electron beam was made to scan along a horizontal line on the sample surface, the computer used the counts obtained at each point on the line for building up a histogram (called a line profile), revealing variations in the elemental concentration. Later on, this stage was pursued; the electron beam was made to scan an area, which led to digitized maps for each element, representing the distribution of the element across that area of the sample. Examples of both line profiles and digitized maps will be presented in section 5.1.
3.2 EXAFS Spectroscopy

3.2.1 Introduction

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is a technique used to determine short-range interatomic correlations in a solid. It involves the measurement of the X-ray absorption coefficient \( \mu \) of atoms as a function of photon energy \( E \). In general \( \mu \) is a decreasing function of \( E \), but discontinuous increases, i.e. absorption edges, occur when an X-ray photon having higher energy than the binding energy of a core electron is absorbed by the atom, exciting the electron to a continuum state. These absorption edges are known as K-edges when ejected electrons come from the \( n=1 \) shell and L-edges if they come from the less tightly bound \( n=2 \) shell. For an isolated atom, the ejected photoelectron travels as a spherical wave with a wavelength \( \lambda = 2\pi/k \) (where \( k = (2m(E - E_0)/\hbar)^{1/2} \), \( E \) is the incident X-ray photon energy and \( E_0 \) is the threshold energy of the absorption edge) outwards to infinity. However, in the presence of neighbouring atoms, e.g. in condensed matter, this outgoing photoelectron wave will be backscattered from the neighbouring atoms, thereby producing an incoming wave which can interfere either constructively or destructively with the outgoing wave near the absorbing atom (See Figure 3.4). Constructive interference increases the absorption above, while destructive interference reduces it below, the isolated atom value, resulting in an oscillatory behaviour of the absorption coefficient. These oscillations which are known as ‘the extended X-ray absorption fine structure’ can start approximately 50 eV above the absorption edge and extend typically 1000 eV further, and may have a magnitude of 10 \% or more of the edge itself. Fine structure also exist between the threshold and the first ~50 eV of the edge, but because the photoelectron involves with multiple scattering in this region, thereby breaking the single scattering
assumption valid for EXAFS, this structure is called X-ray absorption near edge structure (XANES) to distinguish it from EXAFS. Figure 3.5 presents both XANES and EXAFS in a typical K-edge X-ray absorption spectrum.

EXAFS oscillations, as will be shown later, carry information on local atomic arrangements around the absorbing atom, such as the type and number of neighbouring atoms and their distances away from the absorbing atoms. This was first pointed out by Sayers et al. [8] in 1971, although EXAFS has been known for a long time [9]. Since then, partly due to the major improvements in a theoretical understanding of the phenomenon and partly due to the availability of Synchrotron Radiation Sources producing continuous intense X-rays over a wide spectral range, the use of EXAFS for structural investigations has expanded rapidly into many diverse fields such as inorganic chemistry, biochemistry, catalysis, material science etc. The technique is particularly valuable for studying multicomponent systems (both crystalline and amorphous) for which conventional structural techniques such as X-ray or neutron diffraction provide information averaged over all atomic pairs in the sample and hence sometimes yield ambiguous results. This is because in EXAFS, simply by tuning to the X-ray absorption edge of each atom type in the sample, structural information for each type of atom can be obtained, even in the case of the atom existing in impurity concentration levels [10]. In addition to this useful atom-specific nature, the technique has also other attractive features, such as the relative ease of measurement, the short time scale (~30 min) of the experiments, and the comparatively simple and direct method of analysis.
Figure 3.4: Schematic representation of the production of EXAFS

Figure 3.5: Phosphorus K-edge X-ray absorption spectrum of a-GaP showing XANES resonances and EXAFS oscillations
3.2.2 Theory

The EXAFS function, \( \chi \), defined as the oscillatory part of the absorption coefficient produced by the process of photoexcitation of an electron from a core state can be written as

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}
\]  

(2)

where \( \mu \) and \( \mu_0 \) are the experimentally observed and isolated atom absorption coefficients, respectively. The occurrence of this phenomenon was first explained by Kronig who germinated two alternative theories: long-range order (LRO) theory [11] and short-range order (SRO) theory [12]. LRO theory utilized the energy gaps at the Brillouin zone boundaries whereas SRO theory was based on photoelectron scattering by neighbouring atoms. Both theories predicted fine-structure oscillations but were too simple, with the result that lack of agreement between the theories and experiment created confusion over the exact theoretical form of the EXAFS function. The confusion which lasted over half a century ended in favour of SRO theory when Sayers et al [8] pointed out that a Fourier transform of the EXAFS with respect to the photoelectron wavenumber \( k \) should peak at distances corresponding to nearest-neighbour coordination shells of atoms. The theoretical expression they used for the description of the EXAFS was:

\[
\chi(k) = \frac{A(k)}{k} \sum_j \frac{N_j}{R_j^2} |f_j(k, \pi)|^2 \sin(2kR_j + \delta + \psi) \exp(-2\sigma_j^2 k^2) \exp(-\frac{R_j}{\lambda})
\]  

(3)

where different terms account for different factors contributing to the EXAFS signal. The EXAFS oscillations are mainly due to the sine term in which \( 2kR_j \) is the phase shift introduced by the photoelectron wave travelling from the
absorbing atom to the neighbouring scattering atom and back. This term would be adequate if the photoelectron wave were moving in a constant potential. However, because the wave experiences the atomic potential of the absorbing atom twice (i.e. once going out and once coming back) and also the atomic potential of the scattering atom once during the trip, the terms $2\delta$ and $\psi$, respectively, were added as additional phase shifts. The amplitude of the oscillations depends on the number of scattering atoms $N_j$ in a shell $j$ at a distance $R_j$ from the absorbing atom and also their electron scattering strength $f_j(k,\pi)$, the latter depending on both the atomic number of the scattering atom and the photoelectron energy. The amplitude of the oscillations is attenuated because of the Debye-Waller term $\exp(-2\sigma_j^2k^2)$ where $\sigma_j^2$ is the mean square deviation from the interatomic distance $R_j$. In crystalline materials, $\sigma_j^2$ accounts for thermal vibrations of the atoms while for amorphous materials it has additional contributions due to the inherent static or structural disorder. These contributions can be estimated by assuming that the distribution of the interatomic distances is Gaussian. This assumption is valid for thermal vibrations and for weak static disorder but may be poor for a highly disordered system. Further attenuation in the amplitude of the oscillations occurs due to the term $\exp(-2R_j/\lambda)$ which describes the fact that the excited photoelectron has a short mean free path $\lambda$ in the material. This is because the photoelectron during the travelling between the absorbing and scattering atoms may undergo inelastic scattering by electrons in the scattering atoms, thus losing its coherence and its ability to contribute to the EXAFS signal. This is known as extrinsic inelastic loss and can be modelled in terms of a constant imaginary part of the potential, $V_{PI}$, so that $\lambda=k/V_{PI}$. There are also losses caused by intrinsic inelastic processes which involve the excitation and ionization of other electrons on the absorbing atom following the creation of the core hole. These are usually referred to as shake-up and shake-off events, respectively, and are taken into account by the term $A$. In addition, the
extrinsic and intrinsic inelastic processes can interfere one another. However, recent work [13] has shown that their interference is significant only very close to the absorption edge, and may therefore be ignored in EXAFS work.

Equation (3) assumes that the photoelectron waves are plane and single scattering of the photoelectrons take place, whereas in fact the wave is spherical and multiple-scattering events (see Figure 3.6) may occur. An exact theory for \( \chi \) taking the above factors into consideration was developed by Lee and Pendry [14] who used an electron scattering theory which described the process in terms of the wavefunction of the photoelectron and by Ashley and Doniach [15] who used a Green's function formalism. Both theories are equivalent and give the same results. The main conclusion of these two analyse is that, for much EXAFS work, only single-scattering events need be considered. However, for XANES and also for cases where one atom is shadowed by another, that is when neighbouring atoms are arranged in a linear or nearly colinear array, multiple-scattering paths (double and triple) must be included. This necessitates the use of exact curved wave theory. Unfortunately, because of the mathematically complex nature of the exact theory, a large amount of computer time is required for the calculation of \( \chi \), which makes it impractical for interactive data analysis. Therefore, several approximate theories allowing for faster calculations have been developed.

(a) The Plane Wave Approximation (PWA): When the energy of the photoelectron is sufficiently high or the interatomic distances sufficiently large, the curvature of the actual spherical wave may be neglected and the wavefunction of the outgoing photoelectron can be approximated by a plane wave. This approximation is the basis of the plane wave approach and, in fact, takes the theory back to equation (3) (for the case of single scattering).

The PWA produces a simplified theory which enables straightforward data analysis, but it is limited to the high-energy part of the spectrum. Also, comparative results with a curved wave theory show that the PWA is
Figure 3.6: Schematic representation of (a) single-scattering (b) double-scattering events

Figure 3.8: Schematic layout of the experimental set-up at station 7.1
particularly poor for orders of scattering above single ones [16], the theoretical errors occurring in the description of the phase of photoelectron.

(b) The Small Atom Approximation (SAA): In this approximation [14,17] the spherical wave incident on a scattering atom is still approximated by a plane wave, but one which has the correct phase and amplitude at the centre of the scattering atom. Thus, the simplicity of the PWA and its low computational timescales are retained and also the phase problem is avoided. The approximation will be the more accurate the smaller the scattering atom and the higher the photoelectron energy, since at high energies the effective size of the scattering atom decreases by the photoelectron’s ability to penetrate deeper into the atom before scattering. Using this approximation, higher-order scattering contributions can be calculated rapidly and accurately.

(c) The Fast Curved Wave Theory (FCW): The Fast Curved Theory [16,18] does not use any approximation and is an exact theory, treating the wavefunctions as spherical. Hence, it is valid for the entire photoelectron energy range (including low k). The theory is, in fact, an application of the exact curved wave theory of Lee and Pendry [14] to amorphous and polycrystalline materials. The inherent disorder of these materials allows for angle-averaging of the scattered photoelectron wave, which reduces the number of the calculations and consequently the computing time. For single scattering, computing times are comparable to those obtained from the PWA but although double- and triple-scattering contributions may be similarly simplified, they still remain too complex to be calculated interactively with present computing facilities.
3.2.3 Experimental Details

EXAFS experiments are usually performed using synchrotron radiation, because its high intensity allows one to take the spectrum in a short time (~30 min) with a very high signal-to-noise ratio. The radiation has also other useful properties like high collimation, plane polarization and precisely pulsed time structure, each of which are important for different types of X-ray experiments.

In this study, the EXAFS experiments were carried out using the synchrotron radiation source at the SERC Daresbury Laboratory in the UK (see Figure 3.7). The source is actually the electron storage ring, NINA, which is capable of holding a beam of electrons at energies up to 2 GeV and currents of approximately 200 mA for many hours. The ring consists of 16 dipole magnets which bends the electron beam along a circular path. It is this bending of the beam that causes emission of the continuous synchrotron radiation (so-called white radiation) ranging from the infrared to the far X-ray region. The radiation is then coupled to the experiment through beam ports tangent to the ring and beamlines (stations) with their associated optics. Twenty-nine stations are available around the ring. Two of these, 7.1 and 3.4, were used for probing Ga and P K-edges of the a-GaP samples, respectively.

The Ga K-edge experiments at the 7.1 station were carried out in transmission mode. Figure 3.8 presents a schematic layout of the experimental set-up. The white radiation from the storage ring was monochromatized using a Si (111) double-crystal monochromator which satisfies the Bragg condition

\[ m\lambda = 2nd \sin \theta \]  

(4)

where \( m \) is the order of the reflection, \( \lambda \) is the X-ray wavelength, \( n \) is the refractive index, \( d \) is the spacing of the planes in the crystal and \( \theta \) is the angle.
Figure 3.7: An overview of the electron storage ring, SRS, at the SERC Daresbury Laboratory
of incidence. Only first-order reflection is desired. Therefore, higher order reflections than the first (harmonics) were rejected by detuning the monochromator crystals about 70%. The entrance and exit slits were used for defining the horizontal and vertical size of the white and monochromatic beam, respectively, so that the scatterer can be minimized. Both slits and the monochromator were kept in evacuated chambers. After monochromatization, the X-ray beam was passed through the first ionization chamber which measured the incident beam intensity $I_o$, then the sample, and finally the second ionization chamber which measured the transmitted beam intensity $I$. The absorption coefficient $\mu$ was determined from the well-known expression

$$\mu x = \ln \left( \frac{I_o}{I} \right)$$

(5)

where $x$ is the thickness of the sample. The full spectrum was acquired by sequentially changing the angle $\theta$, and thus the photon energy, through the region of interest and by monitoring $I_o$ and $I$ in each step, via a computer data acquisition system. The signal-to-noise ratio in the spectrum was optimized ensuring that the necessary thickness condition is satisfied, that is $\mu x = 2$ at the absorption edge. For the a-GaP samples, which had been deposited onto a mylar substrate over a wide area, it was necessary to fold them many times until the optimal thickness of $\sim$40-50 $\mu m$ was obtained.

The P K-edge experiments at the 3.4 station were performed by the electron drain current method which is a modification of the total yield technique. The station uses soft X-rays ranging from 0.8 to 4 keV. The fact that these low-energy X-rays are attenuated strongly by the atmosphere requires the beamline optics, sample and detector to be kept in ultra-high vacuum, thus placing a constraint on the experimental set-up. The system consisted of a Ge (111) double-crystal monochromator with harmonic rejection set at 70% and a chromium-coated toroidal mirror positioned at a grazing angle to focus
the beam in the vertical direction onto the films. The films used had been deposited on conductive copper plates and then connected to the sample holder using a layer of silver paint so that the drain current resulting from the electrons ejected due to the absorption of X-ray photons could flow through the sample to the substrate and so to the sample holder. The measurement of this drain current produces an output signal which is proportional to the absorption coefficient \( \mu(E) \).

3.2.4 Data Analysis

All EXAFS data collected for this study were analysed using computing facilities available at the SERC Daresbury Laboratory. Transmission data from the station 7.1 were energy calibrated by the EXCALIB program [19]. This program also allows the summing of a series of spectra and the editing of glitches and discontinuities. Summation of the energy calibrated spectra produced at station 3.4 were performed using the general graphics package, PLOTEK.

Normalisation of the EXAFS spectra was carried out by the EXBACK program [19]. The program fits low-order polynomials to the smoothly varying background absorption \( \mu_0 \) of the pre- and post-edge data and subtracts these to leave the EXAFS function \( \chi(E) \) (see Figure 3.9). A first-order polynomial was usually used for the pre-edge and a third-order polynomial for the post-edge. The accuracy of the fitted background was checked by a Fourier transform of the background-subtracted plot. The program also converted \( \chi(E) \) into \( \chi(k) \) using equation (1), where the edge energy \( E_0 \) was taken to be the point at which the first derivative of the absorption is a maximum. However, in the later stages of the data analysis, \( E_0 \) was floated.
Figure 3.9: Subtractions of (1) pre- (2) post-edge backgrounds to yield the EXAFS function $\chi(E)$.
around this value to improve the accuracy of the estimated interatomic
distances.

Structural information from the EXAFS spectra $\chi(k)$ was obtained
using the EXCURV90 interactive analysis program [20]. The program is based
on a non-linear least-squares fitting of the theoretical spectra calculated
according to the fast curved wave theory (considering only single scattering),
described in section 3.2.3, to the experimental spectra in k-space. Prior to the
fitting, both the theoretical and experimental spectra were multiplied by some
power of $k$ to give $k^n\chi(k)$ ($n=1,2,3$) so as to compensate for the diminishing
amplitudes at the high-$k$ values. The amplitude correction factors, i.e. A and
VPI, were obtained from the EXAFS analysis of a crystalline GaP sample and
the phase shifts of both the absorbing and scattering atoms were taken from
the EXAFS data bank present in the program. During the fitting, these
parameters were kept fixed, but correlated pairs $R_jE_0$, which together control
the phase of $\chi$, and $N_j2\eta^2$, which together control the amplitude of $\chi$, were
varied alternately, refining the difference between the theoretical and
experimental spectra in each step, until a minimum in the fit index was
found. The fit index, $FI$, is defined by

$$FI = \frac{1}{100N_p} \sum_{i=1}^{N_p} \left( \frac{[\chi_i(\text{theo.}) - \chi_i(\text{exp.})]k^n}{n} \right)^2$$

where $N_p$ is the number of data points in the spectrum and $n$ is the $k$-
weighting factor mentioned above. The final set of parameters obtained from
this procedure provide the structural information that it is desired to extract
from the EXAFS data. The uncertainties in these were estimated using a
statistical test described by Joyner et al [21]. This test provides a contour map
of the fit index as functions of two correlated fitting parameters, on which the
Figure 3.10: A contour map of the fit index for the correlated parameters \( N_1, A_1 \). The heavy line indicates the 95% confidence region.
95% confidence region (± 2σ uncertainty) is marked. An example is shown in Figure 3.10.

Also, as part of the program, a Fourier transform of the both theoretical and experimental spectra could be performed in order to observe the real-space radial distribution function. This transform was phase-corrected, i.e. the effects of the atomic potentials on the phase of the photoelectron wavefunction were included, and hence the peaks appeared at the true interatomic distances.

3.2.5 Composition Measurements

In the present work, in addition to extraction of the conventional structural information, EXAFS has been used to find the compositions of the samples. For this purpose, only the absorption spectrum of the P K-edge can be used because, for this edge, the drain current is obtained from the first 100 Å or so below the sample surface and therefore contains no contribution from the substrate. Therefore, the relative step height of μ(E) can be written as the sum of the atomic absorption of each element. For a-Ga_{1-x}P_{x},

$$\mu(E) = (1 - x)\mu_{Ga} + x\mu_{P}$$

(7)

By taking the ratio of values of μ(E) just above and just below the edge and the atomic absorption coefficients given by [22], the compositions x were calculated. The results were consistent with those obtained from the EDAX technique described in section 3.1.2.
3.2.6 XANES

XANES is the near-edge structure observed in an X-ray absorption spectrum, which covers the range between the threshold and the point at which EXAFS begins. The spectral range defined is quite arbitrary, reflected in the limits being different for each system. Nevertheless, XANES is generally accepted as extending to an energy of the order of 50 eV above the edge, and can be readily distinguished from EXAFS by its strong, sharp features.

In physical terms, the main difference between XANES and EXAFS lies in the fact that in XANES the ejected photoelectron is strongly backscattered by neighbouring atoms, generating multiple-scattering processes shown in Figure 3.6 while in EXAFS only the single-scattering process takes place. In addition, in XANES the photoelectron wave must be considered as a spherical wave, the plane-wave approximation used in some cases for EXAFS being no longer valid. It is therefore obvious that the theory describing EXAFS cannot simply be extended to XANES, which requires a more complicated treatment [23] including full multiple-scattering calculations. Similarly, the data analysis and their interpretation is not as straightforward as is EXAFS [24]. Despite these difficulties, the interest in XANES grows for several reasons:

(i) The spectra provide not only conventional structural information such as bond lengths, coordination numbers as in diffraction or EXAFS spectroscopy but also orientational information such as bond angles and the relative positions of neighbouring atoms.

(ii) From the chemical shift of the spectra, the effective atomic charge on the absorbing atom can be determined.

(iii) The spectra can also be interpreted in terms of the local partial electronic structure i.e. the density of states DOS.
The use of XANES for the investigation of amorphous materials is of great importance because the knowledges obtained can further the understanding of these materials. A recent work [25] has already demonstrated that XANES can successfully be applied for checking the validity of the proposed structural models and for detecting microphase segregation in complex amorphous alloys. In the present study, XANES was used to obtain information on the partial conduction band density of states.
3.3 Infrared Spectroscopy

Infrared spectroscopy is a technique widely used for the determination of the nature of chemical bonding in solids. It is based on the interaction of the IR radiation with the atoms in the solid through their characteristic vibrational modes. These vibrational modes include stretching, bending, rocking, etc. of the atoms at frequencies determined by both the local spatial geometry of the atoms involved in the motion and the inter-atomic forces amongst them. According to classical electrodynamics, in order for the IR radiation to interact with one of these vibrations, (1) it must have a frequency the same as that of the vibration (2) the vibration must be associated with an alteration in the electric dipole moment. The interaction excites the vibrational mode and produces energy transfer in which the incident radiation energy is absorbed. Such a mode is called infrared active, and can be observed in an infrared spectrum as an absorption band. Vibrations which do not cause an alteration in the electric dipole moment cannot be excited by the IR radiation. These are called infrared inactive, and can be studied by Raman spectroscopy.

An infrared spectrum containing absorption bands provides local, or, short-range atomic structural information about the solid under investigation. The characteristic frequencies at which absorption bands occur are related to the nature of local atomic bonding configurations. Also, the area under the absorption bands associated with each bonding arrangement can give an estimate of the concentration of that bonding configuration. Following the work of Brodsky et al. [30], for each type of bonding the concentration $N$ is written as

$$N = \frac{c n \omega_0 \mu}{2 \pi^2 e^2} \int \frac{\alpha(\omega)}{\omega} d\omega$$

where $c$ is the speed of light, $n$ the refractive index, $\omega_0$ the characteristic frequency, $\mu$ the reduced mass, and $e$ effective charge for the bonding unit in...
the matrix. The accuracy of these calculations depends partly on the value of $e^*$ which must be determined by taking the local fields into account and partly on the absorption band itself which may contain additional absorption arising from other vibrational modes or from causes like cation motion [31].

Infrared spectroscopy is equally applicable to both crystalline and amorphous solids. In crystals, as a consequence of periodicity the wavevector $k$ is a good quantum number which must be conserved. Because of this, the IR radiation interacts only with phonons that have $k=0$ (i.e. at the centre of the Brillouin zone), giving rise to sharp lines in the IR spectrum. On the contrary, for amorphous materials due to their inherent disorder, $k$ is not a good quantum number and the $k$-selection rule breaks down, which enables many more phonons other than at the zone centre to be excited. Therefore, an IR spectrum of an amorphous solid is a much broadened version of the corresponding crystalline spectrum.

In the present study, infrared transmission and reflection spectra of the amorphous GaP films deposited on polished crystalline Si substrates were measured over the wavenumber range 4000-200 cm$^{-1}$ ($\lambda=2.5$-50 $\mu$m) using a Model 580B double-beam Perkin Elmer infrared spectrophotometer. During the transmission measurements, an uncoated c-Si wafer was placed in the path of reference beam in order to eliminate the effect of the substrate. For the reflection measurements, a Perkin Elmer specular reflectance accessory was attached to the spectrophotometer. Also, a Model CD3 air dryer was used to flush dry air into the sample compartment so that both water vapour and carbon dioxide, which cause extra absorption bands and complicate the spectra, could be removed. The spectra obtained were analysed qualitatively i.e. the observed vibrational modes were assigned to the types of bonding present in the network of the films. The results will be presented and discussed in Chapter 5.
References

Chapter 4: Experimental Techniques Used for Optical and Electrical Properties

4.1 Optical measurements

4.1.1 Reflection-Transmission method

4.1.1.1 Refractive index and film thickness

4.1.1.2 High absorption coefficients

4.1.2 Photothermal deflection spectroscopy

4.1.2.1 Introduction

4.1.2.2 Principles

4.1.2.3 Theory

4.1.2.4 Experimental setup

4.1.2.5 Low absorption coefficients

4.2 Conductivity measurements
4 Experimental Techniques Used for Optical and Electrical Properties

The experimental techniques used in the present study for investigating the optical and electrical properties of the sputtered amorphous GaP films are described in this chapter. These include the conventional Reflection-Transmission (R-T) method, the most recently developed Photothermal Deflection Spectroscopy (PDS) technique, and the high- and low-temperature conductivity measurements. Most emphasis is given to PDS because this sensitive spectroscopic technique was installed for the first time in the Department of Physics and Astronomy at the University of Leicester by the author herself during the course of this study. The results obtained from all the above techniques are presented and discussed in Chapter 6.

4.1 Optical Measurements

4.1.1 Reflection-Transmission Method

The use of reflection and transmission spectra for determination of the optical constants of a thin film has long been known and is regarded as the conventional technique. In principle, the method is straightforward in a sense that the only requirement for obtaining the refractive index $n$ and the absorption coefficient $\alpha$ is to solve the well-known Fresnel equations [1]. In practice, however, due to the presence of the substrate supporting the film, these equations are so complicated that they cannot be solved analytically. A variety of numerical procedures, such as vector diagrams [2] and computer search routines [3], have been developed. Unfortunately, these usually lead to multiple solutions and necessitate an efficient criterion in order to identify the correct solution. Recently, a different approach was proposed by Cisneros et
al [4], in which the existence of multiple solutions is avoided by using the extrema of the interference fringes in the reflectance spectra. This method which will be described briefly in the next section was used for the determination of the refractive index of the GaP films studied in this work.

The reflection and transmission spectra of the films were taken at room temperature in the range 200-2500 nm with a double-beam Perkin Elmer 330 spectrophotometer. A typical example is shown in Figure 4.1 where the oscillatory behaviour corresponds to interference fringes resulting from multiple reflections from the air-film, film-substrate and substrate-air interfaces (Figure 4.2). The extrema (minima and maxima) of these fringes occur when [5]

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

(1)

where \( \ell \) is the geometrical thickness of the film, \( m=1,2,3... \) is a fringe order number and \( \lambda_m \) is the wavelength corresponding to the extremum of order \( m \). \( \delta_{af} \) and \( \delta_{fs} \) are phase angles for reflections at the air-film and film-substrate interfaces, respectively and are given by

\[ \delta_{af} = \tan^{-1} \left[ \frac{2k}{\left( n^2 - 1 - k^2 \right)} \right] \]  

(2a)

\[ \delta_{fs} = \tan^{-1} \left[ \frac{2n_3k}{\left( n^2 - n_3^2 + k^2 \right)} \right] \]  

(2b)

where \( n \) is the refractive index of the film and \( n_3 \) is that of the substrate. \( k \) is the extinction coefficient related to \( \alpha \) by \( k = \alpha \lambda / 4\pi \) where \( \lambda \) is the wavelength of the light in vacuum. As the above expressions indicate, the fringes carry information on the optical constants \( n \) and \( k \) and on the geometrical thickness \( \ell \) of the films.
Figure 4.1: Typical reflection $R$ and transmission $T$ spectra for a-GaP film.

Figure 4.2: Schematic representation of multiple reflections
4.1.1.1 Refractive index and film thickness

In order to use the method of Cisneros et. al [4] for the determination of \( n \) and \( \ell \), both the film and substrate are assumed to be weakly absorbing i.e transparent or almost transparent. In other words, \( R + T = 1 \) where \( R \) and \( T \) are the measured reflectivity and transmission, respectively. In this case, the values of the reflectivity at the extrema of the interference fringes are given by

\[
R_{\text{even}} = \left(\frac{1 - n_3}{1 + n_3}\right)^2 \\
R_{\text{odd}} = \left(\frac{n_3 - n^2}{n_3 + n^2}\right)^2
\]

where 'even' and 'odd' refer to the order of the fringes. In these equations, maxima occur for odd-integer orders when \( R_{\text{max}} > R_{\text{substrate}} \) and for even-integer orders when \( R_{\text{min}} < R_{\text{substrate}} \); note that \( R_{\text{even}} = R_{\text{substrate}} \). For Corning 7059 glass, \( n_3 = 1.53 \) and \( R_{\text{even}} = 0.044 \). \( R_{\text{max}} \) and \( R_{\text{min}} \) are both greater than this value; hence \( R_{\text{odd}} = R_{\text{max}} \) and we can write

\[
R_{\text{max}} = \left(\frac{n_3 - n^2}{n_3 + n^2}\right)^2
\]

The positive roots of this equation are

\[
n' = \left\{\frac{n_3\left[1 - R_{\text{max}}^{1/2}\right]}{1 + R_{\text{max}}^{1/2}}\right\}^{1/2} \\
n'' = \frac{n_3}{n'}
\]
It was found for the GaP films that $n'<1$ and $n''>n_3$. Since $n$ is expected to be greater than unity for the frequencies used in optical work, the first root $n'$ was rejected as a solution, thus $n=n''$.

Assuming that variations in the $n$ and hence in the optical thickness $d(=n\ell)$ from one extremum to the next in the long-wavelength region away from the absorption edge are small, we can write

$$d_{m-1} = d_m = d_{m+1} \quad (6a)$$

or

$$(m - 1)\lambda_{m-1} = m\lambda_m = (m + 1)\lambda_{m+1} \quad (6b)$$

From eq. (6b), the following alternative formulae for $m$ are obtained

$$m = \frac{\lambda_{m-1}}{\lambda_{m-1} - \lambda_m} \quad (7a)$$

$$m = \frac{\lambda_{m+1}}{\lambda_m - \lambda_{m+1}} \quad (7b)$$

$$m = \frac{\lambda_{m-1} + \lambda_{m+1}}{\lambda_{m-1} - \lambda_{m+1}} \quad (7c)$$

Using the approximate values given by eqs. (7) and the fact that the orders of the maxima and minima have definite and opposite parities, the correct integer values of $m$ can be chosen. It then becomes possible to calculate the optical thickness at the extrema

$$d_m = m\lambda_m/4 \quad (8)$$
Thus knowing the refractive index $n$ and the corresponding optical thickness $d$, the geometrical thickness $\ell$ of the films can be readily determined from $\ell = d/n$.

### 4.1.1.2 High Absorption Coefficients

If the transmitted light passing through the film-substrate system is calculated taking into account the multiple reflections shown in Figure 4.2, one obtains

$$T_{\text{meas.}} = \frac{(1 - R_1)(1 - R_2)(1 - R_3)}{1 - R_2 R_3} e^{-\alpha \ell}$$

(9)

where $R_1$, $R_2$, $R_3$ are the reflection coefficients at the air-film, film-substrate and substrate-air interfaces respectively, given by

$$R_1 = \left[\frac{(n - n_1)/(n + n_1)}\right]^2$$

$$R_2 = \left[\frac{(n - n_3)/(n + n_3)}\right]^2$$

$$R_3 = \left[\frac{(n_3 - n_1)/(n_3 + n_1)}\right]^2$$

In the short-wavelength region where the absorptance of the film is high due to the absorption edge, the multiple reflections disappear and only the reflections at the air-film interface become significant. In this case, eq. (9) can be approximated by

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

(10)
This expression was used to evaluate the absorption coefficient for values higher than $10^5 \text{cm}^{-1}$.

### 4.1.2 Photothermal Deflection Spectroscopy

#### 4.1.2.1 Introduction

In the field of amorphous semiconductors, there exists an increasing demand for determining optical absorption coefficients at photon energies below the optical gap (usually $\alpha < 10^3 \text{cm}^{-1}$) because this region contains important information on band tailing near the band edges and defect states in the pseudo-gap. However, experimental determination of low absorption coefficients in thin films is difficult. The most commonly used method is to average the interference fringes in the long-wavelength region of the $R$ and $T$ spectra and then to calculate $\alpha$ through the full but cumbersome relations such as eq. (9). According to Al-Sharbaty [6], this leads to large errors in $\alpha$ since the $R$ and $T$ spectra cannot be measured accurately enough. In order to increase the measurement sensitivity for $T$, a set of films with various thicknesses may be used. Even then, the minimum $\alpha$ that could be attained reliably is $\sim 10^2 \text{cm}^{-1}$ for a 1 $\mu$m thick film.

Other methods, for instance photoconductivity, has also been employed to deduce the nature of optical absorption below the fundamental gap. Photoconductivity is given by

$$\sigma \propto \eta \mu \tau \left(1 - e^{-\alpha \ell}\right)$$

where $\eta$ is the efficiency of generating mobile carriers, $\mu$ their mobility, $\tau$ their lifetime and $\ell$ the film thickness. Since $\tau$ is a function of both the generation
rate and $\alpha$, difficulties arise in deducing $\alpha$ from eq. (11). Furthermore, to extract $\alpha$ from such measurements requires the assumption that the product $\eta\mu \tau$ is constant whereas, in fact, it depends on photon energy. Therefore, photoconductivity measurements do not yield accurate absorption coefficient values particularly when the photon energy is low.

The limitations of all these methods led Bocca, Fournier and Badoz [7] to develop a new technique, photothermal deflection spectroscopy (PDS), for measuring small absorption coefficients. PDS whose basis will be described below, can readily measure absorptance values as low as $\alpha \ell = 10^{-5}$ and this limit can be further increased to $\alpha \ell = 10^{-7}$ if a pulsed laser is used as a light source. For thin films with a typical thickness of 1 $\mu$m, these detection limits imply that absorption coefficients as low as $10^{-1}$-$10^{-3}$ cm$^{-1}$ can be determined.

Apart from its high sensitivity, PDS has the advantage of being largely insensitive to light scattering [8]. This is in contrast to traditional reflection and transmission technique in which the scattered and absorbed light are not separable and so the measured absorption coefficient is often considerably larger than the actual coefficient. Another advantage of PDS over R-T technique is that the background absorption resulting from, for example, the substrate can easily be separated from that due to the film absorption [9]. This ability is extremely important particularly when the substrates used are quartz or pyrex.

PDS has also other useful features: contactless measurements allow the technique to be employed in hostile environments such as temperature extremes or caustic substances; 3-D depth profiling of absorption can be performed; also a new type of image which displays unique spatial and thermal information can be obtained and this can be put to use in scanned imaging and microscopy [10].
4.1.2.2 Principles

The physical principle underlying PDS is straightforward as illustrated in Figure 4.3. A solid is irradiated with an intensity-modulated beam of light (pump beam). When the light is absorbed, periodic fluctuations in the temperature of the solid and, through heat transfer, of a thin layer adjacent to the solid surface, occur. These fluctuations induce corresponding gradients in the index of refraction of the solid as well as the adjacent medium, which in turn cause periodic deflection of a second beam (probe beam) propagating through. The magnitude of this periodic deflection can then be related to the absorption coefficient of the solid under investigation.

As can be seen from the above description, one has two choices in performing PDS: collinear and transverse PDS. In the former, the gradient of the index of refraction is both created and probed within the solid whereas in the latter the probing of the gradient of the index of refraction is accomplished in the thin layer adjacent to the solid. However, since the collinear configuration is limited to samples which are transparent to the probe beam, the transverse mode is preferred by many researchers.

4.1.2.3 Theory

Although PDS is a new technique, its theoretical foundations have already been established. In this section, we summarize a unified treatment for both collinear and transverse PDS, given by Jackson et. al [11]. In this treatment, the calculation of the beam deflection is divided into two parts. First, the temperature distribution in the sample is found and then it is solved for optical beam propagation through an inhomogeneous medium.
Figure 4.3: Geometry for collinear and transverse PDS
a) Temperature distribution: Consider the geometry shown in Figure 4.3. Mediums 0 and 2 are optically nonabsorbing. Medium 1 is the absorbing media and can be either a thin film, gas, liquid or solid. For simplicity, all the media are assumed to extend infinitely in the horizontal (radial) direction. The temperature rise in each region $T_i$ above the ambient temperature satisfies the equations

$$\nabla^2 T_0 - \frac{1}{k_0} \frac{\partial T_0}{\partial t} = 0 \quad \text{medium 0} \quad (12a)$$

$$\nabla^2 T_1 - \frac{1}{k_1} \frac{\partial T_1}{\partial t} = -\frac{Q(r,t)}{K_1} \quad \text{medium 1} \quad (12b)$$

$$\nabla^2 T_2 - \frac{1}{k_2} \frac{\partial T_2}{\partial t} = 0 \quad \text{medium 2} \quad (12c)$$

subject to the following boundary conditions:

$$T_0(z=0) = T_1(z=0), \quad T_1(z=e) = T_2(z=e) \quad (13a)$$

$$K_0 \frac{\partial T_0}{\partial z} \bigg|_{z=0} = K_1 \frac{\partial T_1}{\partial z} \bigg|_{z=0}, \quad K_1 \frac{\partial T_1}{\partial z} \bigg|_{z=e} = K_2 \frac{\partial T_2}{\partial z} \bigg|_{z=e} \quad (13b)$$

where $k_i = K_i / \rho_i C_i$ is the diffusivity, $K_i$ is the thermal conductivity, $\rho_i$ is the density and $C_i$ is the specific heat. $Q(r,t)$ is the heat deposited per unit volume oscillating at the frequency $\omega$ in the absorbing medium and is given by

$$Q(r,t) = \frac{1}{2} \frac{4P\alpha}{\pi a^2} \exp(-\alpha z) \exp(-\frac{2r^2}{a^2}) \exp(\omega t) + c.c \quad (14)$$

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 in these equations that, over the interaction region between the pump and probe beams, the probe beam is focussed 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 (12) is solved by making the following substitutions. For medium 0

\[
T_{0}(r, t) = \frac{1}{2} \int_{0}^{\infty} \delta d \delta \delta \delta \quad (15)
\]

for medium 2

\[
T_{2}(r, t) = \frac{1}{2} \int_{0}^{\infty} \delta d \delta \delta \quad (16)
\]

and for medium 1

\[
T_{1}(r, t) = \frac{1}{2} \int_{0}^{\infty} \delta d \delta \delta \quad (17)
\]

where

\[
\Gamma(\delta) = \frac{P \alpha}{\pi \delta K_{1}^{2}} \left[ \frac{e^{-\delta^{2}/\delta}}{\beta_{1}^{2} - \alpha^{2}} \right]^{\gamma}
\]

Substituting into eqs. (12) and satisfying the boundary conditions, it is found that

\[
A(\delta) = -\left[ (1 - g)(b - r) \exp(-\alpha t) + (g + r)(1 + b) \exp(\beta_{1} t) \right] \Gamma(\delta) / H(\delta)
\]

\[
B(\delta) = -\left[ (1 + g)(b - r) \exp(-\alpha t) + (g + r)(1 - b) \exp(-\beta_{1} t) \right] \Gamma(\delta) / H(\delta)
\]

\[
D(\delta) = \Gamma(\delta) \exp(-\alpha t) + A(\delta) \exp(-\beta_{1} t) + B(\delta) \exp(\beta_{1} t)
\]

\[
E(\delta) = \Gamma(\delta) + A(\delta) + B(\delta)
\]

\[
H(\delta) = \left[ (1 + g)(1 + b) \exp(\beta_{1} t) - (1 - g)(1 - b) \exp(-\beta_{1} t) \right]
\]

where

\[
g = K_{0} \beta_{0} / K_{1} \beta_{1} \quad b = K_{2} \beta_{2} / K_{1} \beta_{1} \quad \delta = \alpha / \beta_{1}
\]

The final temperature distribution is obtained by combining eqs. (15)-(20).

The physical interpretation of these formulae is that the temperature can be represented by highly damped waves that decay over the thermal length.
1/K_i: These waves experience both reflection and transmission when they propagate through a boundary.

b) Optical beam propagation: The temperature rise above the ambient temperature produces a spatially varying refractive index

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

where \( (\partial n)/(\partial T) \) is typically \( 10^{-4} \) °C\(^{-1}\) for liquids and \( 10^{-5} \) °C\(^{-1}\) for solids. The propagation of the Gaussian probe beam through such an inhomogeneous medium is given by [12]

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

where \( r_0 \) is the perpendicular displacement of the beam from its original direction, \( n_0 \) is the uniform index of refraction and \( \nabla_\perp n(r, t) \) is the gradient of the index of refraction perpendicular to the beam path. Integration of eq. (22) over the path gives

\[ \Phi = \frac{1}{n_0} \frac{\partial n}{\partial T} \int_{\text{path}} \nabla_\perp T(r, t) ds \]  

where \( \Phi \) is the angular beam deflection. Eq. (23) together with eqs. (15)-(20) represent the 3-D form of \( \Phi \) and are rather complicated. Nevertheless, for the case of the film being thermally thin (i.e. the case of low-frequency modulation and/or a high thermal conducting film), which is of interest to the experimentalists, it is reduced to

\[ \Phi = \left( \frac{dn}{dT} \right) \left( \frac{P}{K \pi^2 T} \right) \left[ 1 - \exp(-\alpha L) \right] \left[ 1 - \exp\left( -\frac{a^2}{A^2} \right) \right] \]  

\[ A \]
Since in the experiments $r/a \approx 1$ (thereby $\Phi$ is maximized), the above expression is further reduced to

$$\Phi = PA[1 - \exp(-\alpha t)]$$  \hspace{1cm} (25)

where $A$ is a constant that includes the thermal properties of the film but independent of the photon energy.

### 4.1.2.4 Experimental Setup

Figure 4.4 and Plate 4.1 show the experimental setup of the transverse PDS installed. The pump and probe beam arrangements are positioned perpendicular with respect to one another. In the pump beam arrangements, the source is a 100 W quartz tungsten halogen bulb (QTH) powered by a stabilized voltage supply. The beam is modulated by a mechanical chopper, and focused by a 100 mm-focal-length mirror onto the slit of an Oriel 77250 grating monochromator. Various order-sorting filters are used to remove unwanted diffraction orders. The resultant beam is focused by two lenses onto the sample held in a suprasil cuvette containing high purity carbon tetrachloride ($\text{CCl}_4$). In the probe beam arrangement, the probe beam, provided by a 0.5 mW He-Ne laser, is brought to a focus by a 63 mm-focal-length lens at a place where the pump beam is incident on the sample. The periodic deflection of this beam is measured by a position detector which consists of a quadrant silicon photodiode and some electronic circuitry. The outputs of the position detector is connected to a Levell d.c. multimeter and an EG&G PARC 5209 lock-in amplifier which is also connected to a PM 3311 (U) Philips digital oscilloscope.
Figure 4.4: Experimental setup of the transverse PDS system
Plate 4.1: Photograph of the PDS apparatus
The operation and specifications of each component of the PDS apparatus, and the factors that affect the signal-to-noise (S/N) ratio are discussed in more detail in the following.

Typical PDS measurements range from 2.5 eV to -0.5 eV. The monochromator used covered this spectral range by means of two interchangeable ruled gratings whose resolutions were 15 nm and 30 nm in the visible and infrared regions, respectively. Higher-order diffractions were rejected using three different longwave pass filters at different parts of the spectral range; 450 nm ≤ λ₁ ≤ 800 nm, 800 nm ≤ λ₂ ≤ 1200 nm, and 1200 nm ≤ λ₃ ≤ 2300 nm. Each of these filters had a transmission higher than 95 % on average, so that the attenuation of the pump beam power was minimised.

A Bentham mechanical chopper was used to modulate the pump beam. The choice of the modulation frequency was made taking into account the S/N ratio. High frequencies enhance the signal stability because of the elimination of the effects of noise originating from the detector, mechanical vibrations etc. On the other hand, lower frequencies increase the signal magnitude. Hence, the optimum frequency which gives the best S/N ratio, represents a compromise between these two frequencies. In our case, 7.2 Hz was found to be the optimum frequency, and this was used throughout the work.

The focussing of the monochromatised and chopped pump beam on the sample was accomplished by two Crown glass lenses. While the first lens, a 125 mm-focal-length-plano-convex, collimated the beam, the second one, an aspheric lens with a focal length of 24 mm, focussed it tightly on the sample. The tight focussing of the pump beam is an important factor that influences the S/N ratio since this ratio is proportional to the intensity (power unit per area) of the pump beam. In the present setup, the image size obtained was 1 mm X 3 mm.
The sample holder assembly used in the experiments is illustrated in Figure 4.5. The samples were ~1 μm thick GaP films deposited on fused silica substrates which were 7-9 mm wide and 25 mm long. Each of them was carefully inserted into the gap formed between the back wall of a Hellma quartz cuvette and the angled edge of an aluminium block placed at the bottom of the cuvette. The cuvette was filled with 99.95 % pure carbon tetrachloride (CCl₄), and covered by several layers of PVC cling film. It was then clamped into the brass holder mounted on an Ealing miniature stage which provided fine lateral and vertical movements. Finally, it was checked that the focussed pump beam was falling onto the middle of the sample.

As a deflection medium, CCl₄ was used. This liquid has no absorption in the energy range of interest (2.5-0.5 eV), and has a large temperature coefficient of the refractive index $\partial n/\partial T$. In addition, it does not alter the properties of the films [9]. These considerations make CCl₄ the preferred deflecting medium. However, special care has to be taken in handling this chemical since it is highly volatile and upon inhalation, it can cause a serious health hazard to heart and lungs. For this reason, the transfer of CCl₄ from its bottle to the cuvette was accomplished in a fume cabinet and the cuvette was sealed very well with the cling film. The latter also helped to keep the cuvette and CCl₄ dust-free and to reduce convection currents.

The geometry of the probe beam arrangement is shown in Figure 4.6 in more detail. The probe beam was a He-Ne laser beam ($\lambda=632.8$ nm) which has a gaussian intensity distribution with a $1/e^2$ diameter, $2R_0$, of 0.48 mm and a divergence angle, $\theta$, of 1.7 mrad. It was brought to a focus at the sample by a laser lens ($f=63$ mm) placed 50 mm ($D_1$) away from the laser source. The focussed spot size, which was calculated from the following expressions [13]

$$R = \frac{4\lambda f}{\pi R_{in}} \quad , \quad R_{in}^2 = (2R_0)^2 + \theta^2 D_1^2$$
Figure 4.5: The sample holder assembly used in PDS experiments. The inset shows the side view of the cuvette and mounted sample.
was 55 μm. The smallness of the spot size allowed the probe beam to be brought as close as 37 μm to the sample surface (i.e. the beam offset $z_0$ was 37 μm). This beam offset was achieved by following the geometrical optic analysis of Frosio et al [14] on a setup similar to ours. They found that the value of $z_0$ depends on the radius $R_0$ of the gaussian probe beam, on the distances $D_1$ and $D_2$, on the focal length $f$ of the lens and on the sample width $s$, and is given by

$$z_0 = f R_0 \left[ \frac{s \lambda}{2 \pi R_0 f^2} \right]^2 \left[ \left( D_1 - f \right)^2 + \left( \frac{\pi R_0 s}{\lambda} \right)^2 \right] + \frac{\lambda^2}{\left[ \lambda^2 \left( D_1 - f \right)^2 + \left( \pi R_0 s \right)^2 \right]}$$

where $D_2 = f$. This equation is represented in Figure 4.7. It can be seen that the minimum offset $z_{0\text{min}} = (\lambda s / \pi)^{1/2}$ and this value can only be attained under the condition that the focal length $f > f_c = R_0 (s / 2 \lambda)^{1/2}$. If $f < f_c$, this minimum value is obtained twice, and if $f > f_c$ then $z_0 > z_{0\text{min}}$ always. For the present setup, $f > f_c$ was used to facilitate manipulations with the sample holder assembly, and the parameters of $D_1$ and $s$ were chosen such that $z_0$ approaches $z_{0\text{min}}$. The choice of the distance between the sample and detector ($D_3 = 30$ cm) was made by considering the dual requirements of a large beam deflection (large S/N) and a small spot size.

As a detector a quadrant silicon photodiode operating with a home-built electronic circuit [15] was used. The photodiode originally had four quadrants which covered a total area of 7 mm². Of these, the two left and also the two right quadrants were electronically joined so that the resultant two quadrants could follow only the lateral movements of the probe beam. Under illumination, the voltages $V_1$ and $V_2$ developed across the resultant quadrants were processed by the electronic circuitry to give an output

$$V_0 = \frac{10 (V_1 - V_2)}{(V_1 + V_2)}$$
Figure 4.6: Geometry for the probe beam arrangement

Figure 4.7: The probe beam offset $z_0$ as a function of distance $D_1$ with the focal length $f$ as parameter.
which, for small deflections was proportional to the probe beam deflection. This output was then fed into a zero-centre d.c. voltmeter and lock-in amplifier. While the former ensured that the mean location of the periodically deflected probe beam spot at the photodiode was centralized between the two resultant quadrants, the latter measured the signal oscillating at the modulation frequency of the pump beam. An oscilloscope which was connected to the lock-in amplifier monitored both the detector and reference signals.

The sources of the background noise in the present setup can be listed as follows:

1. Stray light, which originated directly from the pump beam itself or from reflections of the pump and probe beam from the optical components, cuvette and sample, was found to be impinging on the photodiode and affecting the signal. This light was filtered out by an Oriel He-Ne laser line filter attached to the front of the photodiode.

2. Dust particles and impurities suspended in the CCl$_4$ caused instabilities to the lock-in amplifier because the probe beam, having a diameter of the order of tens of $\mu$m, was completely stopped by a dust particle of the same size. In order to eliminate such particles, high purity CCl$_4$ was used, the samples and cuvette were flushed with CCl$_4$ before assembly, and the cuvette was sealed very securely.

3. Air currents caused by the mechanical chopper were found to deflect the laser beam. Therefore, all the optical paths were enclosed using black pipes and cloths.

4. Mechanical vibrations were another source of noise. In order to suppress them, the height of the components were kept low, the components were screwed onto an optical bench placed on a heavy metal block, and the setup was established in an essentially vibration-free room in the basement of the building.
(5) The pointing stability of the probe laser was found to decrease if the reflections of the laser beam from the cuvette or the He-Ne laser line filter or the detector were let back through the aperture of the laser source. A piece of cardboard was used to stop these reflections.

4.1.2.5 Low Absorption Coefficients

Once the PDS setup was established and aligned, taking measurements was a straightforward routine. However, before measuring each sample, the following preparatory steps had to be carried out.

First, the cuvette and aluminium block were ultrasonically cleaned with acetone and methanol. The sample was rinsed with some CCl₄ and then mounted in the cuvette as described in the preceding section. Before clamping the cuvette into the sample holder assembly, it was checked that the probe beam intersected the pump beam spot. If it did not, the height of the lens between the laser source and sample was adjusted until it did so. After that, the cuvette was placed in the probe beam, and the probe beam offset z₀ was minimized by moving the sample holder assembly laterally so that the beam spot at the detector was just neither distorted nor eclipsed by the sample. Finally, the optical paths were enclosed using black pipes and clothes, and the CCl₄ and electronics were left to settle down for about two hours.

The measurements were always started at the low-wavelength end where the signal was large. At each pump beam wavelength, the mean position of the deflected probe beam was centralized between the two quadrants of the detector. This was accomplished by moving the detector laterally until the reading of the d.c. voltmeter was zero. The lock-in amplifier was initially used in automatic mode for finding the signal which had the same phase with that of the reference signal, and was then controlled
Figure 4.8: Experimental setup for measurements of the pump beam power
Plate 4.2: A photograph showing the components used for measurements of the pump beam power
manually to allow for changes to better settings and to increase the sensitivity as the signal strength decreased. Throughout the measurements, two gratings and three filter changes were carried out, and the signal typically varied from 100 mV to 10 µV.

According to eq. (25), the signal is dependent on the pump beam power and must be normalized to it if α is to be calculated. This requires the determination of the relative pump beam power at each wavelength at which the PDS measurements were made. In our case, this was accomplished using silicon BPX 65 and PbS detectors for the ranges 450-1000 nm and 1000-2500 nm, respectively. The pump beam was directed on the detectors by means of a concave mirror and an objective lens system. This part of the setup, mounted in the place of the probe beam arrangement, is shown in Figure 4.8 and Plate 4.2. When the BPX 65 was in use, the unmodulated pump beam induced a small photocurrent which was first amplified by a Keithley 427 Current amplifier and then measured by a Leevell multimeter (Figure 4.8(a)). However, when the PbS detector was in use, the photocurrent produced by the modulated pump beam (frequency was 600 Hz) and 50 volt bias voltage was measured through a 1 MΩ load resistor and a lock-in amplifier (Figure 4.8(b)). In both cases, the currents found were converted to incident photon energy using calibration curves of the detector response, as a function of incident wavelength.

An example of power normalized signal, $(\Phi/P)$, plotted against photon energy is given in Figure 4.9. As can be seen, the normalized signal displays interference fringes which, considering the fact that the PDS signal is directly proportional to the absorptance $[A=1-(R+T)]$ of the film, are attributed to multiple reflections of the pump beam within the film [8]. As the photon energy is increased, these fringes becomes weaker, and at energies higher than 1.5 eV where the film is completely absorbing $(A=1-R)$, the normalized signal saturates. The saturation value obtained from the figure determines the
Figure 4.9: Power normalized signal versus photon energy for a-Ga$_{1-x}$P$_x$ ($x=0.98$) film

Figure 4.10: Absorption coefficient spectra deduced from: xxx R-T method, PDS, the deduced absorption spectrum
constant C in eq. (25). Then, it becomes possible to calculate the absorption coefficient \( \alpha \). Figure 10 shows an absorption coefficient spectrum deduced in this way.

The absorption coefficient values determined from the PDS are relative and hence need to be calibrated. For the calibration, the PDS spectrum was first smoothed by averaging the interference fringes on a logarithmic scale and then matched to the corresponding absorption spectrum deduced from R and T measurements in the \( 10^3-10^4 \) cm\(^{-1} \) range. The combination of these two spectra gave the final \( \alpha \) spectrum extending over 3-4 orders of magnitude.

### 4.2 Conductivity Measurements

Electrical conductivity measurements at different temperatures play an important part in research on semiconductors since it is from these quantities that the type, concentration and mobility of the charge carriers are found [16]. In the present study, such measurements for the a-GaP films were carried out using 2-probe technique. Before making the measurements, gold or aluminium electrodes, 12 mm long and 4 mm apart, were evaporated on the film surface in a co-planar configuration in an Edwards 12E6/1514 evaporation system. The films were clamped onto a copper holder in a cryostat (shown in Figure 4.11), and leads were made to the electrodes with fine gold wire attached by a silver-loaded electrically conducting paste. One junction of a copper-constantan thermocouple was silver pasted onto the surface of the substrate as close as possible to the film and the other junction was immersed in an ice/water mixture. The cryostat was fitted into a Delta Design Environmental Temperature Control Cabinet which was capable of altering the temperature from 150 to 520 K within \( \pm 0.5 \) K accuracy using a flow of circulating liquid nitrogen vapour from a pressurized liquid-nitrogen
Figure 4.11: Schematic diagram of the cryostat used in conductivity experiments
dewar and an internal heater, respectively. The cryostat was then evacuated to below $10^{-6}$ Torr by an Edwards E02 oil diffusion pump (with liquid-N$_2$ trap) backed by an Edwards E2M5 rotary pump and flushed with helium gas several times, finally, before being filled with an overpressure (~2-3 psi) of helium.

During the measurements, a constant voltage of 40 volts from a Coutant stabilized power supply was applied to the film, and the current induced was read by a Keithley 616 electrometer. The temperature of the film was monitored by a digital millivoltmeter connected to the thermocouple. The measurements were always started when the film was cold. As the temperature of the film was gradually increased to room temperature and above that, at each step the temperature was stabilized before recording the current readings. The conductivity was then calculated from $\sigma = \frac{dl}{LV}$ where $d$ is the separation between the electrodes, $L$ is the length of the electrodes, $V$ is the voltage, $I$ is the current and $\ell$ is the film thickness.
References

[15] For designing and building the electronic circuitry required for the position detector, Dr. T. Harris and Mr. M.A. Harrison from the electronic workshop of the Department of Physics and Astronomy are acknowledged.
Chapter 5: Results: Structural Properties of a-GaP(T₃) films

5.1 Macrostructure
5.2 Microstructure
5.3 Atomic structure
   5.3.1 EXAFS spectroscopy
   5.3.2 IR spectroscopy
5 Results: Structural Properties of a-GaP(T$_g$) films

This chapter presents the structural characteristics of a-GaP(T$_g$) films as obtained from TEM and SEM-EDAX experiments and from EXAFS and IR spectroscopies. While on the macroscopic scale all the films are homogeneous, continuous and smooth, on the microscopic scale, TEM gives evidence for the presence of structural inhomogeneities, namely voids, and SEM-EDAX reveals the extent of the compositional inhomogeneities. On the atomic scale, EXAFS provides direct information such as coordination numbers, bond lengths and variations in the bond lengths, and indirect information about bond angles and their variation. The evidence points towards a chemically ordered network for a-GaP, a result confirmed by IR spectroscopy which probes the nature of local atomic bonding configurations.

5.1 Macrostructure

A typical bright-field transmission electron microscope image taken at low magnification (M=5000) is shown in Plate 5.1. It can be seen that the films are macroscopically homogeneous, continuous and very smooth.

5.2 Microstructure

Plate 5.2 presents bright-field transmission electron microscope images taken at high magnification (M=33000) and the corresponding diffraction patterns for a-GaP films produced at several different deposition temperatures T$_g$. The diffraction patterns all have the same appearance, exhibiting a few diffuse rings which confirms that the films are amorphous.
Plate 5.1: Typical bright-field electron micrograph taken at low magnification
The bright-field electron micrographs in real-space, however, reveal changes with the deposition temperature, indicating an alteration in the microstructure of the films. The contrast (dark and light regions) which appears in some electron micrographs normally implies the existence of local density fluctuations in the network of the films [1]. Such fluctuations may arise for two reasons: (1) small crystals oriented in different directions or (2) voids may be embedded in the network. For our case, the former was ruled out because of the amorphous diffraction patterns obtained, and so we consider the observed contrast provides evidence for the presence of voids in the a-GaP (T$_g$) films. The dark and light regions were assigned to the film and voids, respectively. The sizes of the dark regions were measured for the a-GaP film prepared at 200 °C and found to be between 280 and 580 Å. As is seen from the Plate 5.2, these regions become smaller as the deposition temperature is lowered.

The electron micrograph of the film prepared at the lowest deposition temperature (i.e. 20 °C) reveals no features associated with voids, instead it is very smooth and continuous. This could mean either the network is void-free or the voids are too small to be detected by the TEM used, which has a resolution of the order of 100 Å. The latter was shown to be the case by the small-angle X-ray scattering (SAXS) experiments carried out on this sample [2]. The SAXS experiments also determined the void sizes to be 60 Å in diameter on average. Considering also the electron micrographs of the other two samples produced at higher deposition temperatures, we may infer that the voids are small in dimensions when T$_g$ is low. As T$_g$ is increased, while some voids are eliminated, the others merge into larger ones which can then be readily detected by TEM. The same conclusion was also drawn by Shevchik [3] for sputtered and electro-deposited a-Ge from changes in SAXS during their annealing.
Plate 5.2: Diffraction patterns and high-magnification bright-field electron micrographs of a-GaP($T_s$) films: $T_s=20 \, ^\circ\text{C}$ (at the top), $T_s=150 \, ^\circ\text{C}$ (in the middle) and $T_s=200 \, ^\circ\text{C}$ (at the bottom)
As was mentioned in Chapter 2, the amorphous GaP films investigated in this study were sputtered from a stoichiometric polycrystalline GaP target. Following the general consensus of the sputtering technique, which produces films with compositions the same as that of the target, we expect the compositions of the deposited a-GaP films to be stoichiometric to within a few percent. This was checked by energy-dispersive X-ray analysis (EDAX) using a SEM and also by EXAFS spectroscopy as described in sections 3.1.2 and 3.2.5, respectively. Both methods were consistent with one another. EDAX also revealed that 1-2 % Ar was incorporated into the films during their deposition. These Ar atoms are not bonded to neither Ga nor P atoms (as indicated by IR spectroscopy) but are trapped in the network, presumably in the voids.

Apart from the microscopic structural inhomogeneities discussed above, for the case of compound materials segregation of the constituent elements into different parts of the network, i.e. phase separation, may also occur. The presence of such compositional inhomogeneities in the a-GaP films were searched for using EDAX. For this purpose, line profiles and digitized maps representing the distribution of the both Ga and P along a line or across an area on the sample surface, respectively, were constructed as explained in section 3.1.2. Figure 5.1 presents two examples of the line profiles obtained, where x=100 is approximately 1 mm. For most films, as seen in Figure 5.1 (a), both the Ga and P contents are found to be relatively independent of position, which indicate compositionally homogeneous networks. For some films, however, while the Ga content is quite uniform, the P content shows somewhat larger fluctuations (see Figure 5.1 (b)). Plate 5.3 presents the corresponding digitized maps in which the sequence of black, red, yellow and blue colours illustrate the progressive increase in the elemental concentration. Plate 5.3 (a) is an example of a compositionally homogeneous sample whereas Plate 5.3 (b) is of the one which shows variations in the P content. These
Figure 5.1(a): Line profiles of (a) P, (b) Ga for a-GaP(T_s=20 °C)
Figure 5.1(b): Line profiles of (a) P, (b) Ga for a-GaP($T_s=200$ °C)
variations do not indicate the existence of phase separation in these films since they are not compatible with the variations in the Ga content. Instead they may be a consequence of plasma instabilities occurring during the deposition process.

The absence of phase separation in the a-GaP film deposited at 20°C was also confirmed by SAXS experiments performed on this particular sample. The I(q) versus q plot which was obtained from the data analysis revealed no additional peaks at high q values, which would otherwise be taken as evidence for phase separation [4].
Plate 5.3(a): Digitized maps of (a) P, (b) Ga for a-GaP(T_S=20 °C)
Plate 5.3(b): Digitized maps of (a) P, (b) Ga for a-GaP(T_s=200 °C)
5.3 Atomic Structure

5.3.1 EXAFS Spectroscopy

Figures 5.2 and 5.3 give examples of X-ray absorption spectra for the Ga and P K-edges of the a-GaP films, taken at the 7.1 and 3.4 stations of the SERC Daresbury Laboratory respectively. It is clearly seen that the background absorption $\mu_0$, which has contributions not only from absorption by other elements and from other edges of the same element but also from the experimental set-up itself (i.e. detectors, harmonic contamination in the beam etc.), influences the overall appearance of the absorption spectra. Figure 5.4 (a) and (b) and 5.5 (a) and (b) show EXAFS functions, $\chi(k)$ (extracted from the absorption spectra and then weighted by $k^3$) and the radial distribution functions (RDFs) (calculated by Fourier transformation of the EXAFS function at both Ga and P K-edges) for two amorphous samples deposited at different values of $T_s$. Data for a crystalline GaP sample, which was used as a standard throughout the work, are shown in Figure 5.4 (c) and Figure 5.5 (c). From a comparison of these figures, it can be noted that none of the fine structure of the EXAFS function for the crystalline sample is present in the EXAFS function for the amorphous samples. Similarly, while the Fourier transforms of the EXAFS from the crystal show strong features up to the third shell, only the first-shell peak is strong in the amorphous case. These results are expected in the absence of periodicity and hence confirm the amorphous nature of the films.

The EXAFS spectra obtained, which generally had a usable $k$ range from 3 to 13.5 Å$^{-1}$ for both Ga and P edges, have been analysed by the least-squares curve-fitting procedure as described in section 3.2.4. During the analysis, the factor A, correcting for amplitude reductions due to events that result in absorption but not EXAFS and the so-called VPI parameter
Figure 5.2: Typical Ga K edge X-ray absorption spectrum of a-GaP.

Figure 5.3: Typical P K edge X-ray absorption spectrum of a-GaP.
Figure 5.4(a): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform $FT$ for a-GaP($T_s=20 \, ^\circ C$) at the Ga K edge
Figure 5.4(b): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform $FT$ for a-GaP($T_s=200$ °C) at the Ga K edge.
Figure 5.4(c): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform $\text{FT}$ for c-GaP at the Ga K edge.
Figure 5.5(a): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for a-GaP($T_s$=20 °C) at the P K edge
Figure 5.5(b): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform $FT$ for $a$-GaP ($T_s=200 \, ^\circ C$) at the P K edge.
Figure 5.5(c): The $k^3$-weighted EXAFS function $\chi$ and Fourier transform FT for c-GaP at the P K edge.
representing the photoelectron lifetime, were fixed at 0.75 and -5 for the Ga and 0.65 and -3.5 for the P K-edges, respectively. These values were obtained from the analysis of c-GaP. The parameter $E_0$ which adjusts for the position of the absorption edge was allowed to float freely. The scattering phaseshifts of each atom type in the fitting process were calculated within the EXCURV90 program. The fitting process always included not only Ga-P bonds but also P-P and Ga-Ga bonds at the beginning. However, in every case, at the end of the analysis, the existence of P-P and Ga-Ga bonds were rejected by the fitting procedure, which provides evidence that wrong bonds are not found in the structure of the samples on a significant scale. Other structural information, namely the coordination numbers, the length of the Ga-P bond and the spread of the bond lengths (i.e. the Debye-Waller factor) have also been determined, and are shown in Figures 5.6, 5.7 and 5.8, respectively. Figure 5.6 confirms that a-GaP is four-fold coordinated; in other words, it consists of tetrahedral units. This structure is maintained at higher deposition and annealing temperatures. The Ga-P bond length is also independent of the $T_d$ and $T_a$ temperatures as can be seen from Figure 5.7. The values we found for the Ga-P bond lengths lie around 2.33 and 2.31 Å in the case of a-GaP, and 2.33 and 2.325 Å in the case of c-GaP, the two values corresponding to data taken at the Ga and P edges, respectively. Our crystalline bond length is about 0.03 Å less than the value extracted from diffraction experiments [5]; we believe that this arises from a slight difference in the phaseshift used. However, because the same phaseshift is used for all amorphous samples as well as the crystal, this discrepancy does not affect any of the conclusions made here. In any case there is a 0.02 Å difference in the nearest-neighbour distance determined using the two edges, which is probably within the experimental errors. However, comparison of the amorphous bond length with that of the crystal using the two edges is important since it provides information concerning the existence or otherwise of chemical order on a
Figure 5.6: Coordination numbers determined at the Ga and P K edges versus $T_s$ and $T_a$. The points marked with c and an arrow are for c-GaP.
Figure 5.7: Lengths of the Ga-P bond determined at the Ga and P K edges versus T_s and T_a. The points marked with c and an arrow are for c-GaP.
smaller scale than deduced from the fitting process. If a-GaP is chemically disordered, we should detect P-P bonds (2.2 Å) at the P edge and Ga-Ga bonds (2.44 Å) at the Ga edge, in addition to bonds between Ga and P atoms. Therefore, we would expect to see an increase in the measured Ga-P bond length at the Ga edge and a decrease in the measured P-Ga bond length at the P edge compared to the bond lengths in the crystal, since EXAFS gives an average value for bond lengths. However, we could see only a 0.015 Å difference between the crystalline and amorphous bond lengths at the P edge, which is well below the experimental error of 0.03 Å, and no difference at all at the Ga edge. Thus, we conclude from the bond length data that a-GaP is chemically ordered.

The question of chemical order or disorder can also be discussed using the bond-conservation criterion

$$c_i N_{ij} = c_j N_{ji}$$

where $c_{ij}$ are the compositions of the type of atoms $i,j$ forming a bond and $N_{ij}$ is the number of $j$ atoms bonded to an $i$ atom. The criterion expresses the fact that the number of bonds in a sample is the same whether one enumerates them from the point of view of the $i$ or $j$ atom. This criterion has been applied to a-GaP by using the coordination numbers shown in Figure 5.6 and the composition values obtained from EDAX. It was found that the above equation is satisfied within the experimental error. Therefore, again we conclude that a-GaP is chemically ordered. Further evidence supporting this conclusion will be given in the next section.

The disorder in the network of the a-GaP films has been changed gradually from the amorphous to the crystalline state by increasing the deposition and annealing temperature. Changes can be seen in the Debye-Waller factors of the first and second shell given in Figures 5.8 and 5.9 for
Figure 5.8: Debye-Waller factors of the first shell as a function of $T_s$ and $T_a$ for the Ga and P K edges. The points marked with c and an arrow are for c-GaP.
data obtained from both edges. As can be seen from Figure 5.8, the values determined for the Debye-Waller factors, $\sigma_i^2$, of the first shell at the Ga and P edges are consistent with one another. This is expected since they both show the spread of the same bond length, namely the Ga-P bond, and thus we have a consistency check on the fitted values. The values of $\sigma_i^2$ decrease with increasing deposition and annealing temperature and approach the crystalline values, indicating a reduction in the configurational (static) disorder of the bond length. Figure 5.9 also shows that the variations of the next-nearest-neighbour distances at both edges, i.e. the Ga-Ga distance on the Ga edge and P-P distance on the P edge, are different. The effect of this result on the structure is important and will be discussed in terms of bond angles later.

For amorphous materials, the Debye-Waller factor determined experimentally has contributions from both thermal and static disorder:

$$\sigma^2(\text{exp.}) = \sigma^2_{\text{thermal}} + \sigma^2_{\text{static}}.$$  

Assuming that there is no static disorder in the crystalline state, the above equation becomes $\sigma^2_{\text{thermal}} = \sigma^2_{\text{cry.}}(\text{exp.})$. Then the static disorder of the amorphous materials can be easily determined. Using the values of the Debye-Waller factor of the first shell, both $\sigma^2_{\text{thermal}}$ and $\sigma^2_{\text{static}}$ of a-GaP were found to be about 0.003 Å². This much static disorder causes a 0.007 Å change in the bond length of 2.33 Å. This means that the length of the Ga-P bond in the amorphous state is hardly different from the length of the same bond in the crystal, a feature which is true for many amorphous materials. The fact that we still have an amorphous structure suggests a wide spread in bond angles. In the present work, we have attempted to find the mean value of the bond angle as well as its spread. Figures 5.10 (a) and (b) show three tetrahedra units joined to each other in 3D and a small part of its top view in
Figure 5.9: Debye-Waller factors of the second shell as a function of $T_s$ and $T_a$ for the Ga and P K edges. The points marked with c and an arrow are for c-GaP.
2D, respectively. By using the nearest-neighbour distance (2.33 Å) and the next-nearest-neighbour distances (3.8 Å for both Ga-Ga and P-P distances), the mean value of the bond angle $\beta$ has been determined as 109.3°, which is the bond angle in the crystalline state. When the spread in the bond angle was being calculated from the Debye-Waller factor of the second shell, $\sigma_2^2$, however, it was found necessary to introduce two different spreads, $\Delta \beta_1$ and $\Delta \beta_2$, around the same mean value, $\beta$, due to the differences in the values of the Debye-Waller factors of the second shell at the Ga and P edges. In the calculation of $\Delta \beta_1$ and $\Delta \beta_2$, the contribution of thermal disorder of the second shell ($\sigma_{\text{thermal}}^2 = 0.011 \text{ Å}^2$) has been subtracted from the experimental Debye-Waller factor as has been done for the first shell, and thus the static bond-angle spreads were obtained. The values of the static bond-angle spreads shown in Table 5.1 should be compared to the thermal bond-angle spread which is 1.2° for all samples. It was found that the angle $\beta_2 = \beta \pm \Delta \beta_2$ varies more than the angle $\beta_1 = \beta \pm \Delta \beta_1$, and both angle spreads decrease with increasing deposition and annealing temperature. This result shows that the bond angle at Ga is more rigid than that at P.

Table 5.1: The static bond-angle spreads, $\Delta \beta_1$ at the Ga edge and $\Delta \beta_2$ at the P edge, in samples with different deposition (T$_d$) and annealing (T$_a$) temperatures. The temperature T refers to either T$_d$ or T$_a$. ($\beta_1 = \beta \pm \Delta \beta_1$, $\beta_2 = \beta \pm \Delta \beta_2$).

<table>
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<th>T(°C)</th>
<th>20</th>
<th>100</th>
<th>150</th>
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<th>200</th>
<th>270</th>
<th>400</th>
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<td>4.8</td>
<td>3.7</td>
<td>2.6</td>
<td>1.5</td>
<td>0.4</td>
<td>0.3</td>
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<tr>
<td>$\Delta \beta_2$</td>
<td>17.3</td>
<td>17.0</td>
<td>16.3</td>
<td>15.7</td>
<td>14.6</td>
<td>—</td>
<td>—</td>
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</table>
Figure 5.10: (a) Three GaP tetrahedra units in 3D, (b) Top view of a small part of (a) in 2D together with radii of the first and second shell associated with the Ga and P K edges
5.3.2 Infrared Spectroscopy

Figures 5.11 and 5.12 present the infrared transmission and reflection spectra for some of the amorphous GaP samples prepared at different deposition temperatures \( T_d \) and also of the samples annealed at temperatures \( T_a \), respectively. The spectrum of c-GaP is also included in the figures for the purpose of comparison. The observed bands in c-GaP have been assigned to various vibrational modes using published assignments \([6]\), and given in Table 5.2. In the case of the amorphous samples, most of these modes have been smeared out either partially or completely, leaving only a few features in the entire wavenumber range of 4000-200 cm\(^{-1}\).

For the sample deposited at 20 °C, the main feature observed in its transmission spectrum is the absorption band at 345 cm\(^{-1}\). This has been attributed to the stretching (TO mode) of the Ga-P bond \([7,8]\). This mode appears as a broad ill-defined peak in the reflection spectrum. As \( T_d \) or \( T_a \) are raised, the peak progressively becomes sharper and increases in intensity, and its equivalent in the transmission spectrum also becomes sharper and shifts to 370 cm\(^{-1}\), approaching the fundamental stretching frequency of 375 cm\(^{-1}\) for c-GaP. The sharpening of the TO mode indicates a reduction in the static disorder, mainly the bond-angle disorder, in the amorphous network. This result is consistent with the EXAFS work. The shift of the TO mode from 345 to 370 cm\(^{-1}\) can be associated with an increase in bond strength. Using the simple harmonic oscillator approach, the force constant \( k \), which is a measure of bond strength, was calculated for the wavenumbers before and after the shift. It was found that \( k \) increased by 15\%, meaning that the Ga-P bonds becomes stronger with increasing order in the network. As is known, c-GaP has the zincblende structure in which the s and p orbitals hybridize as sp\(^3\) in order to maximize the bond energy and to make the bond as strong as possible. In the case of a-GaP, the sp\(^3\) hybridization is somewhat different.
Figure 5.11: Infrared transmission spectra of (a) a-GaP(T_s=20°C), (b) a-GaP(T_s=200 °C), (c) a-GaP(T_a=400 °C), (d) c-GaP
Figure 5.12: Infrared reflection spectra of (a) a-GaP($T_s=20^\circ$C), (b) a-GaP($T_s=200^\circ$C), (c) a-GaP($T_a=400^\circ$C), (d) c-GaP.
from that of c-GaP, resulting in weaker bonds. This is presumably due to variations in the bond angle.

The other feature observed in the transmission spectrum of the room-temperature deposited sample is the small, broad absorption band located at about ~590 cm$^{-1}$. It, too, becomes sharper, and an additional small feature appears at ~500 cm$^{-1}$, as $T_9$ or $T_3$ are increased. From the comparison of these two features with those seen in the spectrum of c-GaP, we attribute them to combination modes of the Ga-P bond.

The possible existence of wrong bonds, i.e. P-P and Ga-Ga bonds, has been investigated in the spectra obtained for the amorphous samples. Wrong bonds are not expected to occur in the crystalline state and even if they did they would be infrared inactive. However, the selection rules are relaxed in the amorphous state owing to the lack of periodicity and wrong bonds, if present, should be seen in the IR spectrum. If we had P-P bonds in our samples, we would have expected to see structure at ~270, ~360 and ~450 cm$^{-1}$, or, at least, at one of these wavenumbers [9]. None of these features was seen and hence we conclude that a-GaP contains no P-P (or at least a concentration less than 10% of the total number of bonds, which is the detectable limit of the IR spectroscopy), i.e. it is chemically ordered.

Table 5.2: Identification of the vibrational modes observed in the transmission spectrum of c-GaP. The errors in the quoted wavenumbers are a few cm$^{-1}$.

<table>
<thead>
<tr>
<th>$v$(cm$^{-1}$)</th>
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<td>LO+TA$_2$</td>
</tr>
<tr>
<td>442</td>
<td>TO+TA$_2$</td>
</tr>
<tr>
<td>475</td>
<td>LO+TA$_1$</td>
</tr>
<tr>
<td>492</td>
<td>TO+TA$_1$</td>
</tr>
<tr>
<td>Frequency</td>
<td>Phonon Process</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------</td>
</tr>
<tr>
<td>555</td>
<td>LO+LA</td>
</tr>
<tr>
<td>572</td>
<td>TO+TA</td>
</tr>
<tr>
<td>720</td>
<td>LO+LO</td>
</tr>
<tr>
<td>735</td>
<td>LO+TO</td>
</tr>
<tr>
<td>750</td>
<td>TO+TO</td>
</tr>
<tr>
<td>784</td>
<td>3-phonon process</td>
</tr>
</tbody>
</table>
References


[2] The SAXS experiments were carried out on station 8.2 at the Daresbury Laboratory using X-rays with a wavelength of 1.5 Å. The measurements were performed using a camera length of 1.5 m, which gave a scattering vector range of 0<q<0.5 Å, and the data collected with the aid of a quadrant detector. More technical details about the station 8.2 can be found in: H.C. Gerritsen and C. Robertus (1990), Applications of Synchrotron Radiation, R. Catlow and N. Greaves (eds), (Blackie, Glasgow). For the SAXS experiments on the a-GaP (T_e=20 °C) film, Dr. S.J. Gurman and Mr. B.T. Williams are acknowledged.


Chapter 6: Results: Optical and Electrical Properties of a-GaP(T$_4$) films

6.1 Optical properties
6.2 Electrical properties
6.3 Discussion
6.4 Density of states
6 Results: Optical and Electrical Properties of a-GaP(T$_s$) films

In this chapter, the electronic properties of the a-GaP films, deduced from optical spectroscopy techniques, namely Reflection-Transmission (R-T) and Photothermal Deflection Spectroscopy (PDS), and from conductivity measurements, are presented as a function of deposition and annealing temperature. In order to explain these properties, a model for the nature and distribution of the energy states (DOS) in the forbidden band gap, which is based on theoretical studies, is proposed. Information on the DOS in the conduction band is also extracted from the XANES data. This is then combined with the XPS, UPS and K$_\alpha$ X-ray emission data taken from the literature, which provide the DOS in the valence band, so that a complete picture of the electronic DOS of the films can be obtained.

6.1 Optical Properties

The dispersion of the refractive index $n$ for a-GaP films deposited at different temperatures is presented in Figure 6.1. The refractive index of c-GaP taken from [1] and [2] is also included for comparison. It is seen that $n$ increases with photon energy as the fundamental absorption edge is approached, and the values for the amorphous films at a given photon energy decrease towards the crystalline value as $T_s$ is increased.

Figure 6.2 shows the optical absorption coefficient $\alpha$ deduced from both R-T and PDS measurements as a function of photon energy for five amorphous films deposited at different temperatures and a crystalline wafer. The data reported in [3] for bulk c-GaP has also been added to the figure (broken curve) to display the direct and indirect optical gaps, which occur at 2.78 eV and 2.26 eV, respectively. The tailing of the absorption below 1 cm$^{-1}$
Figure 6.1: Dispersion of the refractive index for a-GaP($T_s$) films. Data for c-GaP are from [1] and [2].
Figure 6.2: Absorption coefficient spectra deduced from R-T and PDS measurements for a-GaP(T$_S$) films and a c-GaP wafer. The broken line refers to the data for bulk c-GaP reported in [3]
indicates a wide energy range for defects or impurity states in the optical gap of the crystal. With regard to the absorption edges of the amorphous films, the striking feature is that they are all shifted by a large amount (~1.6 eV) towards lower photon energies compared with that of the crystal. This shift is, in fact, the largest found amongst the amorphous group-IV and III-V semiconductors and is the principal reason why, in previous studies [4,5], the existence of wrong bonds has been invoked. Also, the edge itself is very broad and becomes even broader with increasing deposition temperature, which is in contrast to the behaviour of a-Si and a-Ge.

The absorption edge spectra of the amorphous samples are seen to consist of two regions: a power-law and an Urbach region. The power-law region, i.e. the non-exponential part of the absorption coefficient data ($\alpha \geq 10^4$ cm$^{-1}$), was used to determine the optical gaps. The data were fitted to the relation given below for the Tauc gap $E_T$:

$$ (\alpha h \omega)^{1/2} = B(h \omega - E_T) $$

where $B$ is a constant. Also, the values of photon energy corresponding to $\alpha = 10^4$ cm$^{-1}$ have been used to determine the so-called $E_{04}$ gap. Both $E_T$ and $E_{04}$ are used in the literature in the absence of a more specific marker. Figure 6.3 shows the variation of both $E_T$ and $E_{04}$ with the deposition temperature. For samples prepared at room temperature, the Tauc gap is 1.0 eV and increases first gradually, then rapidly at about 150-170°C, reaching 1.36 eV when $T_s$ is 200°C. $E_{04}$ follows the same trend. These optical gap values seem to be in good agreement with the value of 1.17 eV given for the magnetron-sputtered samples of Matsumoto et al [6] but larger than 0.42 eV reported in the early work of Connell et al [4]. Gheorghiu and Theye [7] have found 1.2-1.4 eV for as-deposited and 1.5-1.7 eV for annealed flash-evaporated samples.
Figure 6.3: Variation of the optical gaps, E04 and E17, with deposition temperature.
The Urbach region, i.e. the exponential part of the absorption coefficient data ($\alpha \leq 10^3 \text{ cm}^{-1}$), was fitted to the relation of the form

$$\alpha = \alpha_0 \exp(\hbar \omega / E_U)$$

in order to determine the Urbach slope $E_U$. The values obtained for $E_U$ are 112, 118, 125, 158 and 187 meV for the films deposited at $T_G=20, 100, 150, 170$ and $200^\circ\text{C}$, respectively. To our knowledge, there are no data available in the literature for comparison. The increase in the slope of the absorption edge with increasing $T_G$ is surprising and will be discussed in section 6.3.

6.2 Electrical Properties

Figure 6.4 presents the variation of conductivity as a function of inverse temperature for $a$-GaP films prepared at different deposition temperatures $T_D$ and with annealing at temperatures $T_A$. For all the films, the conductivity cannot be described by the simple activated form of $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ with a single activation energy $E_a$, but instead exhibits curvature on a $\ln \sigma$ versus $1/T$ plot over the entire temperature range studied. The curvature can be interpreted as a continuously varying activation energy: $E_a$ increases from 0.23 eV to 0.36 eV with rising $T$ for a sample deposited at $20^\circ\text{C}$ and from 0.11 eV to 0.48 eV after annealing this sample at $270^\circ\text{C}$. Values for the pre-exponential factor $\sigma_0$, which normally provides information on the conduction mechanism involved, were obtained from extrapolations of the tangents to the curves at the high-temperature ends; they lie between 2 and 50 $\Omega^{-1}\text{cm}^{-1}$ for the $T_D, T_A$ range of 20-270$^\circ\text{C}$. The low values of $\sigma_0$, in addition to the curvature of the conductivity plots, virtually rules out the possibility that the conduction is via extended states in either the valence and
Figure 6.4: Conductivity as a function of inverse temperature for a-GaP films with different temperatures of $T_S$ and $T_A$. 
conduction bands, such transport normally being associated with values of $\sigma_0$ in the range $10^2$-$10^4$ cm$^{-1}$.

A relation of the form $\sigma = \text{const.} \exp\left[\frac{-T_0}{T}^{1/4}\right]$, which is used to describe variable-range hopping conduction at the Fermi level, has also been tested. The plots of $\ln\sigma$ versus $T^{-1/4}$ were linear up to very high temperatures, with $T_0=3\times10^9$ for as-deposited samples and slightly higher for samples deposited or annealed at a higher temperature. However, the density of states calculated from the values of $T_0$ (assuming a localization length of 10 Å) were unreasonably high, which suggests that variable-range hopping at the Fermi level is not the mechanism for conduction either.

A possible mechanism for electrical conduction in these films is that of transport in a band tail, but with the conduction path moving downwards in the tail states as $T$ is lowered, producing a gradually decreasing activation energy. Such a mechanism is also consistent with the low values of $\sigma_0$.

In Figure 6.4, a kink can be seen at the high-temperature end of some of the curves. This kink, which was observed only during the heating cycle, was found to occur at 115°C for samples deposited at room temperature and was shifted towards higher temperatures for samples prepared at high deposition temperatures and for annealed samples. It was attributed to an 'in situ annealing effect', which is indicative of a loose structure possibly stemming from the presence of voids in the network. Figure 6.4 also shows a reduction in the conductivity of samples prepared at high $T_a$ or annealed at high $T_a$.

It appears that our conductivity data is quite different from the only conductivity report [6] in the literature for sputtered a-GaP, although the values of optical gap are in good agreement with those reported by the same group, as was mentioned earlier. The measurements of Matsumoto and Kumabe [6] reveal a kink at a critical temperature $T_c$ of 150°C, above and below which activated conduction occur. They have assigned the activation
energy above $T_c$ to intrinsic activation, and that below $T_c$ (0.42 eV) to the energy between extended and gap states. For flash-evaporated films prepared at room temperature, an exponential variation of conductivity has been observed [8], whereas annealed samples showed an activated behaviour with a single activation energy 0.4-0.5 eV above room temperature, indicating transport in extended states beyond the mobility edge [7]. However, since the pre-exponential factor was not compatible with the value expected for extended-state conduction and $E_A$ was much smaller than half the optical gap $E_T$, the same results were also interpreted as activated hopping in band tails [5]. At low temperatures, the conductivity data was found to follow the law $\sigma = \sigma_0 \exp(T_0/T)^n$ with $n=1/4$ and $T_0$ of the order of $10^9$ K for as-deposited samples and $n=1/2$ for annealed samples [5].

6.3 Discussion

Recently, O'Reilly and Robertson [9] have reported a comprehensive theoretical study on amorphous III-V semiconductors. Using the tight-binding recursion method, they calculated the local density of states for bulk material and also for defect sites. The calculations for the bulk sites show that both the valence and conduction band edges should not be affected by any variations in bond angle, and hence theoretically little change in the band gap is expected from this source. However, since experimentally the optical gaps are found to be smaller than those in the corresponding crystals, O'Reilly and Robertson invoke the presence of significant numbers of defect states. Two types of defect, namely dangling bonds and wrong bonds, have been studied. It was found for a-GaP that the unrelaxed singly occupied P and Ga dangling bonds give rise to states at or close to the valence and conduction band edges, respectively. These bonds can become doubly occupied, whereupon they
relax by altering their environment from four-fold to three-fold coordination, accompanied by a change of the tetrahedral bond angle of 109° to the preferred angles of 97° and 120° for P and Ga dangling bonds, respectively. In this case, the corresponding states move into the valence and conduction bands. The singly occupied dangling bonds can also interact with one another forming either weak bonds or creating dangling-bond-defect complexes, which are likely to occur at the inner surfaces of voids. The calculations have shown that complexes of two adjacent P dangling bonds produce states nearer to midgap. Furthermore, O'Reilly and Robertson have shown that isolated wrong bonds, i.e. Ga-Ga and P-P, give rise to states near the valence and conduction band edges, respectively, whereas clusters of wrong bonds produce states near midgap. Figure 6.5 illustrates a schematic diagram of the density of states of c-GaP close to the band edges, together with the calculated positions of the states that arise from different types of defects possible in an amorphous GaP network [9]. For sputtered a-GaP samples, the EXAFS and IR data presented in the previous chapter have shown that there are no or very few wrong bonds in the network. This result is supported by the ESR study of Hoheisel et al [10] who assigned resonance signals to dangling bonds rather than wrong bonds. Therefore, the states due to isolated wrong bonds should be insignificant in the density-of-states picture. On the contrary, since our samples were found to contain voids, we expect a significant number of dangling bonds. Hoheisel et al [10], however, have found the spin density of P and Ga dangling bonds to be of the order of $10^{18}$ and $10^{17}$ cm$^{-3}$, respectively, which suggest that most of the dangling bonds are either relaxed or have linked to one another in such a way that the remaining number of unpaired electrons is very few.

One can note in Figure 6.5 that the states arising from both the unrelaxed and relaxed dangling bonds have accumulated towards the band edges, producing a high density of tail states, which inevitably results in a
Figure 6.5: A schematic diagram for the density of states of c-GaP close to the band edges and closure of the band gap arising from the different types of defect states for a-GaP ($T_s=20^\circ C$) (curves a), a-GaP ($T_s=200^\circ C$) (curves b). Ga(dbc) defects are positioned by analogy with P(dbc).
reduction in the band gap and hence a shift of the absorption edge towards lower energies. However, it is clear that these states alone are insufficient to account for the observed 1.6 eV shift of the edge. In order to explain such a large shift, the states due to defect complexes (e.g. P(db)c, Ga(db)c), which are located nearer to midgap, should be taken into account. Since these defect complexes will be associated with only a small absorption, they can be related to the low-energy part of the absorption edge spectra, whereas the isolated dangling bonds are associated with the high-energy part of the edge. It is probably easier to eliminate the isolated defects rather than the defect complexes. Hence, as the deposition or annealing temperature is increased, the isolated defects are for the most part annealed out, resulting in a larger shift in the high-energy part of the absorption edge [11] compared to the shift in the low-energy part of the edge back towards the crystalline position. Therefore, the Urbach edge becomes broader with increasing $T_s$. If $T_s$ is increased above 400°C, these defect complexes are eventually annealed out and the Urbach edge then becomes sharper as demonstrated by Davey et al [3] on evaporated films.

As seen in Figure 6.5, there is no particular gap state with a high density in the pseudo-gap and the residual density of states is actually fairly low compared to say a-Si or a-Ge. This can explain the absence of subgap absorption in the absorption edge of a-GaP. It is also consistent with the lack of evidence for variable-range hopping in the conductivity data. The conductivity, instead, is more likely to be dominated by a transport mechanism that takes place in the wide band tails. With annealing and increasing deposition temperature, since there will be removal or relaxation of the defects and hence a lowering of the density of states, as seen in Figure 6.5, the conductivity is reduced relative to the room-temperature deposited sample but hopping in the tail states still occurs. The activation energies
found cannot be used to relate the conductivity data to the optical data in order to obtain information about the position of the Fermi level.

The optical properties of a semiconductor can be correlated to its structural properties using the refractive index data. This is done by relating the static refractive index \( n(0) \) (at zero frequency) to the plasma frequency \( \omega_p \) of the valence electrons by the following expression [13]

\[
\left( n(0) \right)^2 = 1 + \frac{2}{3} \left( \frac{\hbar \omega_p}{E_g} \right)^2
\]

where \( E_g \) is the Penn gap which represents an average separation between valence and conduction bands and is therefore a measure of the bond strength. The plasmon energy of a-GaP is found to be smaller than that of the crystal [14], and hence the increase in \( n(0) \) for a-GaP, as shown in Figure 6.1, indicates a reduction in its Penn gap. The figure also shows a decrease in \( n(0) \) for amorphous samples with increasing deposition temperature \( T_s \), which could arise from either a decrease of \( \hbar \omega_p \) or an increase of \( E_g \) or both. In principle, changes in the Penn gap can result from variations in bond length \( (E_g \propto r^{-2.5}) \), coordination number \( (E_g \propto N^2) \) and bond-angle distribution [12]. The first two effects are ruled out by our EXAFS data on sputtered a-GaP, which revealed, within experimental uncertainties, no changes in bond length and coordination number. However, a considerable reduction in the spread of the bond angle was observed as \( T_s \) increased from 20 to 200°C. From IR spectroscopy, it was found that this reduction in the spread of the bond angle is associated with a 15% increase in the strength of the Ga-P bond. Using the above equation, this should reduce \( n(0) \) by about 12%. However, experimentally a decrease of only 5% is found when \( T_s \) is increased from 20 to 200°C. This suggests that the rise in \( E_g \) is partially compensated by an increase in \( \hbar \omega_p \). An increase in \( \hbar \omega_p \) is expected when densification, arising
both from a reduction in void concentration and from local atomic rearrangements, occurs with increasing $T_a$.

The above arguments apply only if the voids are small enough to be accessible to the electrons. If the voids are large, effective-medium theory predicts an overall increase in $n(0)$ when their concentration is reduced by annealing [12]. Although we cannot rule out a contribution of this nature, the experimental result of a decrease in $n(0)$ on annealing shows that the effect cannot be dominant. Small-angle X-ray scattering experiments on the samples after annealing are in progress in order to clarify this point.

6.4 Density of States

A XANES spectrum which is the part of the X-ray absorption spectrum close to the absorption edge (see section 3.2.5) actually represents the density of states of the conduction band. XANES is, therefore, complementary to the techniques such as X-ray emission or X-ray and UV photoelectron spectroscopy (XPS and UPS) which give information on the density of states of the valence band.

Figures 6.6(a) and (b) show the XANES of P and Ga K edges for both amorphous and crystalline samples, i.e. the partial density of states of the conduction band for each type of atom. The first striking thing about these figures is much smearing of the features present in the XANES of $c$-GaP in the amorphous case. The first peaks which occur at 10364 and 2144 eV for Ga and P edges, respectively, are associated with the antibonding $p$-like bands since they correspond to $1s \rightarrow p$ transitions. The second and third peaks at the P edge, which become more pronounced with increasing temperature, correspond to the antibonding mixed $s$-$p$ and $s$-like bands, respectively.
Figure 6.6: XANES for (a) The P K edge, (b) The Ga K edge. The curves have been displaced for clarity.
However, the latter two peaks seen in the crystalline case at the Ga edge do not recover with temperature up to 200°C.

In Figure 6.7, the XANES spectra of both crystalline and amorphous GaP at the P edge (d), (e) are plotted together with the Kp X-ray emission spectrum [15] of P in c-GaP (a), XPS [16] of c-GaP (b) and UPS [14] of a-GaP (hv=21.2 eV) (c). From a comparison of these spectra (an allowance for differences amongst the spectra should be made because of the different techniques used), we firstly note that the density of states of the valence (a), (b) and the conduction bands (d) of c-GaP are mirror images of one another as expected from a bonding-antibonding picture. However, a comparison of the density of states of the valence band (c) with the conduction band (e) of a-GaP prepared at room temperature shows that while the valence band has fewer features than that of the crystal, the conduction band loses its structure nearly completely. The same result has been found for a-Ge and a-Si [17]. Secondly, the density of states of the conduction bands for both amorphous and crystalline samples are broadened compared to the density of states of the valence bands due to transitions from the deep-lying d levels of Ga (binding energy=-18.7 eV [16]) to the conduction band [18].
Figure 6.7: (a) Kβ X-ray emission spectrum [15] of P in c-GaP, (b) XPS [16] of c-GaP, (c) UPS [14] of a-GaP (hv=21.2 eV), (d) XANES of c-GaP at the P K edge, (e) XANES of a-GaP at the P K edge.
References

[11] The absorption edge shifts towards higher energies slowly below \( T_s = 150^\circ C \), but between 150 and 170\(^\circ\)C a rapid shift occurs. The dependence of \( \alpha \) and other film properties, such as refractive index and spread in bond angle, on \( T_s \) in this way suggests that film growth during deposition is controlled by an activated process in which local surface reorganizations occur above a critical deposition temperature [12].
Chapter 7: Summary and Suggestions for Future Work

7.1 Summary

7.2 Suggestions for future work
7 Summary and Suggestions for Future Work

7.1 Summary

In this thesis a detailed investigation of amorphous GaP, a remarkable yet little-studied amorphous III-V semiconductor, has been presented.

The a-GaP samples were prepared in thin-film form by radio-frequency sputtering. During the preparation, a r.f. power of 250 W and an argon pressure of 3-4 mTorr were used and temperature of the substrates was varied from room temperature to 200 °C. Sputtering under these conditions for $5\frac{1}{2}$ hours yielded films with thicknesses of 1-1.2 μm. Some room-temperature prepared films were subsequently annealed at higher temperatures (200-400 °C) in a vacuum of $10^{-5}$ mTorr for two hours.

The structure of these films was investigated by a variety of experimental techniques. Transmission electron microscope (TEM) experiments at low magnification revealed that the films were macroscopically homogeneous, continuous and smooth. However, under high magnifications, contrast (dark and light regions) appeared in some of the bright-field electron micrographs and this is interpreted as evidence for the presence of microscopic inhomogeneities, namely voids, in the a-GaP network. The results of small-angle X-ray scattering (SAXS) experiments have confirmed this assertion, and the sizes of the voids have been determined to be ~60 Å in diameter on the average, for room-temperature deposited samples. For samples produced at higher deposition temperatures, TEM experiments have shown that some voids are eliminated while others merge to create larger ones.

A scanning electron microscope (SEM) together with an energy dispersive X-ray analyser (EDAX) was used for the compositional analysis of the films. It was found that all samples are stoichiometric to within a few
percent and 1-2% Ar is trapped in the network. Line profiles and digitized maps of Ga and P, which represent the distribution of these elements along a line and across an area on the sample surface respectively, did not show any compositional inhomogeneities such as phase separation but a small degree of non-uniformity in the case of P was found.

Extended X-ray absorption fine structure (EXAFS) measurements were performed for both the Ga and P K-edges to obtain information about the local atomic structure in the films. The technique revealed that the Ga and P atoms are surrounded by four P and Ga atoms respectively, arranged in a tetrahedral geometry. The existence of wrong bonds, Ga-Ga and P-P bonds, is not significant (less than 2-3% - the detectable limit of the technique) i.e. a-GaP is predominantly chemically ordered. This result is in contrast to the case of flash-evaporated samples in which wrong bonds in concentrations as high as 25% have been found [1,2]. In addition, EXAFS revealed that the configurational disorder of the a-GaP network results from variations in the bond angles, in particular those around the P atoms, rather than variations in bond lengths, and that this disorder decreases with increasing deposition and annealing temperature.

Infrared (IR) transmission and reflection spectra of the films were measured over the wavenumber range 4000-200 cm\(^{-1}\) (\(\lambda=2.5-50\ \mu\text{m}\)) to investigate further the local atomic bonding configurations. Features in the IR spectra associated with Ga-P vibrational stretching modes were identified and these were found to be sharpen and shift with increasing deposition and annealing temperature. These changes are interpreted as a strengthening of bonds related to a reduction in bond-angle disorder. No vibrations associated with wrong bonds were observed, a result in agreement with the conclusions from the EXAFS data.

Optical transmission and reflectivity measurements on the films were used to determine the dispersion of the refractive index and the optical
absorption edges as a function of deposition temperature $T_g$ of the films. For low values of absorption coefficients, the technique of photothermal deflection spectroscopy (PDS), using equipment constructed by the author, was used. The optical gap of the amorphous films lies at about 1-1.2 eV which is much smaller than even the indirect gap of crystalline GaP (2.26 eV). The gap increases by several tenths of an electronvolt as $T_g$ is raised from room temperature to 200 °C. At the same time, the Urbach slope decreases—a behaviour which is in striking contrast to that obtained for amorphous tetrahedral semiconductors.

The electrical conductivity of the films displays a non-Arrhenius behaviour with temperature. The decreasing activation energy with temperature is interpreted in terms of a conduction path with shifts relative to the Fermi energy.

A model for the density of electronic states, which considers states associated with defects, has been proposed to account satisfactorily for all the structural, optical and electrical data obtained during these investigations.

### 7.2 Suggestions for Future Work

1. An interesting finding of this study was that while there is little disorder in the bond length in a-GaP, there are wide distributions in the bond angles which is more pronounced around P atoms than around Ga atoms. Similar results were also found for a-GaAs [3] in which material the bond angle distribution around As atoms is much larger than around Ga atoms. These results suggest that the essential flexibility of the a-III-V network, which is needed to form a covalent random network without much strain, is provided by bond-angle disorder, in particular that around group-V atoms. The
implications of this on the topology of the a-III-V network would be worth investigating by means of modelling studies.

2. Determination of the dependence of the structural, optical and electrical properties of a-GaP films on departures from stoichiometry and on incorporation of hydrogen could be very useful for understanding the relation between the properties of the films and conditions that are likely to influence the density of defects. This study has, in fact, already been initiated by the author.

3. Investigations of defects by means of ESR and luminescence techniques would be useful for a better understanding of the electronic states.

4. Addition of elements that might produce doped n- and p-type material could be attempted. Suggested elements, which could be co-sputtered from the surface of the GaP target, are Zn (for n-type) and S, Se or Te (for p-type). Some results suggesting the effectiveness of Zn in this respect have already been reported [4].
References

Publications


A structural study on a-GaP prepared at different temperatures

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Abstract. A series of nearly stoichiometric a-GaP films has been prepared by R F sputtering on to substrates held at temperatures from 20-200 °C. Extended x-ray fine absorption (EXAFS) at both the Ga and P K edges, infrared absorption, and optical edge data have been used to understand the structures of these films. The stoichiometric amorphous network of GaP, which was found to be fourfold coordinated as expected, showed no chemical disorder. The development of the atomic order of the network with increasing deposition temperature and annealing, from the amorphous to the crystalline state, has been followed. The results are discussed in terms of the bond lengths and angles and the strength of the Ga-P bonds.

1. Introduction

Crystalline III-V semiconductors are important materials owing to their technological applications in the microelectronic and optoelectronic industries. Their amorphous counterparts have become of interest recently, not only because of their possibility for applications, but also because of their contribution to fundamental research on non-crystalline systems.

The structural disorder in the amorphous materials is the basic factor that determines their properties and can be categorized as being either chemical or configurational. Configurational disorder refers to the variations in bond lengths and angles, which affect the localization of the states at the band edges and the band gap. Chemical disorder relates to the proportion of each type of chemical bond present and influences the electronic valence and conduction band densities of states and, as for configurational disorder, the size of the band gap. In contrast to amorphous group-IV elements which have only configurational-type disorder, amorphous III-V compounds, being binaries, can also contain chemical disorder. This has been investigated for amorphous GaAs [1, 2, 3], GaP [4] and InP [5] by EXAFS. In the case of a-GaAs, since the shape of the scattering factors for both Ga and As atom are nearly identical, it is very difficult to draw conclusions about chemical disorder. However, in the case of a-GaP the scattering factors of Ga and P atoms are very different so that EXAFS becomes a more sensitive test of chemical disorder. Chemical disorder in flash-evaporated a-GaP has already been reported [6].

Only a few IR studies on a-GaP [7, 8] and a-GaP:H [9, 10] have so far been made. In one of these [7] IR spectra have been obtained from 6 to 300 K. In the present work, the change in the IR absorption bands of a-GaP with increasing deposition...
temperature and on annealing (up to 673 K) have been investigated and the results compared with c-GaP.

The aim of the present work is to investigate the structure of sputtered amorphous GaP films using EXAFS and infrared techniques.

2. Sample preparation

The films used for both EXAFS, infrared analysis and optical measurements were prepared by RF sputtering at the same time to eliminate deposition-dependent variations. The base pressure before flushing argon into the chamber was $2 \times 10^{-7}$ mTorr, and the pressure during sputtering was 3-4 mTorr. The power applied to the 4" stoichiometric polycrystalline GaP target was 250 W. For infrared and optical measurements, polished crystalline silicon wafers and fused-silica substrates respectively were used. The distance between the target and substrates was kept at 5 cm. For EXAFS measurements on the P edge, the films were deposited on Cu plates because of the need to have a conductive substrate required for the drain current measurement, whereas for the Ga edge, mylar was used as a substrate, the films being folded over many times until the optimal thickness 40-50 μm was obtained for the x-ray transmission measurements made at this edge.

Films were deposited on substrates held between room temperature and 200°C. (These films will be referred to as a-GaP($T_d$) where $T_d$ is the deposition temperature.) Some samples prepared at room temperature were subsequently held at higher temperatures (200-400°C) for two hours at a base pressure of $10^{-5}$ mTorr in order to investigate the structure of annealed samples. (These films will be referred to as a-GaP($T_a$) where $T_a$ is the annealing temperature.)

The deposition rates were between 30 and 40 Å min$^{-1}$ depending on the deposition temperature. The thicknesses of the films (1-1.2 μm) were determined both by an optical technique, in which the interference fringes in reflection were used, and by a mechanical method using a Tàysurf. The thicknesses determined by both methods agreed to within 5%.

The compositions of the samples were determined by both energy-dispersive x-ray analysis (EDAX) using a DS 130 scanning electron microscope (SEM) and EXAFS in which the step heights of the absorption spectra taken at the P K edge were used. Both methods were consistent with one another. The compositions of the films were found to fluctuate around stoichiometry within 2-4%. The uniformity of the composition across the films was also checked by taking line profiles for both Ga and P in EDAX. The line profiles showed that for some films the P content, but not the Ga content, varies somewhat across their width. A few per cent argon was found to be trapped in the films.

The amorphicity of the samples was checked both by a JOEL Jem 100Cx transmission electron microscope, from which characteristic diffuse-ring diffraction patterns were obtained, and by the EXAFS technique itself. The transmission electron microscope was also used to look at the surfaces of the films in order to probe any phase separation. Within the resolution of the microscope, the surfaces of all samples were smooth and showed no phase separation except one prepared at 200°C whose surface was slightly rough and displayed features which we associated with regions where an excess of P exists.
3. Experimental details and data analysis

3.1. EXAFS

The x-ray absorption spectra of samples for both the Ga and P K edges were obtained using the 2 GeV Synchrotron Radiation Source at the SERC Daresbury Laboratory.

The Ga K edge experiments in the nearly hard-x-ray region (~ 10.370 eV) were carried out at the 7.1 beam line station in the transmission mode at room temperature. In the beam line, the white x-ray beam is collimated at the entrance slit, monochromatized using a Si(111) crystal with harmonic rejection set at 70%, and passed through the folded sample whose thickness, \( d \), was about 40-50 \( \mu \text{m} \). Both the incident \( I_0 \) and transmitted beam intensity \( I \) were measured by ion chambers filled with argon gas. The x-ray absorption spectra were obtained by comparing the transmission beam intensity to the incident beam intensity as the energy region was scanned.

The P K edge experiments in the soft-x-ray region (~ 2150 eV) were made at room temperature at the 3.4 beam line station where the electron drain current method, which is a modification of the total electron yield technique, is used. At station 3.4, the white beam is monochromatized using a Ge(111) crystal and focused on the sample by a chromium-coated mirror placed at a grazing angle. Because of the strong attenuation of such low-energy x-rays by the atmosphere, the mirror, the monochromator and the samples have to be maintained in ultra-high vacuum. The absorption of x-ray photons by the sample causes electron ejection. As a result, a drain current, which is proportional to the absorption coefficient \( \mu(E) \), can be collected and measured.

The EXAFS function, \( \chi(E) \), was obtained from the absorption spectrums \( \mu(E) \) by making pre- and post-edge background subtractions using the available software program, EXBACK. For both of these subtractions, different-order polynomials have been fitted. The normalized EXAFS function \( \chi(k) \) was first converted into \( \chi(k) \) using

\[
\frac{\hbar^2 k^2}{2m} = (E - E_{\text{edge}}) + E_0
\]

where \( E \) is the incident photon energy, \( E_{\text{edge}} \) is the threshold energy of that particular absorption edge and \( E_0 \) is the energy offset, being the difference between the energy of a \( k = 0 \) photoelectron and the lowest unoccupied energy level. \( \chi(k) \) is then multiplied by \( k^2 \) in order to compensate for the diminishing amplitudes of the experimental spectrum at high \( k \)-values. In order to obtain structural information, the program EXCURVE90 was used to make a comparison of the least-squares fitting of the \( k^2 \)-weighted experimental spectrum to the theoretical spectrum which was calculated using the single-scattering curved wave theory [11]. The basic formula describing the theoretical EXAFS spectra is

\[
\chi(k) = (-A(k)/k) \sum_j \left( N_j f_j(k) \right) \exp(-2\sigma_j^2 k^2) \\
\times \exp(-2R_j \lambda) \sin(2kR_j + 2\delta + \psi).
\]

Here \( f_j(k) \) is the backscattering amplitude from each of the \( N_j \) neighbouring atoms of the \( j \)th type, with a Debye-Waller factor of \( \sigma_j^2 \), at a distance \( R_j \) away. \( \delta \) is the phase shift experienced by the photoelectron during its passage through the
central-atom potential, and \( \psi \) is the phase of the backscattering factor. The term 
\[ \exp(-2R_j/\lambda) \]
is due to inelastic losses in the scattering process with \( \lambda \) being the 
electron mean free path. \( \lambda \) can be written in terms of a constant imaginary 
part of the potential, \( \text{vpi} \), as \( \lambda = k/\text{vpi} \). \( A(k) \) is the amplitude reduction factor due to 
many-body effects such as shake-up and shake-off processes at the central atom [12].

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many-body effects such as shake-up and shake-off processes at the central atom [12].

During the fitting, the values used for both \( A(k) \) and \( \text{vpi} \) were 0.75 and -5 at the 
Ga and 0.65 and -3.5 at the P K edges respectively, which were the result of the 
least-squares fitting for crystalline GaP, and the phasestrips of both the absorbing and 
neighbouring atoms were calculated in the program. The least-squares refinements 
of the experimental and theoretical spectra were terminated when the least-squares 
fit index was minimized. The fit index, \( F \), is defined by

\[
F = \left( \frac{1}{100N_p} \right) \sum \left[ \left| \chi_i(\text{calc}) - \chi_i(\text{exp}) \right| \right]^2
\]

where \( N_p \) is the number of data points in the spectrum, and \( n \) is a \( k \)-weighting 
factor, which was kept at 3 throughout this work. The uncertainty in the final set of 
parameters resulting from such a procedure has been found as pairs of \( (N_j, \sigma_j^2) \) and 
\( (R_j, E_j) \) by using a statistical test described by Joyner et al [13]. In the test, the 
error bars of the paired fitting parameters are given by the 95% confidence region 
(\( \pm 2\sigma \)) of a contour map of the fit index.

In the present work, in addition to the extraction of the conventional structural 
information, EXAFS has been used to find the compositions of the samples. For this 
purpose, only the absorption spectrum of the P K edge can be used, because the 
drain current is then obtained from the first 100 \( \AA \) or so below the sample surface, 
containing no contribution from the substrate. Therefore, the relative step height 
of \( \mu(E) \) can be written as the sum of the atomic absorption of each element. For 
Ga\(_{1-x}\)P\(_x\),

\[
\mu(E) = (1 - x)\mu_{Ga} + x\mu_{P}.
\]

By taking the ratio of values of \( \mu(E) \) just above and just below the edge and the 
atomic absorption coefficients given by [14], the compositions \( x \) were calculated.

The absorption edge itself and the spectrum \( \sim 25 \text{ eV} \) above it had to be excluded 
from the EXAFS function since the theory used for EXAFS takes into account only the 
single-scattering process, whereas in the region close to the edge multiple-scattering 
processes are dominant. However, this region (called the XANES region) was used to 
obtain information on the partial conduction band density of states.

3.2 Infrared spectroscopy

Infrared spectra of the samples in the frequency range 4000–200 cm\(^{-1}\) were obtained 
at room temperatures by using a Model 580B double-beam Perkin–Elmer infrared 
spectrophotometer. A c-Si wafer was used in the path of reference beam in order to 
eliminate the effect of substrates. Also during the scans, dry air was flushed into the 
sample compartment to remove water vapour which causes extra absorption bands 
and complicates the spectra.
3.3. The optical measurements

The reflection and transmission of the films in the UV/visible/near-infrared region were measured at room temperature using a Model 330 Perkin-Elmer spectrophotometer. Assuming that the films are weakly absorbing, the absorption coefficients, $\alpha$, of the films were calculated from the following formula

$$ T \equiv (1 - R) \exp(-\alpha t) $$

where $T$ and $R$ are the measured transmittance and reflectance, respectively, and $t$ is the film thickness.

4. Results and discussion

Figures 1 and 2 show the $k^2$-weighted EXAFS function $\chi$ and Fourier transform for crystalline and amorphous GaP at the Ga and P K edges. It is not surprising that all the fine structure of the EXAFS function of the crystalline state has disappeared in the EXAFS functions of the amorphous state. Similarly, while the Fourier transforms of the EXAFS from the crystal show strong features up to the third shell, only the first-shell peak is strong in the amorphous case. This is expected in the absence of periodicity and can be used as a test of amorphicity.

![Figure 1. The $k^2$-weighted EXAFS function $\chi$ and Fourier transform FT for crystalline (on the left) and amorphous (on the right) GaP ($T_i = 20^\circ C$) at the Ga K edge.](image)
The EXAFS data in the $k$-range $3-13.5 \, \text{Å}^{-1}$ for both the P and Ga edges of the samples prepared at high deposition temperatures $T_d$ and also of the samples annealed at temperatures $T_a$, have been analysed as described in section 3.1. During the data analysis not only Ga-P bonds but also P-P and Ga-Ga bonds were added into the fitting process. However, in every case, the program EXCURV90 rejected the existence of the P-P and Ga-Ga bonds, which shows that wrong bonds are not found in the structure of the samples on a significant scale. (The sensitivity of EXAFS is such that the existence of bonds down to 5% can be detected with the large data range used.) The coordination numbers, the length of the Ga-P bond and the spread of the bond lengths (the so-called Debye-Waller factor) have been determined, and are shown in figures 3, 4 and 5, respectively. Figure 3 confirms that a-GaP is fourfold coordinated; in other words, it consists of tetrahedral units. This structure is maintained at higher deposition and annealing temperatures. The Ga-P bond length is also independent of the $T_d$ and $T_a$ temperatures as can be seen from figure 4. The values we found for the Ga-P bond lengths lie around 2.33 and 2.31 Å in the case of a-GaP, and 2.33 and 2.325 Å in the case of c-GaP, the two values corresponding to data taken at the Ga and P edges, respectively. Our crystalline bond length is about 0.03 Å less than the value extracted from diffraction experiments [15]; we believe that this arises from a slight difference in the phaseshift used. However, because the same phaseshift is used for all amorphous samples as well as the crystal, this discrepancy does not affect any of the conclusions made here. In any case there is a 0.02 Å difference in the nearest-neighbour distance determined using the two edges, which is probably within the experimental errors. However, comparison of the amorphous bond length with that of the crystal using the two edges is important since it forms the basis of our
discussion concerning the existence or otherwise of chemical order on a small scale in this amorphous III-V compound. If a-GaP is chemically disordered, we should detect P-P bonds (2.2 Å) at the P edge and Ga-Ga bonds (2.44 Å) at the Ga edge, in addition to the bonds between Ga and P atoms. Therefore, we would expect to see an increase in the measured Ga-P bond length at the Ga edge and a decrease in the measured P-Ga bond length at the P edge compared to the bond lengths in the crystal, since EXAFS gives an average value for bond lengths. However, we could see only a 0.015 Å difference between the crystalline and amorphous bond lengths at the P edge, which is well below the experimental error of 0.03 Å, and no difference at all at the Ga edge. Thus, we conclude from the bond length data that a-GaP is chemically ordered.

The question of chemical order or disorder can also be discussed using the bond-conservation criterion

\[ c_i N_{ij} = c_j N_{ij} \]

where \( c_{i,j} \) are the compositions of the type of atoms \( i,j \) forming a bond and \( N_{ij} \) is the number of \( j \) atoms bonded to an \( i \) atom. The criterion has been applied to a-GaP by using the coordination numbers determined from EXAFS and the composition
values obtained from EDAX. It was found that the above equation is satisfied within the experimental error. Therefore, again we conclude that a-GaP is chemically ordered.

Infrared spectroscopy can provide information on both the nature and the number of bonds of each type and hence can be used to investigate the existence, if any, of wrong bonds. The transmission spectra of a-GaP at high wavenumbers shows structure associated with the interference fringes. Therefore, only the range 1000-200 cm\(^{-1}\) is shown in figure 6(a) in which the main feature is due to the stretching mode of the Ga-P bond. Wrong bonds, i.e. P-P and Ga-Ga, are infrared inactive in the crystalline state. However, because the selection rules are relaxed in the amorphous state owing to the lack of periodicity, all modes can contribute to the spectra. Thus, wrong bonds, if present, should be seen in the IR spectrum. If we had P-P bonds in our a-GaP samples, we would have expected to see structure \cite{16} at \(\approx 270, \approx 360\) and \(\approx 450\) cm\(^{-1}\), or, at least, at one of these wavenumbers. None of these features was seen and hence, we conclude that a-GaP contains no P-P bonds (or at least less than 10\% of the total bonds, which is the detectable limit of the IR spectroscopy), i.e. it is chemically ordered. The disorder in the network of the a-GaP films has been changed gradually from the amorphous to the crystalline state by increasing the deposition and annealing temperature. Changes can be seen in the Debye-Waller factors of the first and second shell given in figures 5 and 7 for data obtained from both edges. As can be seen from figure 5, the values determined for the Debye-Waller factors of the first shell, \(\sigma_1^2\), at the Ga and P edges are consistent with one another. This is expected since they both show the spread of the same bond length, namely the Ga-P bond, and thus we have a consistency check on the fitted values. The values of \(\sigma_1^2\) decrease with increasing deposition and annealing temperature and approach the crystalline values, indicating a reduction in the configurational (static) disorder of the bond length. The result is also consistent with the optical data in figure 8, where the optical band gap is seen to increase with the increasing deposition temperature from the amorphous band gap value towards that of the crystal. Figure 7 also shows that the variations of the next-nearest-neighbour distances at both edges, i.e. the Ga-Ga distance on the Ga edge and P-P distance on the P edge, are different. The effect of this result on the structure is important and will be discussed in terms of bond angles below.

For amorphous materials, the Debye-Waller factor determined experimentally has
A structural study of $\alpha$-GaP

Figure 6. (a) Transmission spectra of (a) $\alpha$-GaP ($T_i = 20^\circ C$), TO mode at 345 cm$^{-1}$; (b) $\alpha$-GaP ($T_i = 200^\circ C$); (c) $\alpha$-GaP ($T_i = 400^\circ C$), TO mode at 370 cm$^{-1}$ for (b) and (c); (d) c-GaP, three-phonon process at 784 cm$^{-1}$, TO + TO at 750 cm$^{-1}$, LO + TO at 735 cm$^{-1}$, TO + LO at 720 cm$^{-1}$, TO + TA at 572 cm$^{-1}$, LO + TA at 555 cm$^{-1}$, TO + TA$_1$ at 492 cm$^{-1}$, LO + TA$_1$ at 475 cm$^{-1}$, TO + TA$_2$ at 442 cm$^{-1}$, LO + TA$_2$ at 425 cm$^{-1}$. The errors in the quoted wavenumbers are a few cm$^{-1}$. (b) Reflection spectra of (a) $\alpha$-GaP ($T_i = 20^\circ C$); (b) $\alpha$-GaP ($T_i = 200^\circ C$); (c) $\alpha$-GaP ($T_i = 400^\circ C$); (d) c-GaP; the TO mode at 370 cm$^{-1}$ is consistent with (a).

contributions from both thermal and static disorder

$$\sigma^2(\text{exp}) = \sigma^2_{\text{thermal}} + \sigma^2_{\text{static}}.$$  

Assuming that there is no static disorder in the crystalline state, the above equation becomes $\sigma^2_{\text{thermal}} = \sigma^2_{\text{exp}}(\text{exp})$. Then the static disorder of the amorphous materials can be easily determined. Using the values of the Debye-Waller factor of the first shell, both $\sigma^2_{\text{thermal}}$ and $\sigma^2_{\text{static}}$ of $\alpha$-GaP were found to be about 0.003 Å$^2$. This much static disorder causes a 0.007 Å change in the bond length of 2.33 Å. This means that the length of the Ga–P bond in the amorphous state is hardly different from the length of the same bond in the crystal, a feature which is true for many amorphous materials. The fact that we still have an amorphous structure suggests a wide spread in bond angles. In the present work, we have attempted to find the mean value of the bond angle as well as its spread. Figures 9(a) and (b) show three tetrahedra units joined to each other in 3D and a small part of its top view in 2D, respectively. By using the nearest-neighbour distance (2.33 Å) and the next-nearest-neighbour distances (3.8 Å for both Ga-Ga and P-P distances), the mean value of the bond angle $\beta$ has been determined as 109.3°, which is the bond angle in the crystalline state. When the spread in the bond angle was being calculated from the Debye-Waller factor of the second shell, $\sigma^2_{\beta}$, however, it was found necessary to introduce two different spreads around the same mean value, $\Delta \beta_1$ and $\Delta \beta_2$, due to the differences in the values of the Debye-Waller factors of the second shell at the
Figure 7. Debye-Waller factors of the second shell as a function of deposition or annealing temperature for the Ga and P K edges. The points marked with c and an arrow are for c-GaP and added into the figure for comparison. All data were taken at room temperature.

Ga and P edges. In the calculation of $\Delta\beta_1$ and $\Delta\beta_2$, the contribution of thermal disorder of the second shell ($r^2_{\text{thermal}} = 0.011 \text{Å}^2$) has been subtracted from the experimental Debye-Waller factor as has been done for the first shell, and thus the static bond-angle spreads were obtained. The values of the static bond angle spreads shown in Table 1 should be compared to the thermal bond-angle spread which is 1.2° for all samples. It was found that the angle $\beta_1 = \beta \pm \Delta\beta_1$, and both angle spreads decrease with increasing deposition and annealing temperature. This result shows that the bond angle at Ga is more rigid than that at P.

Figure 9. (a) Three GaP tetrahedra units in 3D. (b) Top view of a small part of (a) in 2D together with radii of the first and second shells associated with the Ga and P K edges.
A structural study of a-GaP

Table 1. The static bond angle spreads, $\Delta \beta_1$ at the Ga edge and $\Delta \beta_2$ at the P edge, in samples with different deposition, $T_d$, and annealing, $T_a$, temperatures. The temperature $T$ refers to either $T_d$ or $T_a$.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>20</th>
<th>100</th>
<th>150</th>
<th>170</th>
<th>200</th>
<th>270</th>
<th>400</th>
</tr>
</thead>
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<tr>
<td>$\Delta \beta_1$</td>
<td>5.4</td>
<td>4.8</td>
<td>3.7</td>
<td>2.6</td>
<td>1.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>$\Delta \beta_2$</td>
<td>17.3</td>
<td>17.0</td>
<td>16.3</td>
<td>15.7</td>
<td>14.6</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Infrared spectroscopy can again be used to follow the development of the order in the network. Figures 6(a) and (b) compare the transmission and reflection spectra of a-GaP ($T_d = 200$ °C), a-GaP ($T_a = 200$ °C) and c-GaP ($T_a = 400$ °C) with each other as well as with c-GaP. The observed bands in c-GaP have been assigned to different modes using published assignments [17], (see figure 6(a)). In the case of the amorphous samples, most of the fine structure seen in the IR spectra of c-GaP has been smeared out either partially or completely, but, with increasing deposition and annealing temperature, the TO mode becomes sharper and shifts to higher wavenumber and more structure gradually starts appearing at 500 and 600 cm$^{-1}$ in the IR transmission spectra. Similarly, the IR reflection spectra start showing more structure around 650 cm$^{-1}$ and the reflection coefficient at 370 cm$^{-1}$ increases. The shift of the fundamental stretching mode from 345 to 370 cm$^{-1}$, which is known as the fundamental stretching frequency of c-GaP, can be associated with the increase in bond strength. Using the simple harmonic oscillator approach, the force constant $k$, which is a measure of bond strength, was calculated for the wavenumbers before and after the shift. It was found that $k$ increased by 15% after the shift, meaning that the Ga-P bonds are becoming stronger with increasing order in the network. As is known, c-GaP has the zincblende structure in which the s and p orbitals hybridize as sp$^3$ in order to maximize the bond energy and to make the bonds as strong as possible. In the case of a-GaP, the sp$^3$ hybridization is somewhat different from that of c-GaP, resulting in less strong bonds. This is presumably due to the variations in the bond angle.

A XANES spectrum which is the part of the x-ray absorption spectrum close to the absorption edge actually represents the density of states of the conduction band. XANES is, therefore, complementary to the techniques such as x-ray emission or x-ray and UV photoelectron spectroscopy (XPS and UPS) which give information on the density of states of the valence band.

Figures 10(a) and (b) show the XANES of P and Ga K edges for both amorphous and crystalline samples, i.e. the partial density of states of the conduction band for each type of atom. The first striking thing about these figures is that there is a lot of smearing of the features present in the XANES of c-GaP in the amorphous case. The first peaks which occur at 10364 and 2144 eV for Ga and P edges, respectively, are associated with the antibonding p-like bands since they correspond to Is $\rightarrow$ p transitions. The second and third peaks at the P edge, which become more pronounced with increasing temperature, correspond to the antibonding mixed s-p and s-like bands, respectively. However, the latter two peaks seen in the crystalline case at the Ga edge do not recover with temperature up to 200°C.

In figure 11, the XANES spectra of both crystalline and amorphous GaP at the P edge (d), (e) are plotted together with the K$_\alpha$ x-ray emission spectrum [18] of P in c-GaP (a), XPS [19] of c-GaP (b) and UPS [20] of a-GaP ($h\nu = 21.2$ eV) (c). From
Figure 10. XANES for (a) The P K edge; (b) The Ga K edge. The curves have been displaced for clarity.

Figure 11. (a) X-ray emission spectrum [19] of P in c-GaP; (b) 10% [20] of c-GaP; (c) P in [21] of a-GaP (hν = 21.2 eV); (d) XANES of c-GaP at the P K edge; (e) XANES of a-GaP at the P K edge.

A comparison of these spectra (an allowance should be made amongst the spectra because of the different techniques used), we firstly note that the density of states of the valence (a), (b) and the conduction bands (d) of c-GaP are mirror images of one another as expected from a bonding-antibonding picture. However, a comparison of the density of states of the valence band (c) with the conduction band (e) of a-GaP prepared at room temperature shows that, while the valence band has fewer features than that of the crystal, the conduction band loses its structure nearly completely. The same result has been found for a-Ge and a-Si [21]. Secondly, the density of states of the conduction bands for both amorphous and crystalline samples are broadened.
A structural study of a-GaP

compared to the density of states of the valence bands due to transitions from the deep-lying d levels of Ga (binding energy = -18.7 eV [19]) to the conduction band [22].

5. Conclusions

In this paper, we have presented a detailed structural study of nearly stoichiometric sputtered a-GaP films prepared at a temperature range of 20-200°C and annealed up to 400°C. The local structure and bonding of these films have been investigated by using EXAFS at both the Ga and P K edges and infrared spectroscopy. The results were also correlated with optical edge data.

In the amorphous network of GaP, Ga and P atoms are found to be tetrahedrally coordinated, as expected. The existence of wrong bonds, i.e. Ga-Ga and P-P bonds, in the structure has been discussed and it is concluded that a-GaP contains no (or very few, below the detectable limits of the techniques used) wrong bonds, i.e. it is chemically ordered.

It was also found that there is no appreciable disorder in the bond length but there are very wide spreads in the bond angles due to the amorphous nature of these films. The bond angle spread at P in particular is much larger than that at Ga which shows that a P-centred tetrahedron is not as rigid as a Ga-centred tetrahedron. The disorder in the network of the films has been changed gradually from the amorphous to the crystalline state by increasing the deposition and annealing temperatures. There are no changes in the coordination numbers and in the Ga-P bond length with increasing deposition and annealing temperature but there is a decrease in the bond angle spread, an increase in the optical band gap and an increase in the strength of the Ga-P bond.

Finally, our XANES spectra have been combined with the XPS, UPS and Kα x-ray emission spectra taken from the literature so that a complete picture of the electronic valence and conduction band densities of states of the a-GaP films can be obtained.

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References


Transport and optical properties of a-GaP prepared at different substrate temperatures

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Abstract. The electronic properties of a series of nearly stoichiometric sputtered a-GaP films have been investigated as a function of increasing deposition and annealing temperatures up to 270 °C. The optical absorption coefficient (10 cm<sup>-1</sup> < α < 10<sup>5</sup> cm<sup>-1</sup>) as a function of photon energy, deduced both from transmission (T) and reflection (R) measurements and from photothermal deflection spectroscopy (PDS), shows a very large shift of the edge towards lower energies relative to that of c-GaP. The electrical conductivity data have an activation energy that varies continuously with temperature. The results are related to the atomic structure of films which was reported earlier by Elgun, Gurman and Davis and also to the microstructure which is shown to contain voids. In addition, a density-of-states picture based on theoretical calculations by O'Reilly and Robertson is used for interpretation of the results.

1. Introduction

Crystalline GaP is widely used in technological applications such as light-emitting diodes and high-temperature transistors. It is also one of the basic materials for alloy semiconductor lasers and superlattice devices. Similarly, their amorphous counterparts have become of technological interest recently, and they have already been used in the fabrication of electroluminescent diodes where green light is obtained [1]. Furthermore, junction diodes composed of p-type a-GaP:H films doped with Zn on n-type c-GaP substrates show good rectification properties [2]. Yet, from the fundamental research point of view, chemical disorder and other defects in the a-GaP structure, which influence the valence- and conduction-band densities of states and therefore the electronic properties, have not been completely resolved.

Identification and quantification of chemical disorder as exemplified by wrong bonds have attracted considerable attention since such defects are considered to be probable for topological reasons. An early model of a continuous random network with odd-membered rings, namely the Polk model, necessarily requires wrong bonds in the a-GaP network. Later on, Dixmier et al [3] showed that the Connell–Temkin model, which is again a continuous random network but with even-membered rings only, was more appropriate. This suggests that a-GaP is chemically ordered. However, it seems that the existence of chemical disorder depends strongly on the sample preparation of technique. For flash-evaporated samples, a proportion of wrong bonds as high as 25% has been reported [4]. In contrast, Elgun et al [5] found no (or very few, below the detection limits of extended x-ray absorption fine structure (EXAFS) and infrared (IR) spectroscopy) wrong bonds for rf-sputtered a-GaP samples.

Another probable defect is the dangling bond. There have been only a few studies to identify and quantify these in a-GaP. They can exist in isolation as well as at the inner
surfaces of voids in the network, which may occur in order to relieve strain, and have been
identified by electron spin resonance (ESR) [6]. According to O'Reilly and Robertson [7],
about 2% dangling bonds for each constituent atom may be expected.

Reports on a-GaP prepared by a variety of vapour-deposition techniques can be found
in the literature. Evaporated a-GaP films have been studied most extensively [8-11], and
their structure and electronic properties have been investigated in a systematic way. Glow-
discharge samples have also been prepared [12]. For RF-sputtered a-GaP, there have been
some preliminary results [13-15] on electronic properties in a limited range. Recently, we
have reported [5] a detailed structural study of RF-sputtered, nearly stoichiometric, a-GaP
as a function of deposition temperature. In this paper, we present the optical and electrical
properties of these films, and discuss the results in relation to the structure in order to obtain
more information about the effect of the defects on the density of states in the valence and
conduction bands.

2. Experimental procedures

2.1. Sample preparation

The samples used in this study were prepared by RF sputtering, which was carried out in
an argon atmosphere at a pressure of 3-4 mTorr. The base pressure of the system was
2 \times 10^{-7} \text{ mTorr}. An RF power input of 250 W was applied to the 4" stoichiometric
polycrystalline GaP target, which was positioned 5 cm away from the substrates. The
temperature of the substrates during deposition was varied between room temperature and
200 °C, and the corresponding deposition rates were in the range 30-40 Å min^{-1}. Annealing
at higher temperatures was carried out in a vacuum of 10^{-7} \text{ mTorr} for 2 h.

Films for optical and electrical measurements were deposited on fused silica and Corning
7059 glass substrates respectively, and had thicknesses of 1-1.2 μm. Electron-microscope
samples (~1 μm thick) were deposited on mica, then floated off in water and transferred
to Cu grids. A 260 μm thick undoped c-GaP sample, supplied by the Philips Research
Laboratories, was used for comparative optical measurements.

The thicknesses of the films were determined both by an optical technique, in which the
interference fringes in reflection were used, and by a mechanical method using a Talyurf.
The results agreed to within 5%.

2.2. Methods of measurement

The DC conductivity measurements were performed using the two-probe technique for
which gold or aluminium electrodes were evaporated onto the film surface in a co-planar
configuration. Leads were made to the electrodes with fine gold wire attached by a silver-
loaded electrically conducting paste. The current–voltage curves were found to be linear.
The conductivity measurements were carried out using a stabilized power supply and a
Keithley 616 electrometer in the temperature range 1500-520 K in a cryostat filled with an
overpressure (~2-3 psi) of helium after being evacuated to 10^{-6} \text{ mTorr}.

The optical transmission $T$ and reflection $R$ measurements were made at room
temperature in the ultraviolet (uv)/visible/near-infrared region with a Perkin-Elmer 330 double-
beam spectrophotometer. In all the samples investigated, $T$ and $R$ displayed interference
fringes due to multiple reflections within the film and substrate, which became more
pronounced at lower energies. The extrema of the fringes in the reflection were used
to calculate the refractive index $n$ and thickness $t$ of the films by the method proposed in
The absorption coefficients in the range of $10^{-10}$ to $10^5$ cm$^{-1}$ were determined from the approximate formula

$$T = (1 - R) \exp(-\alpha t)$$

where the measured transmission $T$ and reflection $R$ values were taken from the region in which fringing is slight or absent, in order to minimize the error in $\alpha$.

Low absorption coefficients down to $10^5$ cm$^{-1}$ were obtained using photothermal deflection spectroscopy (PDS), a method introduced by Jackson et al. [17]. The PDS measurements were carried out in the transverse mode with a 100 W tungsten-halogen lamp as the pump beam, which was modulated at a frequency of 7 Hz, and a 0.5 mW helium-neon laser as the probe beam. The deflection medium was CCl$_4$, and both Si and PbS detectors were used for normalization of the pump beam intensity. The PDS spectra were calibrated by adjusting to the absorption coefficient values deduced from $T$ and $R$ measurements in the $10^5$ cm$^{-1}$ range. The combination of $T$, $R$ and PDS data gave an optical absorption spectrum extending over three to four orders of magnitude in $\alpha$.

3. Results

3.1. Microstructure

The compositions of the films were determined by a DS 130 scanning electron microscope to which an energy-dispersive X-ray analyser (EDAX) was attached and also by EXAFS measurements. The latter method is described in detail in [5]. All samples were found to be stoichiometric to within a few percent. EDAX was also used to probe the compositional fluctuations of the films. For this purpose, line profiles shown in figure 1 have been taken across the films for both Ga and P atoms. It was found that for some films, while the Ga content is stable, the P content shows small fluctuations, possibly due to plasma instabilities during the deposition process.

The microstructure of the films was also investigated using a Joel Jem 100CX transmission electron microscope. The electron diffraction patterns confirmed that the films are amorphous. Bright-field electron micrographs in real space have revealed the presence of voids. Figure 2(a) shows a micrograph for an a-GaP film prepared at 200 °C, in which dark and light regions correspond to the film and voids, respectively. The sizes of the dark regions were measured and found to be between 280 and 560 Å. In order to demonstrate that these regions are not small crystals oriented in different directions, the diffraction pattern of the same film is shown in figure 2(b).

It seems that the deposition temperature $T_s$ should be higher than 200 °C to obtain void-free a-GaP films. As the deposition temperature was lowered, it was observed that the dark regions became smaller, implying an increase in the void concentration. It was also inferred that the void sizes decrease with decreasing $T_s$. For films deposited at room temperature, the voids could not be seen by transmission electron microscopy with a resolution of order 100 Å. Small-angle scattering experiments on this sample have revealed voids 60 Å in diameter on average. The small-angle scattering experiments have also revealed no additional peak at high $q$ in the $f(q)$ versus $q$ plots, which would be taken as indicative of phase separation [18].
3.2. Optical properties

The dispersion of the refractive index $n$ for a-GaP films deposited at different temperatures is presented in figure 3. The refractive index of c-GaP taken from [19] and [20] is also included for comparison. It is seen that $n$ increases with photon energy as the fundamental absorption edge is approached, and the values for the amorphous films at a given photon energy decrease towards the crystalline value as $T_s$ is increased.

Figure 4 shows the optical absorption coefficient $\alpha$ deduced from both $R-T$ and PDS measurements as a function of photon energy for amorphous films deposited at different temperatures and a crystalline wafer. The data reported in [8] for bulk c-GaP have also been added to the figure (broken curve) to display the direct and indirect optical gaps, which occur at 2.78 eV and 2.26 eV, respectively. The tailing of the absorption below 1 cm$^{-1}$ indicates a wide energy range for defects or impurity states in the optical gap of the crystal. As for the absorption-edge spectrum of the amorphous film, the striking feature is that it shows a very large shift (~1.6 eV) towards lower photon energies compared with that of...
Transport and optical properties of a-GaP

Figure 2. (a) Bright-field electron micrograph of an a-GaP \((T_s = 200 \, ^\circ C)\) film. Dark and light regions correspond to film and voids, respectively. (b) Electron diffraction pattern of the same film.

the crystal. In fact, this is the largest shift found amongst amorphous group-IV and III–V semiconductors. This is why previous studies [14,21] have invoked the existence of wrong bonds in the network. Also, the edge itself is very broad and becomes even broader with increasing deposition temperature as opposed to the case for a-Si and a-Ge.

The absorption-edge spectra of the amorphous samples are seen to consist of two regions, namely power-law and Urbach regions. The power-law region, i.e. the non-exponential part of the absorption coefficient data \((\alpha \geq 10^4 \, \text{cm}^{-1})\), was used to determine the optical gaps. The data were fitted to the relation given below for the Tauc gap \(E_T\):

\[
(\alpha \hbar \omega)^{1/2} = B (\hbar \omega - E_T)
\]

where \(B\) is a constant. Also, the photon energy values corresponding to \(\alpha = 10^4 \, \text{cm}^{-1}\) have been used for the \(E_{04}\) gap. Figure 5 shows the variation of both the optical gaps, \(E_T\) and \(E_{04}\), with the deposition temperature. For samples prepared at room temperature, the Tauc gap is 1.0 eV and increases first gradually, then rapidly at about 150–170 °C, reaching 1.36 eV when \(T_s\) is 200 °C. \(E_{04}\) follows the same trend. These optical gap values seem to be in good agreement with the value of 1.17 eV given for the magnetron sputtered samples
Figure 3. Dispersion of the refractive index for a-GaP films deposited at different temperatures. Data for c-GaP from [19] and [20] is included for comparison.

Figure 4. Absorption coefficient spectra deduced from $T$, $R$ and $ros$ measurements for a-GaP films prepared at different deposition temperatures and for a c-GaP wafer. The broken line refers to the data for bulk c-GaP reported in [8].

of Matsumoto et al [15] but bigger than the 0.42 eV reported in the early work of Connell et al [14]. Gheorghiu and Theye [10] have found 1.2–1.4 eV for as-deposited and 1.5–1.7 eV for annealed flash-evaporated samples.
The Urbach region, i.e. the exponential part of the absorption coefficient data ($\alpha \leq 10^3 \text{ cm}^{-1}$), was fitted to the relation of the form

$$\alpha = \alpha_0 \exp\left(\frac{\hbar\omega}{E_u}\right)$$

in order to determine the Urbach slope $E_u$. The values obtained for $E_u$ are 112, 118, 125, 158 and 187 meV for $T_s = 20, 100, 150, 170$ and 200 °C, respectively. To our knowledge, there are no data available in the literature for comparison.

### 3.3. Electrical conductivity

Figure 6 presents the variation of conductivity as a function of inverse temperature for a-GaP films prepared at different deposition temperatures $T_s$ and with annealing temperatures $T_a$. For all the films, the conductivity cannot be described by the simple activated form of $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ with a single activation energy $E_a$, but instead exhibits a curvature over the entire temperature range studied, resulting in a continuously varying activation energy. $E_a$ increases from 0.23 eV to 0.36 eV with rising $T_s$ for samples deposited at 20 °C and from 0.11 eV to 0.48 eV after annealing at 270 °C. Values for the pre-exponential factor $\sigma_0$, which normally provides information on the conduction mechanism involved, were obtained from extrapolations of the tangents to the curves at the high-temperature ends; they lie between 2 and 50 $\Omega^{-1} \text{ cm}^{-1}$ for the $T_s$, $T_a$ range of 20-270 °C. The low values of $\sigma_0$, in addition to the curvature of the conductivity plots, rule out the possibility that the conduction is via extended states in either the valence or conduction bands.

A relation of the form $\sigma = \text{constant} \exp\left(-\left(T_0/T\right)^{1/4}\right)$, which expresses variable-range hopping conduction at the Fermi level, has also been tested. The plots of $\ln \sigma$ versus $T^{1/4}$ were linear up to very high temperatures, with $T_0 = 3 \times 10^9$ for as-deposited samples and slightly higher for samples deposited or annealed at a higher temperature. However, the density of states calculated from the values of $T_0$ (assuming a localization length of 10 Å) were unreasonably high, which led us to believe that variable-hopping at the Fermi level is not the mechanism for conduction either.

A possible mechanism for these films seems to be transport taking place in a band tail, in which the conduction path moves down in the tail states at $T$ is lowered, producing a
The conductivity data are quite different from the only conductivity report [15] in the literature on sputtered a-GaP, although the optical-gap values are in good agreement as we mentioned earlier. The measurements of Matsumoto and Kumabe [15] reveal a kink at a critical temperature \( T_c \) of 150 °C, above and below which activated conduction occurs. They have assigned the activation energy above \( T_c \) to intrinsic activation, and that below \( T_c \) (0.42 eV) to the energy between extended and gap states. For flash-evaporated films prepared at room temperature, an exponential variation of conductivity has been observed [22], whereas annealed samples showed an activated behaviour with a single activation energy of 0.4-0.5 eV above room temperature, indicating transport in extended states beyond the mobility edge [10]. However, since the pre-exponential factor was not compatible with extended-state conduction and \( E_a \) was much smaller than half the optical gap \( E_g \), the same results were also interpreted as activated hopping in band tails [21]. At low temperatures, the conductivity data were found to follow the law \( \sigma = \sigma_0 \exp(-E_a/kT)^n \) with \( n = \frac{1}{2} \) and \( T_0 \) of the order of 10^9 K for as-deposited samples, and \( n = \frac{1}{2} \) for annealed samples [21].

In figure 6, a kink can be seen at the high-temperature end of some of the curves. This kink, which was observed only during the heating cycle, was found to occur at 115 °C for samples deposited at room temperature and was shifted towards higher temperatures for samples prepared at high deposition temperatures and in annealed samples. It was attributed to \textit{in situ} annealing effects, which are indicative of a loose structure possibly stemming from the presence of voids in the network. Figure 6 also shows a reduction in the conductivity values for samples prepared at high \( T_s \) and \( T_a \).

Gradually decreasing activation energy. Such a mechanism is also consistent with the low values of \( \sigma_0 \).
4. Discussion

Recently, O'Reilly and Robertson [7] have reported a comprehensive theoretical study on amorphous III–V semiconductors. Using the tight-binding recursion method, they calculated local densities of states of bulk and defect sites. The calculations for the bulk sites show that both the valence- and conduction-band edges should not be affected by any variations in bond angle, and hence theoretically little change in the band gap is expected from this source. However, since experimentally the optical gaps are found to be smaller than those in the corresponding crystals, they invoke the presence of significant numbers of defect states. Two types of defect, namely dangling bonds and wrong bonds, have been studied. It was found for a-GaP that the unrelaxed singly occupied P and Ga dangling bonds give rise to states at or close to the valence- and conduction-band edges, respectively. These bonds can become doubly occupied, whereupon they relax by altering their environment from fourfold to threefold coordination, accompanied by a change of the tetrahedral bond angle of 109° to the preferred angles of 97° and 120° for P and Ga dangling bonds, respectively. In this case, the corresponding states move into the valence and conduction bands. The singly occupied dangling bonds can also interact with one another either forming weak bonds or creating dangling-bond–defect complexes, which are likely to occur at the inner surfaces of voids. The calculations have shown that a complex of two adjacent P dangling bonds produces states nearer to midgap. Furthermore, they have revealed that isolated wrong bonds, i.e. Ga–Ga and P–P, give rise to states near the valence- and conduction-band edges, respectively, whereas clusters of wrong bonds produce states near midgap. Figure 7 illustrates a schematic diagram of the density of states of c-GaP close to the band edges together with the calculated positions of the states that arise from different types of defect possible in an a-GaP network [7]. For sputtered a-GaP, our EXAFS and IR data [5] have shown that there are no or very few wrong bonds in the network. This result is supported by the electron spin resonance (ESR) study of Hoheisel et al [6] who assigned resonance signals to dangling bonds rather than wrong bonds. Therefore, the states due to isolated wrong bonds should be insignificant in the density-of-states picture. On the contrary, since our samples were found to contain voids, we expect a significant number of dangling bonds. Hoheisel et al [6], however, have found the spin density of P and Ga dangling bonds to be of the order of $10^{18}$ and $10^{17}$ cm$^{-3}$, respectively, which suggests that most of the dangling bonds are either relaxed or they have linked to one another in such a way that the remaining number of unpaired electrons is very few.

One can note in figure 7 that the states arising from both the unrelaxed and relaxed dangling bonds have accumulated into the band edges, producing a high density of tail states, which inevitably results in a reduction in the band gap and hence a shift of the absorption edge towards lower energies. However, it is clear that these states alone are insufficient to account for the observed 1.6 eV shift of the edge. In order to explain such a large shift, the states due to defect complexes (e.g. P(db)$_{2}$, Ga(db)$_{2}$), which are located nearer to midgap, should be taken into account. Since these defect complexes cause a small absorption, they can be related to the low-energy part of the absorption-edge spectra, whereas the isolated dangling bonds are associated with the high-energy part of the edge. It is probably easier to eliminate the isolated defects rather than the defect complexes. Hence, as the deposition or annealing temperature is increased, the isolated defects are for the most part annealed out, resulting in a larger shift in the high-energy part of the absorption edge [23] compared to the shift in the low-energy part of the edge back towards the crystalline position. Therefore, the Urbach edge becomes broader with increasing $T_{r}$. If $T_{r}$ is increased above 400 °C, these defect complexes are eventually annealed out and the Urbach edge becomes sharper as demonstrated by Davey and Pankey [8] on evaporated films.
As seen in figure 7, there is no particular gap state with a high density in the pseudo-gap and the residual density of states is very low. This can explain the absence of subgap absorption in the absorption edge of a-GaP, as compared to the case for a-Si:H. It is also consistent with the absence of a variable-range hopping mechanism in the conductivity data. The conductivity, instead, is more likely to be dominated by a transport mechanism taking place in such wide tails. With annealing and increasing deposition temperature, since there will be removal or relaxation of the defects and hence a lowering of the density of states, as seen in figure 7, the conductivity is reduced relative to the room-temperature-deposited sample but hopping in the tail states still occurs. The activation energies found, however, cannot be used to correlate the conductivity data to the optical data in order to obtain information about the position of the Fermi level.

The optical properties of a semiconductor can be correlated to its structural properties using the refractive-index data. This is done by relating the static refractive index \(n(0)\) (at zero energy) to the plasma frequency \(\omega_p\) of the valence electrons by the following expression [25]:

\[
n(0)^2 = 1 + \frac{1}{2}\left(\frac{\hbar\omega_p}{E_g}\right)^2
\]

where \(E_g\) is the Penn gap, which represents an average separation between valence and conduction bands and is therefore a measure of the bond strength. The plasmon energy of a-GaP is found to be smaller than that of the crystal [26], and hence the increase in \(n(0)\) for a-GaP, as shown in figure 3, indicates a reduction in its Penn gap. The figure also shows a decrease in \(n(0)\) for amorphous samples with increasing deposition temperature \(T_d\), which could arise from either a decrease of \(\hbar\omega_p\) or an increase of \(E_g\) or both. In principle, changes in the Penn gap can result from variations in bond length \(E_g \propto r^{-2}\)`, coordination number \((E_g \propto N^2)\) and bond-angle distribution [24]. The first two effects are ruled out by our EXAFS...
Transport and optical properties of a-GaP

data on sputtered a-GaP [5], which revealed, within experimental uncertainties, no changes in bond length and coordination number. However, a considerable reduction in the spread of the bond angle was observed as $T$ increased from 20 to 200 °C. From IR spectroscopy, it was found that this reduction in the spread of the bond angle is associated with a 15% increase in the strength of the Ga-P bond [5]. From the above equation, this should reduce $n(0)$ by about 12%. However, experimentally a decrease of only 5% is found when $T$ is increased from 20 to 200 °C. This suggests that the rise in $E_g$ is partially compensated by an increase in $\hbar\omega$. An increase in $\hbar\omega$ is expected when densification, arising both from a reduction in void concentration and from local atomic rearrangements, occurs with increasing $T$.

The above arguments apply only if the voids are small enough to be accessible to the electrons. If the voids are large, effective-medium theory predicts an overall increase in $n(0)$ when their concentration is reduced by annealing [24, 27]. Although we cannot rule out a contribution of this nature, the experimental result of a decrease in $n(0)$ shows that the effect cannot be dominant. Small-angle x-ray scattering experiments on the samples after annealing would be informative.

5. Conclusions

In this paper, we have presented the electronic properties of nearly stoichiometric sputtered a-GaP films prepared at different deposition temperatures and after annealing. It was shown that the principal optical results and also the conductivity of the samples can be explained by a density-of-states picture taking into account the defect states, mainly dangling bonds and their complexes, located at positions calculated by O'Reilly and Robertson [7].

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References

The absorption edge shifts towards higher energies slowly below $T_\text{c} = 150 \degree C$, but between 150 and 170 $\degree C$ a rapid shift occurs. The dependence of $\alpha$ and other film properties, such as refractive index and spread in bond angle, on $T_\text{c}$ in this way suggests that film growth during deposition is controlled by an activated process in which local surface reorganizations occur above a critical deposition temperature [24].
The effect of varying substrate temperature on the structural and optical properties of sputtered GaAs films

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Abstract. Stoichiometric GaAs films have been prepared by RF sputtering over an appreciable range of substrate temperature $T_s$. The structural and optical properties of these films have been investigated by means of a variety of experimental techniques. Transmission electron microscope (TEM) experiments reveal that for $T_s \geq 70^\circ$C the structure consists of nanocrystals embedded in an amorphous network. EXAFS, XPS and infrared experiments are consistent with each other, indicating that configurational disorder in the amorphous network of the GaAs films decreases as $T_s$ is raised. Most of the disorder relates to bond-angle disorder; the spread in bond angle around Ga atoms is found to be less than that around As atoms for a given substrate temperature. The changes observed in the fundamental absorption edge with increasing $T_s$ are discussed in relation to various possible defects in amorphous GaAs.

1. Introduction

Previous work on amorphous III–V semiconductors has focused mostly on stoichiometric (or near-stoichiometric) compounds. Early x-ray diffraction studies on such compounds [1] showed, as in the case of a-Si and a-Ge, that although they lacked the long-range order of the corresponding crystal structure they retained tetrahedral short-range order. The first continuous random network (CRN) model proposed for the structure of a-Si and a-Ge (by Polk [2]) contains a considerable number of odd-membered rings; in the case of amorphous III–V compounds, this would necessarily introduce a proportion of wrong bonds, i.e. bonds between like atoms. A CRN model introduced by Connell and Temkin [3], consisting only of even-membered rings, was suggested to be possibly more appropriate. Electron diffraction studies on near-stoichiometric a-GaAs, a-GaP, a-GaSb and a-InP by Dixmier et al [4] supported this view.

The adoption of the Connell–Temkin CRN implies a high degree of chemical order. Further information on the extent of chemical ordering in amorphous III–V materials has been obtained from a variety of experiments. On the basis of EXAFS [5] and optical [6] measurements, Theye and co-workers concluded that flash-evaporated (stoichiometric) a-GaAs contained few wrong bonds. This is in general agreement with an EXAFS and optical study by Baker et al [7] on sputtered a-Ga$_{1-x}$As$_x$ (0.5
Although the inability to distinguish between Ga and As scatterers somewhat hampered EXAFS analysis; the extension to As-rich specimens allowed the authors to detect a change in coordination around As atoms from about four at compositions close to stoichiometry towards about three in very As-rich films (Ga atoms remained fourfold coordinated over the composition range investigated). In the case of a-GaP, however, contrary results have been obtained by different groups. EXAFS studies [5,8] on approximately stoichiometric flash-evaporated a-GaP provide evidence for both Ga-Ga and P-P bonds, with the proportion of wrong bonds apparently as high as 25%. The electron diffraction experiments of Dixmier et al. [4] suggest that this partial chemical disorder is not forced on the network by topological considerations; instead, the authors attribute it to 'extrinsic' disorder arising from the particular method of sample preparation. Indeed, recent EXAFS and optical experiments on sputtered (approximately stoichiometric) a-GaP [9] indicate a much higher degree of chemical ordering, with no wrong bonds detectable (at least within the sensitivity of the EXAFS and infrared experiments carried out in this study).

The preparation conditions, in particular the substrate temperature, necessary for the deposition of amorphous (as opposed to microcrystalline) III-V materials differ quite widely among the various reports in the literature. In the case of GaAs, Paul et al. [10] found that films sputtered from an Ar/H2 plasma were partially crystalline when the substrate temperature was around or above 25 °C; a temperature of 4 °C was required to produce fully amorphous material. However, Hargreaves et al. [11] were able to prepare a-GaAs by sputtering at up to 30 °C. Furthermore, MBE-deposited GaAs can apparently be prepared in amorphous form at substrate temperatures as high as 200 °C or more [12]. In view of the differences in preparation conditions mentioned above, it appeared to us to be of interest to prepare a set of sputtered GaAs films over an appreciable range of substrate temperatures \( T_s \), in an attempt to determine the point at which the deposited films first show signs of microcrystallinity (at least for our deposition system). There appear to have been few systematic investigations into the effect on the structural and electronic properties of amorphous III-V semiconductors of varying preparation conditions such as \( T_s \), which would be expected to produce changes in the configurational disorder of the amorphous network (i.e. variations in bond angle and bond length). The second principal aim of our work was therefore to study the effect of reducing the degree of configurational disorder in amorphous GaAs films, through increases in \( T_s \). In what follows, we present and discuss the results of TEM, EXAFS, optical (including infrared) and XPS measurements on a set of GaAs films prepared over a wide range of substrate temperature.

2. Preparation

The GaAs films were prepared by rf sputtering in an argon atmosphere at a pressure of ~4 mTorr. The base pressure of the system was 2 × 10^-7 Torr or better. An rf power of 75 W was applied to the target which was a crystalline GaAs wafer, 2 inches in diameter. The sputtered films were deposited onto a variety of substrates: Corning 7059 for optical measurements, c-Si for infrared work, mylar for EXAFS experiments and Al foil for composition and XPS measurements. Substrate temperatures \( T_s \) above and below room temperature were achieved by means of a substrate table heater and temperature controller and by water-cooling respectively. The \( T_s \) range investigated
was 14 °C-240 °C. The thicknesses of the deposited films lay between 0.09 and 0.16 μm.

3. Microstructure

The composition of the GaAs films was determined by energy dispersive x-ray analysis (EDAX) using a DS130 scanning electron microscope (SEM). All samples were found to be essentially stoichiometric, with deviations from stoichiometry of no more than 3 or 4 at.%. No significant variations in composition were found between different areas of the same sample, suggesting that the GaAs films were compositionally homogeneous, at least down to a scale of 5 μm x 5 μm (the area probed by the EDAX measurements).

![Figure 1. Electron diffraction pattern for GaAs sample prepared at 53 °C.](image1)

![Figure 2. Electron diffraction pattern for GaAs sample prepared at 72 °C.](image2)

The microstructure of the sputtered GaAs samples was also investigated by means of transmission electron microscopy (TEM) experiments, carried out using a Jeol JEM 100 CX instrument. For each sample, the composition was checked in situ by EDAX prior to carrying out TEM measurements. In the case of films prepared at substrate
temperatures of ~50 °C or less, the diffraction patterns consist of a few diffuse rings, as in figure 1, confirming the amorphicity of these samples; micrographs recorded in real space, as opposed to reciprocal space, show no evidence for any nanocrystals of diameter greater than 20 Å, the resolution of the microscope. At a slightly higher substrate temperature $T_s$ of ~70 °C, the rings in the electron diffraction pattern become much thinner with brighter regions (see figure 2), while the micrograph reveals the presence of regularly distributed and similarly sized inhomogeneities (presumed to be nanocrystallites) of ~20 Å in diameter. As $T_s$ is further raised, the rings fade and bright spots appear in the diffraction patterns, as in figure 3, which indicate an increasing degree of microcrystallinity. The micrographs reveal that the size of the nanocrystallites increases with rising $T_s$, although from 120 °C onwards they become more irregularly distributed and show a greater variation in size. The average nanocrystallite diameter reaches 100 Å at $T_s \approx 180$ °C. Without a clear idea of the thickness of the TEM samples, it is difficult to estimate the volume fraction occupied by the nanocrystals; nevertheless, the micrographs indicate that even for the samples deposited at highest $T_s$, amorphous material accounts for a substantial fraction. The diffraction pattern obtained from the sample prepared at 180 °C yielded lattice spacings which correlated well (to within ±0.1 Å) with values obtained for a c-GaAs wafer.

4. Experimental details

4.1. EXAFS

EXAFS measurements on the GaAs samples were carried out using the 2 GeV synchrotron radiation source at Daresbury Laboratory. The x-ray absorption coefficient $\mu$ was measured about both Ga and As K edges on station 7.1, which has a Si(111) double crystal monochromator. Measurements were made using standard transmission geometry, the beam intensities being measured by ionization chambers containing an Ar/He gas mixture. Harmonic rejection was set at 70% by detuning the monochromator. Samples were deposited onto low-absorbing mylar substrates for EXAFS studies; in order to obtain the necessary sample thickness, several layers were stacked together.
The EXAFS spectra were extracted from the measured absorption spectra $\mu(E)$ using the standard Daresbury program EXBACK [13]. This fits low-order polynomials to the pre- and post-edge data to represent the smoothly varying background absorption; these are then subtracted from the measured spectra to yield the EXAFS spectra $\chi(E)$.

A simplified expression, based on plane-wave theory, for the EXAFS function for K edges is given by

$$\chi(k) = -\frac{A(k)}{k} \sum_j \left( \frac{N_j}{\sigma_j^2} \right) f_j(\pi) \exp\left(-2\sigma_j^2 k^2\right) \exp(-2r_j / \lambda) \sin(2kr_j)$$

$$+ 2\delta + \psi$$  \hspace{1cm} (1)

where $k$, the photoelectron wavevector, is related to photon energy by

$$\frac{k^2 \sigma^2}{2\pi} = (\omega - E_{\text{edge}}) + E_0.$$  \hspace{1cm} (2)

The energy of the edge $E_{\text{edge}}$ is taken to be the point at which the first derivative of the absorption is a maximum. $E_0$, an energy offset, is the difference in energy between a $k = 0$ photoelectron and the lowest unoccupied energy level. $N_j$ is the number of atoms of type $j$ at a distance $r_j$ from the absorbing atom, each of which has a back-scattering amplitude $f_j(\pi)$ (a function of both atom type and photoelectron energy). The factor $A(k)$ corrects for amplitude reductions due to events that result in absorption but not EXAFS, such as multiple electron excitations. In practice, $A(k)$ is taken to be independent of energy. The first exponential term in equation (1) is the Debye-Waller factor, describing the effects of vibrational and static disorder; $\sigma_j^2$ is the mean square variation in bond length $r_j$. The second exponential factor in the expression for $\chi$ represents losses due to inelastic scattering, $\lambda$ being the elastic mean free path of the photoelectron. This is modelled in terms of a constant imaginary part of the potential $V_i$ so that $\lambda = kV_i$. This reproduces the $E^{3/2}$ variation of electron mean free path. $\delta$ is the phaseshift experienced by the photoelectron during its passage through the central atom potential, while $\psi$ is the phase of the back-scattering factor.

Values for structural parameters such as $r_j$, $N_j$, etc can be obtained from the experimental EXAFS by fitting the experimental data to calculated EXAFS functions. In the case of our GaAs samples, structural information was obtained by multi-parameter fitting the experimental EXAFS spectra to EXAFS functions calculated using the fast curved-wave theory of Guzman et al [14]. The curve-fitting procedure was carried out with the aid of the EXCURV90 program [13] (readily available at Daresbury), which uses a least-squares analysis. Scattering phaseshifts were calculated within the program. $A(k)$ and $V_i$ were obtained from an EXAFS study on a crystalline GaAs sample, which was also used to check the phaseshifts. The analysis program also contains a statistical package which gives the uncertainties on the structural parameters (often strongly correlated). We always quote the limits of the 95% confidence region, i.e. the $\pm 2\sigma$ uncertainties, where $\sigma$ is the standard deviation.

4.2 XPS

X-ray photoelectron spectroscopy (XPS) data were taken from the as-grown GaAs films on aluminium substrates and from a crystalline GaAs wafer, using Al Ko
radiation at 1486.6 eV in a VG Escalab spectrometer. Scans were made over a binding energy range of 0–1200 eV and were calibrated using the oxygen $1s$ line at 532 eV and the oxygen Auger line at 976 eV. The absolute energy resolution (FWHM or full-width-at-half-maximum) of the instrument was 1.0 eV. The samples were not sputter-cleaned as this causes structural rearrangement. Since the films were not grown in situ, surface oxidation is evident in the core level spectra. At this resolution, however, it is possible to separate out the oxygenated components of the levels since the oxides produce chemical shifts of the order of 1 eV and 4 eV for Ga and As respectively.

4.3. Optical absorption measurements

Infrared transmission spectra for the GaAs films were recorded on a Perkin-Elmer 580B double-beam spectrophotometer over the wavenumber range 4000–180 cm$^{-1}$. The sample chamber was thoroughly purged with dry air during data-taking in order to reduce absorption due to water vapour.

Measurements at visible and near-infrared photon energies were carried out using a Perkin-Elmer 330 double-beam spectrophotometer, the absorption coefficient $\alpha$ being obtained by standard transmission and reflection techniques. $\alpha$ was also measured by PDS (photothermal deflection spectroscopy) in order to extend the range of measurable absorption coefficients to lower values than could be obtained by the transmission and reflection measurements.

5. Results

5.1. EXAFS

Examples of As-edge EXAFS spectra (weighted by $k^2$) for the sputtered GaAs films, together with the associated Fourier transforms, are given in figure 4. Data for a crystalline GaAs sample are also included. The noise level was sufficiently low to give a usable $k$ range out to beyond 13 Å$^{-1}$, except for the crystalline sample where a larger data range was possible. The Fourier transforms are phase-corrected (taken with respect to $2kr + 26 + \psi$) so that the peaks appear at the true interatomic distances. For the sample prepared at 14 °C, the virtual absence of a second peak in the Fourier transform indicates considerable configurational disorder in the structural network. At higher substrate temperatures, a second peak (although a rather small one) is observed which suggests a reduction in the amount of disorder; this will be discussed in more detail later. The second peak in the Fourier transforms of the sputtered samples was always found to be much smaller than for the crystalline case, even at the highest substrate temperatures studied.

A problem associated with the data analysis (outlined in section 4.1) is that Ga and As atoms have very similar back-scattering amplitudes and phaseshifts, since they are very close to one another in atomic number. This means that they are virtually indistinguishable as scatterers. We have therefore assumed that around each Ga or As absorbing atom there is one basic atom type X, where X denotes either a Ga or an As atom. Changing X from As to Ga (or vice versa) hardly affected the fitted structural parameters, altering them by much less than their uncertainties. However, in spite of the difficulty referred to above, the data in a structural study by us on a-Ga$_{x}$As$_{y}$ [7] were not inconsistent with there being relatively few wrong bonds (like-atom bonds)
Structural and optical properties of sputtered GaAs films

Figure 4. As-edge EXAFS spectra (weighted by \( k^2 \)) and associated Fourier transforms (FT) for (a) GaAs sample prepared at 14 °C, (b) GaAs sample prepared at 122 °C and (c) crystalline GaAs sample. The full curves represent the experimental data; the broken curves give the best fit.

at stoichiometry. In fact, by calculating Penn gaps from measured refractive indices and plasmon energies, it has recently been demonstrated that a-GaAs (and a-InP) appear to be chemically ordered [15]. (This technique has been successfully applied to the amorphous alloys SiN [16] and SiO [17], both of which were found to be chemically ordered.) Furthermore, our XRS data (presented in section 5.2) strongly suggest that the sputtered GaAs samples are well chemically ordered.

Analysis of EXAFS data from the GaAs crystal yielded nearest-neighbour distances of 2.43 ± 0.02 Å (from Ga-edge data) and 2.42 ± 0.02 Å (from As-edge data), with a coordination \( N \) and Debye-Waller factor (from both edges) of 4.0 ± 0.5 and 0.005 ± 0.001 Å\(^2\) respectively when the amplitude parameter \( A(k) \) was set at 0.7 and the mean free path parameter \( \Lambda \) at ~3 eV. Both sets of data are consistent, although the deduced bond length is slightly short; the bond length in c-GaAs is 2.45 Å. This points to a slight error in our phaseshifts but does not, however, affect the conclusions in this study.

Fitting the first peak in the Fourier transforms for the sputtered GaAs samples proved fairly straightforward. With values of \( A(k) \) and \( \Lambda \) identical to those used...
for the crystal, both Ga- and As-edge data yielded bond lengths $r_1$ of 2.42 or 2.43 Å (±0.02 Å), a coordination $N_2$ of 4±1 and a Debye-Waller factor $\sigma_r^2$ of 0.006 ± 0.001 Å² in all cases. No significant variation with substrate temperature was found for any of the above parameters. This is in very good agreement with previous work [7] where it was also found that the fitted (first-shell) structural parameters for stoichiometric a-GaAs were nearly identical to those for c-GaAs. In particular, the close similarity in Debye-Waller factors between the two phases indicates that the major contribution to $\sigma_r^2$ in the amorphous samples is thermal or vibrational and that there is little static disorder in the bond length. Most of the configurational disorder in our GaAs samples is therefore associated with bond-angle disorder.

As we have already seen in figure 4, a second peak appears in the Fourier transforms of the EXAFS spectra as the substrate temperature $T_s$ is increased. Clearly, fitting such small features with a reasonable degree of certainty is difficult. In an attempt to provide some quantitative analysis, we allowed the second-shell distance $r_2$ and Debye-Waller factor $\sigma_r^2$ to vary in the fitting procedure but kept the second-shell coordination $N_2$ fixed at 12 (as in c-GaAs). Analysis of As-edge EXAFS spectra for the GaAs films yielded $\sigma_r^2$ values which decreased as $T_s$ was raised. This is illustrated in figure 5, which shows $\sigma_r^2$ as a function of $T_s$. (EXAFS measurements could not be carried out for samples deposited above 200 °C since the mylar substrates became unstable at these temperatures.) Values for $r_2$ (corresponding to the As-As distance assuming chemical ordering) lay between 3.95 and 3.99 Å. The uncertainties in $\sigma_r^2$ and $r_2$ are ±0.01 Å² and ±0.06 Å respectively. Ga-edge data from the crystalline GaAs sample gave second-shell parameters $r_2$ and $\sigma_r^2$ of 3.95 ± 0.03 Å and 0.012 ± 0.004 Å² respectively. The second-shell peaks in the Fourier transforms of Ga-edge spectra were much smaller than for the corresponding As-edge data and were consequently more difficult to fit. In fact, second-shell fits were only possible for $T_s \approx \sim 70$ °C; the deduced $\sigma_r^2$ values are included in figure 5. Although larger than the values deduced from As-edge EXAFS spectra, they appear to follow the same trend. The fitted values of $r_2$ were similar to those found from the As edges, lying between 3.95 and 3.99 Å. Ga-edge EXAFS from the GaAs crystal gave $r_2 = 3.97 ± 0.03$ Å and $\sigma_r^2 = 0.014 ± 0.005$ Å².

The fitted values of the interatomic distances and Debye-Waller factors allow us to calculate the bond angle $\theta$ and variation in bond angle $\Delta \theta$ from simple trigonometric considerations. Both As- and Ga-edge data give $\theta = 109^\circ$ or 110° in all cases, confirming the tetrahedral nature of the structural network. $\Delta \theta_{Ga}$ deduced from As-edge EXAFS (i.e. the variation in bond angle around Ga atoms) is found to decrease from ±5° at substrate temperatures around room temperature to ±7° at $T_s \approx 180$ °C. Ga-edge data indicate that $\Delta \theta_{As}$ (the bond-angle variation around As atoms) decreases from a value which is too large to measure at the lowest $T_s$ values studied to ±9° at $T_s \approx 180$ °C. It should be pointed out that the deduced values of $\Delta \theta$ contain both structural and thermal contributions. Analysis of EXAFS measurements on c-GaAs, which is assumed to have only a thermal contribution to $\Delta \theta$, gave $\Delta \theta$ values of ±5° around both atom types. (Note that the second-shell peak in the Fourier transform disappears when $\Delta \theta$ is approximately double that in the crystal.

It has therefore been possible to show directly from EXAFS measurements that the bond-angle disorder around both atom types in the GaAs films decreases with increasing substrate temperature $T_s$. Over the range of $T_s$ investigated, the variation in bond angle around Ga atoms is less than that around As atoms at a given
Figure 5. Second-shell Debye-Waller factor $\sigma^2$ as a function of $T_s$ (substrate temperature during deposition) for both Ga- and As-edge data. The uncertainties in $\sigma^2$ are ±0.010 Å$^2$.

Figure 6. Infrared transmission spectra for sputtered GaAs samples. The substrate temperatures during deposition label the curves.
Tetrahedral structural units with Ga atoms at the centre are therefore less distorted than As-centred ones. Although TEM experiments revealed the presence of nanocrystallites for \( T_r \approx 70 \) °C, the appearance of a second shell in the Fourier transforms of the EXAFS spectra reflects the increasing configurational order of the amorphous network rather than the appearance of the tiny nanocrystallites. For the sample prepared at \( \sim 180 \) °C are still appreciably larger than the corresponding values found for c-GaAs.

5.2. Core level spectra

The largest changes (with increasing \( T_r \)) in the XPS spectra of the GaAs films are expected in the valence band. However, the spectrometer resolution was relatively low compared to the energy separation of the observed features, and in this binding-energy range the signal-to-noise ratio was also low. We have therefore concentrated on information concerning the core levels, in particular the Ga and As 3d levels.

The Ga and As 3d spectra are similar for all sputtered and crystalline wafer samples; their positions and widths are detailed in table 1. As \( T_r \) is raised, both Ga and As levels show no changes in chemical shift (within experimental error) from those found for crystalline GaAs. This indicates that very few wrong bonds are present in all the samples, even those prepared at low \( T_r \). There is, however, an indication from the energy differences of the Ga and As 3d levels (which are more accurate since the errors involved are mostly systematic) that there could be a small monotonic reduction in the density of wrong bonds with increase in \( T_r \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_r = 53 ) °C</th>
<th>( T_r = 72 ) °C</th>
<th>( T_r = 179 ) °C</th>
<th>Crystalline wafer</th>
<th>Ga*</th>
<th>As*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga 3d</td>
<td>19.2</td>
<td>19.3</td>
<td>19.3</td>
<td>19.3</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>2.0</td>
<td>2.0</td>
<td>1.8</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spin split</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga(3d)</td>
<td>20.3</td>
<td>20.4</td>
<td>20.5</td>
<td>20.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As 3d</td>
<td>41.2</td>
<td>41.2</td>
<td>41.2</td>
<td>41.1</td>
<td>41.8</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>1.9</td>
<td>1.9</td>
<td>1.7</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spin split</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(3d)-Ga 3d</td>
<td>22.0</td>
<td>21.9</td>
<td>21.9</td>
<td>21.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.

Core level energies are given with respect to the Fermi level. All values are in eV and are ± 0.1 eV. Values marked * are from [38].

The FWHM is governed not only by the instrumental linewidth but also by the spread in bond angle, i.e. the contribution from second-nearest neighbours. We find that the FWHM decreases monotonically with increasing \( T_r \), implying a monotonic reduction in bond-angle disorder with increase in \( T_r \) in line with the EXAFS data described in the previous section. The data suggests that even for the sample prepared at 179 °C, the bond-angle disorder is still appreciably greater than that in the crystalline material. Although indicated by the data, it is not possible to say with certainty that the spread in bond angle \( \Delta \theta \) for Ga-centred tetrahedra is less than for As-centred tetrahedra, nor at what substrate temperature the main changes occur, because of the experimental errors involved. However, because of the reduction in FWHM, spin splittings can be measured for the samples deposited at higher \( T_r \), and these are in line with those found for the crystalline material.
The findings described above are in overall agreement with the earlier work of Shevchik et al [19] who presented data for Ga 3d levels in amorphous and crystalline GaAs, deposited at 20 °C and 225 °C respectively, and also with the data of Senemaud et al [20] for an amorphous sample of GaAs which was then annealed to achieve crystallinity.

It would of course be of great interest to calculate \textit{ab initio} the contribution to the chemical shifts expected due to the presence of wrong bonds and, similarly, the line broadening expected due to bond-angle disorder. Such calculations would, however, be very complicated and have not been attempted here. By decomposing the potentials seen by the core electrons into three parts involving that due to core charges on central atoms and nearest neighbours, bonding charge and a lattice contribution, it is possible to get at least a qualitative picture of the changes expected. In the elemental solid the terms will sum to zero, while in the stoichiometric crystal the cationic line shift is measured to be \(-1\) eV with respect to the Fermi level. Wrong bonds are expected to alter all three terms, the variation in bond length and sign of the charge causing the largest changes. Assuming a linear scaling, a shift of 0.1 \pm 0.1 eV between the amorphous and crystalline samples (as measured) implies 10 \pm 10% wrong bonds in the amorphous material. From our other data, it seems likely that the lower bound represents the more probable situation.

Bond-angle disorder is expected to change only the lattice term. Assuming a purely Coulombic interaction and a charge transfer of 0.25 electrons, a broadening of \(E'(eV) = \frac{14.4(q/r)}{r}\) may be expected, where \(q\) is the charge transfer in electrons and \(r\) is the distance from the outer core levels to the second-nearest neighbours in Ångströms. For the Ga 3d levels, this suggests broadenings of around 0.3 eV for a \(\Delta \theta \) of \(\pm 11^\circ\) (assumed value for \(T_s = 53^\circ C\)), 0.2 eV for a \(\Delta \theta \) of \(\pm 9^\circ\) (\(T_s = 179^\circ C\)) and 0.1 eV for \(\pm 5^\circ\) (crystal). These values correspond within error to the changes in FWHM given in table 1.

5.3. Infrared data

Figure 6 shows infrared transmission spectra for some of the GaAs films over the wavenumber range 350-180 cm\(^{-1}\). The strong absorption mode observed in each case is the Ga–As TO normal mode, which in c-GaAs is located at 268 cm\(^{-1}\). No other features were observed over the entire range of wavenumbers available to us (4000-180 cm\(^{-1}\)) for any of the samples.

For the samples deposited at the two lowest temperatures, the TO mode is broad and centred at \(~250\) cm\(^{-1}\). This is in good agreement with previous studies on a-GaAs which show a broadening and shift to lower wavenumber compared to the crystalline case [7,21]. As can be seen from figure 6, the overall effect on the TO mode of raising \(T_s\) is a shift in position towards the crystalline value along with a sharpening and increase in intensity. For the sample prepared at \(-50^\circ C\) (still completely amorphous according to TEM), the peak has shifted to \(~270\) cm\(^{-1}\) although it remains broad on the lower-wavenumber side. As \(T_s\) is further raised, the peaks continue to sharpen, becoming considerably more symmetric, although from figure 7, which shows the FWHM versus \(T_s\), little further sharpening occurs above about 100 °C. Despite the appearance of the nanocrystallites at around 70 °C, the rapid shift to higher wavenumber and the sharpening of the Ga–As TO mode reflects the reduction in configurational (bond-angle) disorder of the amorphous network.

For the samples prepared at the highest substrate temperatures, no additional modes (as would be expected in c-GaAs) were observed.
5.4. Optical gap and the absorption edge

The optical absorption coefficient \( \alpha \) for the GaAs samples, measured by transmission and reflection methods as a function of photon energy \( h\omega \) in the visible and near-infrared region of the electromagnetic spectrum, was fitted to the Tauc relation

\[
(\alpha h\omega)^{1/2} = B(h\omega - E_{\text{opt}})
\]

in order to define an optical band gap \( E_{\text{opt}} \). \( B \) is a constant. Figure 8 shows the deduced values of \( E_{\text{opt}} \) plotted as a function of \( T_c \). For samples deposited at around room temperature, \( E_{\text{opt}} \) is approximately 0.95 eV which agrees reasonably with previous optical studies on a-GaAs [6,7]. Bond-angle disorder in amorphous semiconductors normally give rise to a decrease in band gap; the gradual rise in \( E_{\text{opt}} \) with increasing \( T_c \) therefore appears to be consistent with a reduction in bond-angle variation. However, as O'Reilly and Robertson [22] have pointed out, the bandgap in amorphous III-V semiconductors may also be affected by defect states such as...
dangling bonds; we shall discuss this point further in section 6. It should be noted that the optical gap for the samples prepared at highest $T_e$ is still considerably less than the value in c-GaAs ($\sim$1.5 eV).

Our GaAs films were fairly thin, all film thicknesses lying between 0.09 and 0.16 $\mu$m. This tended to restrict the measurable range of $\alpha$ to rather high values. As mentioned in section 4.3, PDS experiments enable the measurement of lower absorption levels than are usually possible by conventional transmission and reflection techniques. Figure 9 shows examples of absorption curves (log $\alpha$ versus $h\nu$) obtained by PDS, including the data obtained by transmission and reflection measurements, for the sputtered GaAs samples. The higher-energy part of the absorption curves ($\alpha \gtrsim 10^9$ cm$^{-1}$) shifts systematically to higher photon energy with increasing $T_e$, which is consistent with the observed increase in $E_{\mathrm{U}}$ gap. However, at lower absorption levels, there is little or no such shift. The absorption edge therefore appears to broaden as $T_e$ is raised; the Urbach edge parameter $E_{\mathrm{U}}$, obtained by fitting the edge to the exponential relation

$$\alpha = \alpha_0 \exp\left(h\nu/E_{\mathrm{U}}\right)$$

increases gradually with rising $T_e$, from 50 meV for $T_e = 14$ °C to 74 meV for $T_e = 223$ °C, before increasing more rapidly to 120 meV for the sample prepared at 240 °C. At first sight, this broadening appears to be at odds with our other data as an increase in order normally gives rise to a sharpening of the absorption edge in amorphous semiconductors. However, as we shall discuss in the following section, this may not necessarily be so in amorphous III–V semiconductors.

![Figure 9. Absorption edge spectra for GaAs films sputtered at (a) 14 °C and (b) 240 °C.](image)
amorphous to a nanocrystalline structure with increasing \( T_s \) over the range 20-155 °C; unfortunately, no \( E_g \) data are given for these samples.

6. Discussion

TEM experiments suggest that there is a relatively sharp transition in the structural nature of the sputtered GaAs films between (i) a purely amorphous network for substrate temperatures \( T_s \leq 50 \) °C and (ii) an amorphous network in which there are tiny embedded nanocrystallites for \( T_s \geq 70 \) °C. The size of the nanocrystallites increases gradually with rising \( T_s \). Despite the appearance of such nanocrystallite inhomogeneities at relatively modest substrate temperatures, EXAFS and optical (including infrared) measurements all show that there is still much amorphous material in the structural network over the whole \( T_s \) range studied.

The structural picture for our sputtered GaAs films of nanocrystals embedded in an amorphous network (for \( T_s \geq 70 \) °C) is in good agreement with work by Zallen and co-workers [26-29] who, by means of Raman scattering experiments, investigated the structure of nanocrystalline GaAs layers produced by ion-bombarding crystalline wafers. The Raman spectra of such samples exhibited two-mode behaviour, with the crystalline LO (longitudinal optic) line superimposed on the Raman spectrum of a-GaAs (three broad overlapping bands, centred at approximately 70, 150 and 250 cm\(^{-1}\)). (Back-scattering geometry was adopted on (100)-oriented wafers so that only the \( k = 0 \) LO phonon, situated at 292 cm\(^{-1}\), was Raman active in the crystal.) These results were taken as evidence that the ion-bombarded GaAs layers consisted of a fine-scale mix of a-GaAs and GaAs nanocrystals. From an asymmetric broadening and slight downward shift in wavenumber of the LO line with increasing ion bombardment, estimates were obtained for the size of the nanocrystals; values of between 50 and 100 Å were obtained [29] for various samples, in reasonable agreement with values measured by TEM for our sputtered samples.

Our EXAFS, XPS and infrared data confirm that raising the substrate temperature leads to a decrease in configurational disorder in the amorphous network of GaAs films. The EXAFS results not only demonstrate that most of this disorder relates to variation in bond angle (as opposed to variation in bond length) but also allow us to directly determine the bond-angle spread \( \Delta \theta \). Our data show that \( \Delta \theta \) around both atom types decreases as \( T_s \) is raised but that, at a given \( T_s \), \( \Delta \theta \) around Ga atoms is less than that around As atoms. With the assumption of a good degree of chemical ordering, this difference implies that tetrahedral units in the structure with Ga atoms at the centre become less distorted more easily than As-centred ones. A similar situation has recently been found in sputtered a-GaP films [9], the group V atom showing the greater spread in bond angle.

As was mentioned in section 5.4, bond-angle disorder normally causes some decrease in band gap in amorphous semiconductors. The increase in \( E_{opt} \) (figure 8) and the changes in the absorption curves at higher absorption levels (figure 9) with increasing \( T_s \), therefore appear to be consistent with improving order at higher \( T_s \). However, calculations by O'Reilly and Robertson [22] on the local electronic structure of bulk and defect sites in amorphous III–V compounds (using the tight-binding recursion method) suggest that bond-angle disorder should result in hardly any decrease in band gap for these materials. If this is so, an alternative explanation is required to explain our absorption edge data.
The calculations by the above authors [22] suggest that dangling-bond states in a-GaAs are situated at or close to the band edges, with As dangling bonds near the valence band edge and Ga dangling bonds near the conduction band edge. This situation favours charge transfer from the higher Ga to the lower As dangling-bond level to produce a doubly occupied As level and an empty Ga level. Such transfer causes a downward shift of the As level and an upward shift of the Ga level tending to expel them from the gap. It also results in a relaxation of the bond angle at the dangling-bond sites from the tetrahedral bond angle towards the preferred angles of 97° for As and 120° for Ga. In fact for all the amorphous III-V compounds investigated, O'Reilly and Robertson [22] calculated that relaxed anion dangling bonds occur at or below the valence band edge and relaxed cation dangling bonds occur at or above the conduction band edge. Furthermore, they suggested that such materials should contain a higher proportion of dangling bonds than a-Si. Although a fraction of about 3-4% broken bonds is expected in a-Si in order to reduce strain in the random tetrahedral network, most of these reconstruct to form weak bonds; in amorphous III-V compounds, which also have tetrahedral networks, a similar fraction of dangling bonds might be expected but it is suggested that these now relax rather than reconstruct. The picture described above for dangling bonds in a-GaAs may help to explain the absorption edge data for our GaAs films. As was seen in section 5.4, the optical gap and the region of the absorption curves corresponding to higher absorption levels shifted to higher energy with increasing $T_e$, which is not perhaps surprising for an amorphous semiconductor.

The work of O'Reilly and Robertson [22] also predicts the energy levels of various wrong-bond defects in a-GaAs (and other related compounds). Isolated As-As bonds are calculated to give states just below the conduction band edge while isolated Ga-Ga bonds are predicted to give states just below the valence band edge. Clusters of wrong bonds and defect complexes are expected to produce states nearer midgap. If these calculations are correct, they suggest that the lower-energy part of our absorption curves (figure 9) may be associated with wrong-bond defects. The associated absorption levels are low which implies that we would be dealing with relatively small numbers of such defects (less than could be detected by EXAFS of infrared measurements at any rate). As we saw in section 5.4, the lower energy region of our absorption curves was much less affected by changing $T_e$ than the higher-absorption part; this would indicate that the density of wrong-bond defects is much less affected by increasing $T_e$ than the dangling bond density. If so, this could account for the observed broadening (increase in $E_g$) in our absorption edges as $T_e$ is raised.

7. Conclusions

The structural (tetrahedral) network of sputtered GaAs films is purely amorphous for substrate temperatures $T_s$ up to about 50 °C. For $T_s > 70 °C$, the structure consists of nanocrystals embedded in an amorphous network. The average size of the nanocrystals increases as $T_e$ is raised, reaching ~100 Å at ~180 °C.

Configurational disorder in the amorphous network of the GaAs films decreases with increasing $T_e$. Most of the disorder is associated with bond-angle (rather than bond-length) variation. For a given $T_e$, the spread in bond angle around Ga atoms is less than that around As atoms.
If the band gap in GaAs is little affected by bond-angle disorder (as some calculations suggest), the changes observed in the absorption edge spectra with increasing $T_e$ are consistent with a reduction in dangling-bond density at higher $T_e$.

References

Structural and optical properties of amorphous In$_{1-x}$P$_x$ films

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Structural and optical properties of amorphous In$_{1-x}$P$_x$ films


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Abstract

In$_{1-x}$P$_x$ films have been prepared by rf sputtering with compositions in the range $0.4 < x < 0.9$. The samples are completely amorphous for $x > 0.5$ but In-rich films contained crystallites. Extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy measurements indicate that there is chemical disorder in the structural network of the a-In$_{1-x}$P$_x$ films, although chemical ordering is predominant. Optical absorption data are found to be consistent with this assertion. Partial coordination numbers, deduced from the EXAFS measurements, are interpreted using thermodynamic arguments.

1. Introduction

Early X-ray diffraction studies on stoichiometric amorphous III–V semiconductors [1] showed that, like amorphous silicon (a-Si) and germanium (a-Ge), these materials retained tetrahedral short range order. Continuous random network (CRN) models proposed for the structure of a-Si [2] contain an appreciable number of odd-membered rings, which would necessarily introduce a proportion of 'wrong' bonds, i.e., like-atom bonds in the case of III–V compounds. A CRN model containing only even-membered rings was introduced by Connell and Temkin [3] in order to avoid this problem. The data of electron diffraction experiments on several approximately stoichiometric amorphous III–V compounds by Dumier et al. [4] were consistent with the expectations of the Connell–Temkin CRN.

A high degree of chemical order is implied by the adoption of the Connell–Temkin CRN. This ordering has led to attempts to investigate the degree of chemical order in amorphous III–V compounds by a variety of experimental techniques. In the case of GaAs, Ga–Ga and As–As bonds are difficult to resolve from heteropolar Ga–As bonds by X-ray methods since the close-ness in atomic number of Ga and As means that these atoms scatter virtually identically. Data from extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) core level studies on both sputtered [5,6] and flash-evaporated [7,8] material are consistent with a high degree of chemical ordering. Optical absorption data by Baker et al. [6], for a-GaAs films sputtered at various deposition temperatures, are consistent with the suggestion by...
O'Reilly and Robertson [9] that dangling bond defects may be more significant in this material than wrong bond defects. Less information is available on a-InP, the subject of this study. Measurements of core levels by XPS [10] and of valence band spectra by ultraviolet photoelectron spectroscopy (UPS) [11] indicate that the structure of flash-evaporated material has chemical disorder. However, XPS data from Shevchik et al. [12] provide evidence for a higher degree of chemical ordering in sputtered samples.

In this study, EXAFS and XPS measurements are used to investigate the structure and extent of chemical ordering in sputtered a-In$_{1-x}$P$_x$ films, not only at stoichiometric compositions but over the composition range defined by $0.4 < x < 0.9$. Microstructure in the deposited films is investigated by means of small-angle X-ray scattering (SAXS). The results of optical studies carried out on the same samples are correlated with the structural information obtained from the EXAFS and XPS experiments.

### 2. Preparation

Films of a-In$_{1-x}$P$_x$ were prepared by rf sputtering from a 99.999% pure crystalline InP target of 4 in diameter. The sputtering gas was argon, the pressure during deposition being approximately 4 mTorr. Prior to admitting the sputtering gas, the system was evacuated to a base pressure of $2 \times 10^{-7}$ Torr. The rf power applied to the target was 200 W, at a frequency of 13.56 MHz. In all cases, water-cooling ensured a substrate temperature of approximately 20°C during deposition. A variety of substrates was included in each deposition run: Corning 7059 glass for optical absorption measurements, polished c-Si wafer for infrared experiments, Al for XPS and mylar and copper substrates for EXAFS studies. Samples deposited on mylar were also used in the SAXS experiments.

The composition, $x$, in the a-In$_{1-x}$P$_x$ films could be altered by adding P pieces to the sputtering target, thereby allowing us to produce P-rich samples. Some In-rich samples were also prepared since films deposited at room temperature from a pure target (i.e., with no additional P pieces) were somewhat In-rich ($x = 0.42$). We have therefore been able to study the composition range $0.4 < x < 0.9$. $x$ was measured from the relative change in X-ray absorption at the P K edge, as explained in the following section. Compositions, albeit more surface-related, could also be obtained from the XPS measurements, and were generally consistent with the values deduced from the P edge EXAFS data to within 5 at.%. ($x$-values measured from energy dispersive X-ray analysis (EDAX) experiments, which we normally use, have to be obtained using the P K and In L peaks since the In K peak is beyond the range of our instrument; we generally find that compositions determined by EDAX from mixed K and L peaks overestimate the amount of 'L' element. This was certainly the case for the a-In$_{1-x}$P$_x$ samples, with the In-content overestimated by as much as 20 at.%.)

Transmission electron microscope (TEM) experiments confirmed the amorphous state of the sputtered samples for compositions $x \geq 0.51$, yielding electron diffraction patterns which consisted of a few diffuse rings. In-rich films ($x \leq 0.49$), however, were revealed to be partially crystalline although the size of the 'nanocrystallites' was $\leq 2$ nm. Further details of the TEM measurements are included in a forthcoming publication [13].

### 3. Experimental

#### 3.1. EXAFS

Extended X-ray absorption fine structure measurements on the a-In$_{1-x}$P$_x$ samples were carried out at the 2 GeV synchrotron radiation source at Daresbury Laboratory. The X-ray absorption, $\mu(E)$, was measured about both In and P K edges.

Indium K edge data were recorded in standard transmission geometry [14]. A double crystal Si(220) monochromator was used, with harmonic rejection set at 80% by detuning the monochromator. The incident and transmitted intensities were measured with ion chambers containing a Kr/He gas mixture. Samples for transmission
EXAFS measurements were deposited on thin low-absorbing mylar substrates; several layers of film were stacked together in order to obtain the necessary sample thickness. PK edge measurements were also carried out [15]. The apparatus has a Cr-plated mirror which focuses the beam at the sample. The mirror has a high energy cut-off at about 3.5 keV, which means that harmonic contamination of the monochromatic beam is small compared with the primary beam. An InSb (111) double-crystal monochromator was used to define the energy of the incident beam; the incident intensity being measured by an Al foil [15]. Absorption at the sample was measured using the electron drain current method [16], a variation of the total electron yield technique, which measures the electron drain required to earth the sample after electron emission. Hence, for PK edge measurements, the films were deposited onto copper substrates.

The drain current technique samples, approximately, only the first 10 nm below the surface and hence the measured $\mu(E)$ contains no contribution from the substrate [16]. The relative height of the step in $\mu(E)$ at the PK edge can therefore be used to determine the sample composition, since the total absorption for a sample of composition In$_{1-x}$P$_x$ is given by

$$\mu(E) = (1-x)\mu_{Al}(E) + x\mu_{P}(E),$$  \hspace{1cm} \text{(1)}$$

where $\mu_i$ is the atomic absorption of element $i$. The ratio of $\mu(E)$ just above to $\mu(E)$ just below the edge will, consequently, yield $x$, assuming the atomic absorption coefficients are known. In this work, we used the values given by Viegele et al. [17].

Extended X-ray absorption fine structure spectra, $\chi(E)$, were extracted from the measured absorption spectra, $\mu(E)$, using the standard Daresbury program EXBACK [14]. This fits low-order polynomials to represent the smoothly varying pre- and post-edge background absorption.

The resulting EXAFS spectra were analysed to provide experimental values for structural parameters such as bond length, $r$, coordination number, $N_j$, and mean square variation in bond length, $\sigma_r^2$ (or Debye–Waller factor), by fitting the experimental data to calculated EXAFS functions. In these studies, the experimental $\chi(E)$ were multi-parameter fitted to EXAFS functions calculated using the fast curved-wave theory of Gurnon et al. [18]. The curve-fitting procedure was carried out with the aid of the EXCURV92 program [14] which uses a least-squares analysis. Scattering phase shifts and atomic potentials were calculated within the program; complex energy-dependent potentials (Hedin–Lundqvist potentials) were used. The parameters fitted were $r$, $N_j$, $\sigma_r$, and the position of the Fermi level, $E_F$. The amplitude reduction factor, $A$, which takes account of events that result in absorption but not EXAFS, and a parameter, $W$, which can be regarded as a fine-tuning parameter to allow for any slight errors in the phase shift calculations and also any instrumental broadening, were obtained from an EXAFS data of a crystalline InP sample. Analysis of the crystalline data yielded nearest-neighbour distances ~ 0.254 nm, the bond length in c-InP. The analysis program contains a statistical sub-program which gives the uncertainties on the structural parameters (often strongly correlated). We always quote the limits of the 95% confidence region, i.e., the $\pm 2\sigma$ uncertainties, where $\sigma$ is the standard deviation. Further details of the experimental set-up and data-analysis procedure can be found in Ref. [14].

3.2 XPS

X-ray photoelectron spectroscopy measurements were carried out in a spectrometer (VG Escalab) using Al K$_\alpha$ radiation at 1486.6 eV. Scans were made over the binding energy range 0–1200 eV and were calibrated using the carbon 1s line at 284.6 eV. The absolute energy resolution (full-width at half-maximum or FWHM) of the instrument was 1.0 eV. Although the a-In$_{1-x}$P$_x$ films were not grown in situ, with the result that some surface oxidation was evident in the recorded spectra, the samples were not sputter-cleaned as this causes structural rearrangement. For the P core levels, however, it was possible to separate out the oxygenated components since the oxides produce chemical shifts of about 4 eV. This was, unfortunately, not possible in the case of the In levels since oxygen produces
Fig. 1. Examples of $k^2$-weighted EXAFS spectra $\chi$ and associated Fourier transforms for a-In$_x$P$_{1-x}$ samples. (a) In K edge data for sample with $x = 0.42$. (b) P K edge data for sample with $x = 0.68$. The full lines represent the experimental data; the dashed lines give the least-squares fit.
Fig. 1. (continued).
a much smaller chemical shift (≤ 1 eV) for these levels.

3.3 SAXS

Small-angle X-ray scattering experiments were carried out at Daresbury Laboratory, using X-rays with a wavelength of 0.15 nm. The measurements were performed using a camera length of 1.5 m, which gave a scattering vector range of 0 < q < 5 nm⁻¹; the data were collected with the aid of a quadrant detector. As for the transmission EXAFS measurements, samples for SAXS were folded several times in order to increase the sample thickness and therefore improve the signal-to-noise ratio. Substrate contributions were measured directly from blank areas of the (folded) substrates and subtracted before data analysis.

3.4 Optical measurements

Infrared transmission measurements for the a-In₁₋ₓPₓ films were performed on a double-beam spectrophotometer (Perkin-Elmer 580B) over the wavenumber range 4000–180 cm⁻¹. An air-dryer unit was used to thoroughly purge the sample compartment prior to and during data-taking in order to reduce the absorption due to water vapour.

The absorption coefficient, α, at visible and near-infrared photon energies was deduced by standard transmission and reflection techniques. The measurements were carried out on a double-beam instrument (Perkin-Elmer 330). Such measurements also allow the refractive index, n, to be determined which, together with plasmon energies (obtained from XPS measurements), yield experimental values for the Penn gap. Refractive index and Penn gap data for the a-In₁₋ₓPₓ films will be presented in a forthcoming publication [13]. α was also measured by photothermal deflection spectroscopy (PDS) in order to extend the measurable range of α to lower values than could be obtained in the transmission and reflection measurements.

4. Results

4.1 EXAFS

Examples of In and P edge EXAFS spectra χ (weighted by k³) for the a-In₁₋ₓPₓ samples are given in Fig. 1, along with their associated Fourier transforms. The Fourier transforms are phase-corrected so that the peaks appear at the true interatomic distances. In general, the noise level was such as to allow a k-range ≤ 130 nm⁻¹. The absence in the majority of Fourier transforms of shells at distances corresponding to second nearest neighbours in c-InP (0.413 nm) or more distant neighbours, is consistent with the amorphous state of the samples, e.g., Fig. 1(b), although for

We suggest that the close similarity between the $I(q)$ versus $q$ spectra for InP and GaAs samples plus the lack of a trend with varying composition is consistent with the assumption that the measured SAXS for our $a$-In$_{1-x}$P$_x$ films is due to voids. Further, no evidence for a diffuse ring at higher $q$ (subsidiary peak at higher $q$ in the $I(q)$ versus $q$ plots) was found for any of the samples; such features are indicative of phase separation and have been observed for sputtered $a$-SiNi$_x$:H films [27] and also $a$-GeFe$_x$ samples [28]. EDAX measurements carried out on some of the $a$-In$_{1-x}$P$_x$ films revealed the presence of 1–2 at.% Ar. Included Ar atoms presumably contribute to the observed SAXS and some of these may be trapped in voids.

4.4. Infrared

Infrared transmission spectra for several of the $a$-In$_{1-x}$P$_x$ samples are illustrated in Fig. 8. The main feature observed in each case is a strong absorption mode in the vicinity of 300 cm$^{-1}$; this corresponds to the In–P TO mode (bond-stretch), which in the crystal is at ~305 cm$^{-1}$. In the amorphous samples ($x \geq 0.51$), the TO mode is broadened and shifted, to ~280 cm$^{-1}$. For samples with compositions $x \leq 0.49$, which according to the TEM experiments are partially crystalline, the TO feature is, however, narrower and located at the crystalline wave-number, consistent with a reduced degree of configurational disorder in these samples. As expected, the TO mode decreases in intensity as the samples become increasingly P-rich (for samples of similar thickness). For higher $x$, additional absorption between approximately 400 and 600 cm$^{-1}$ was observed, which we attribute to P–P bonds since P is infrared-active in this region [29]. As for the trend in the total P-coordination with increasing $x$ (see Fig. 5), this indicates (not surprisingly) that the amorphous network in the sputtered films becomes increasingly like that of $a$-P at high P-content.

4.5. The optical absorption edge

Fig. 9 shows $\alpha$ as a function of photon energy, $\hbar\omega$, for several $a$-In$_{1-x}$P$_x$ samples; data from the transmission and reflection and the PDS experiments are combined in these absorption curves. There is a shift to higher energy and a decrease in the width of the absorption edge with increasing P-content, although in a non-uniform manner. Optical band gaps were determined using the Tauc relation [30]

$$\alpha \hbar\omega = B(\hbar\omega - E_T)^2,$$  (5)
where $B$ is a constant, and also from $E_{\text{in}}$ (the photon energy at which $a = 10^4 \text{ cm}^{-1}$). Both $E_T$ and $E_{\text{in}}$ are plotted in Fig. 10 as a function of composition. For approximately stoichiometric material, we find that $E_T$ is $0.82 \pm 0.02 \text{ eV}$ although, nearer $x = 0.6$, it is higher at $0.88 \pm 0.02 \text{ eV}$ (cf. approximately $1.4 \text{ eV}$ in c-InP). The higher value is in reasonable agreement with the value of $0.90 \text{ eV}$ measured by Gheorghiu et al. [20] for slightly P-rich $0.5 < x < 0.6$ flash-evaporated material. The band gap is reasonably constant over quite a large part of the P-rich composition region and is close to the value for the stoichiometric amorphous material, indicating that In-P bonds dominate to high P-contents. This is therefore consistent with the idea that the a-In$_{1-x}$P$_x$ samples are predominantly chemically ordered. An increase in band gap towards the value associated with a-P ($E_T = 1.75 \text{ eV}$ [29]) is only observed for compositions $x > 0.75/0.80$. The rapid decrease in $E_T$ and $E_{\text{in}}$ for the In-rich samples demonstrates that only small numbers of In-In bonds are required to reduce the bandgap. In the light of this finding, the appreciable In-In coordination deduced for P-rich flash-evaporated samples [21,22] seems somewhat surprising. The percolation limit for excess In in stoichiometric InP of 15% (assuming perfect chemical ordering) corresponds to a composition $x$ of 0.425. Since the material is in fact slightly chemically disordered, the percolation limit should be at slightly higher value of $x$, i.e., slightly less In. It is therefore of interest to note that extrapolation of $E_{\text{in}}$ versus $x$ in Fig. 10 to $E_{\text{in}} = 0$ yields $x = 0.45$. (The absorption, $\alpha$, in the In-rich sample $x = 0.42$ was too large to measure in our films, and hence bandgap values could not be deduced.)

From Fig. 9, it is clear that, as for the change in bandgap, the decrease in the width of the absorption edges with increasing P content is also non-uniform, the largest change taking place for compositions around stoichiometry. This is shown by the trend of the Urbach edge parameter, $E_U$, with increasing $x$, illustrated in Fig. 11, where values of $E_U$ are determined by fitting the absorption edges to the exponential relation

$$a = a_0 \exp\left(\frac{h\nu}{E_U}\right).$$

Our value of approximately 90 meV for near-stoichiometric and P-rich material (aside from the most P-rich sample for which $E_U$ is larger) is less than the value of 140 meV measured by Theye et al. [11] for slightly P-rich ($0.54 < x < 0.65$) flash-evaporated samples, although this was reduced to 115 meV upon annealing. We also find smaller values of $\alpha$ at low photon energy than those found by the above authors for corresponding flash-evaporated specimens (for which $\alpha > 200 \text{ cm}^{-1}$ [11]). This implies a somewhat lower density of midgap defect states in the sputtered InP films. According to O’Reilly and Robertson [9], who have calculated the electronic states of bulk and defect sites in amorphous III–V compounds using tight-binding recursion methods, isolated In-In “wrong” bonds should give states approximately in the middle of the bandgap. (States associated with P-P wrong bonds are predicted to lie in the conduction band, close to the band edge.) This is consistent with the large differences observed between the absorption spectra for slightly In-rich and slightly P-rich material. Although there is no (or only a slight) decrease in the width of the absorption edge as $x$
is increased from $0.51 \pm 0.5$ to $0.57 \pm 0.5$ (see Figs. 9 and 11), the shift to higher photon energy (Figs. 9 and 10) results in a decrease in the low energy absorption of about a factor of 4. The density of defect states around midgap, arising from In-In bonds, according to O'Reilly and Robertson [9], decreases with increasing P content for slightly P-rich samples and is thus consistent with chemical disorder.

5. Discussion

Our EXAFS and XPS data reveal a degree of chemical disorder in the structural network of the sputtered a-In$_{1-x}$P$_x$ films. Chemical ordering with In-P bonds is however predominant. Samples with compositions close to stoichiometry remain tetrahedrally coordinated (as in c-InP). Interpretation, using the calculations by O'Reilly and Robertson [9], of the changes in the optical absorption edges as the composition is varied (Fig. 9) also provides evidence for chemical disorder. The presence of In-In bonds, inferred from the optical data for In-rich and approximately stoichiometric samples, lends weight to our suggestion that the failure to detect such bonds in the EXAFS measurements is a consequence of a large range in bond lengths. The bond lengths of the other bond types have a smaller range although slight static disorder was detected for the In-P bonds (at least for $x > 0.51$). Most of the configurational disorder is due to variations in bond angle (including dihedral angle), as is usual for covalent glasses [31]. P-P bonds increase as $x$ is increased. The EXAFS and infrared data show that the network becomes increasingly like that of a-P at high $x$. Microstructural information for our a-In$_{1-x}$P$_x$ samples is provided by TEM and SAXS experiments. TEM experiments reveal that In-rich samples contain crystallites with dimensions of the order of 2 nm. Infrared and EXAFS data are consistent with this. The SAXS data indicate that, apart from voids with diameters in the range 4–8 nm, the samples are compositionally homogeneous.

It is of course important to be aware of possible errors involved in the determination of partial coordinations and the implication of such errors for our arguments concerning the existence of chemical disorder in the a-In$_{1-x}$P$_x$ films. We note, particularly for the samples with compositions close to stoichiometry, that if a quoted $x$-value slightly underestimates the P content (i.e., if the sample is actually slightly more P-rich) then, although EXAFS results suggest that the sample is a little less chemically disordered than originally believed, optical data (with reference to the work of O'Reilly and Robertson [9]) indicate that there is somewhat more disorder. Alternatively, if the P content of a sample is overestimated by the quoted $x$-value, evidence for chemical disorder is slightly reduced in the case of the optical data but somewhat enhanced as far as the EXAFS results are concerned. Composition errors (estimated to be $< 5\%$) therefore do not affect our conclusions about the degree of chemical ordering in the a-In$_{1-x}$P$_x$ samples. Various measurements, including XPS and optical data by Theye and coworkers [10,11], indicate that a-InP prepared by flash evaporation also has some disorder. Nevertheless, the amorphous network of such material is better described by a Connell–Temkin CRN (containing only even-membered rings) than by Polk models (which contain odd- and even-membered rings) as demonstrated by the electron diffraction experiments of Dixmier et al [4]. Partial chemical disorder can therefore be regarded as 'extrinsic', arising from non-equilibrium deposition conditions. It should be pointed out that core level measurements by Shevchik et al. [12] for various amorphous III–V compounds (including InP) prepared by dc sputtering suggested that the numbers of wrong bonds were insignificant (all the samples were approximately stoichiometric). This emphasises the fact that differing preparation techniques and conditions affect the structure of thin film semiconductors.

The measured partial coordinations may be analysed in terms of thermodynamic theory, such as the quasi-chemical approximation (QCA) or a more accurate model given by Gurman [32] which relates partial coordinations to bond energy differences. Such models consider the bonding in amorphous alloys to occur via well-defined covalent bonds. The chemical bond energies are in-
eluded in the internal energy while effects due to
the statistics of bonding within the local struc­
tural units are included in the entropy. The QCA
approximates the entropy to that of a random
alloy and hence may not provide a good descrip­
tion for chemically ordered systems. The ob­
served structure for an alloy is considered to be
that with the minimum Gibbs free energy. It is
recognised that amorphous alloys are not in ther­
mal equilibrium, but it can be argued that their
structure became 'frozen-in' at the glass transi­
tion temperature, \( T_g \); the relevant tem­
perature is
\[ T_g = \frac{E_A}{k} \]
For a binary alloy AB, the QCA
\[ \frac{N_A N_A}{N_B N_B} = \exp(-2\Delta E/kT_g) \]
where
\[ \Delta E = E_{AB} = \frac{1}{2} \left( E_{AA} + E_{BB} \right) \]
and
\[ E_{AB} = \frac{1}{2} \left( E_{AA} + E_{BB} \right) + c (x_A - x_B)^2 \]
where \( E_{AB} \) and \( E_{AA} \) have the same definitions as
previously and \( c \) is a constant whose value is
almost exactly \(-1.0 \text{ eV/bond}\). \( \Delta E \) can therefore
be estimated from the experimental values. For InP, \( \Delta E = -0.17 \text{ eV} \). Although some-
what larger than the experimentally estimated
value, \( \Delta E \) obtained from electronegativities are
subject to some error (up to \( \pm 0.1 \text{ eV} \)) as a result of
uncertainties in electronegativity values; we
therefore consider that agreement between the
two \( \Delta E \) values is satisfactory. In any case, both
are small enough to be consistent with (measur­
able) partial disorder.

6. Conclusions
The structural network of sputtered a-In\(_{0.98}\)P\(_{0.02}\)
films is largely chemically ordered, with In–P
bonds favoured. Chemical ordering is not, how­
ever, complete; the degree of partial chemical
ordering is not, how­
ever, complete; the degree of partial chemical
disorder is consistent with that expected from
thermodynamic models for amorphous covalent
alloys.

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