

PREPARATION, CHARACTERIZATION AND STUDY
OF
AMORPHOUS GaAs THIN FILMS AND RELATED COMPOUNDS

Thesis submitted for the degree of

Doctor of Philosophy

at the University of Leicester

by

Mekhaiel Iessa Manssor

BSc (Mosul University) MSc (UWIST)

Department of Physics and Astronomy

University of Leicester

January 1991

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To my parents, brother and sisters

PREPARATION, CHARACTERIZATION AND STUDY OF AMORPHOUS GaAs THIN FILMS AND RELATED COMPOUNDS

Mekhaïel Iessa Manssor

ABSTRACT

The purpose of this thesis is to investigate the electrical and optical properties of a-GaAs thin films and also the related ternary compounds a-GaAlAs and a-GaAsP. The films were prepared by the technique of r.f sputtering in an argon atmosphere both with and without hydrogen. Experiments carried out include optical absorption, infrared absorption and electrical conductivity. The composition of the films was determined by EDAX. Information on structure and local bonding configurations for the a-GaAsP films was obtained from EXAFS measurements.

Initially investigations were focussed on a-GaAs films prepared at room temperature, and in particular the effect of hydrogenation on film properties. Unhydrogenated a-GaAs has an optical gap of about 1.0 eV, although hydrogenation was found to increase this to about 1.3 eV. Infrared absorption data show that the main hydrogen mode in a-GaAs:H is the Ga-H-Ga bridging mode. It was also found that a-GaAs and a-GaAs:H films could be prepared at elevated substrate temperatures; similar measurements were also carried out on these specimens. Non-stoichiometric (As-rich) GaAs films were also prepared and characterized.

Films of a-GaAlAs were successfully prepared by co-sputtering. For this system an interesting result is that the optical gap was found to decrease initially with increasing Al content before increasing at larger Al contents, in contrast to the crystalline case where the band gap increases monotonically with increasing Al content. Above 30 at.% Al, the films were found to be microcrystalline.

A set of a-GaAsP films was also prepared. EXAFS measurements on these specimens reveal that Ga-P bonds in the amorphous network rapidly maximize at the expense of Ga-As bonds as the P-content increase. In other words the Ga bonding environment appears to be partially ordered. P-P and P-As "wrong" bonds are detected and, at high P-content, possibly also As-As bonds. The EXAFS results were found to correlate

ACKNOWLEDGEMENTS

I am most indebted to my supervisor Professor E.A.Davis for his encouragement, guidance and advice throughout the period of this work. His assistance, particularly in the latter stages of the work, is much appreciated.

I would like to express my gratitude to Dr.S.H.Baker for his much valued assistance and for his comments on the manuscript. I am also grateful to the Department of Physics and Astronomy of Leicester University for providing me with Laboratory facilities and to members of the workshop for their technical assistance.

My thanks to Dr.S.C.Bayliss, Dr.S.J.Gurman and to all members of the CMP research group for their kind cooperation and for helpful discussions.

I also gratefully acknowledge the Ministry of Higher Education and Scientific Research, Iraq, for financial support.

Last, but not least, I must not forget to express my gratefulness to my wife Nawal and my children, Afnan, Alhan, Manhal, Joman and Fallon for their patience during the period of this study.

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CHAPTER ONE

GENERAL INTRODUCTION

1.1 AMORPHOUS SEMICONDUCTORS

Amorphous materials do not possess the long-range periodic arrangement of atoms or molecules found in the crystalline state; (amorphous means having no form or structure, from the Greek morfe-form). However, quite often they show short-range order, extending over a few atomic spacings around a given reference atom, which is determined by the chemical nature of the bonding in the structure.

The most extensively studied and also the best understood amorphous semiconductor so far is amorphous silicon (a-Si). Two important discoveries have made possible the use of a-Si as the basis for electronic devices. The first [1-3] was that hydrogenated a-Si (a-Si:H) films, prepared by the glow-discharge decomposition of silane (SiH_4), possess a very low density of localized states in the mobility gap. This property is probably the most important factor in the subsequent development of the material, since it is an essential requirement for the fabrication of devices. The second important discovery which helped to make amorphous Si a potential material for device applications was reported by Spear and LeComber in 1975 [4]. These authors showed that the electronic properties of a-Si:H prepared by the glow-discharge process could be controlled by substitutional doping with group-V phosphorus (P) atoms or group-III boron (B) atoms in analogy with the situation in crystalline Si. Their work opened up a wide variety of potential applications in electronics and optoelectronics for amorphous semiconductors. This important breakthrough was followed in

1976 by a paper on the first a-Si:H pn junctions, which exhibited a photoresponse typical of photovoltaic cells [5]. Shortly afterwards, Carlson and Wronski [6] demonstrated the first amorphous silicon solar cell. The field is rapidly advancing and new commercial applications of amorphous semiconductors (especially a-Si:H) are beginning to be realised. Products containing a-Si, eg photovoltaic cells and thin-film transistors are now on the market. The present and future applications of a-Si and its alloys are reviewed in reference [7].

1.2 METHODS OF PREPARATION OF AMORPHOUS MATERIALS

Amorphous materials have been prepared in both bulk and thin film forms. There are a large number of techniques for the preparation of thin films of these materials; for example, thermal evaporation, sputtering, glow-discharge, and chemical vapour deposition. Bulk materials are generally prepared by the rapid melt-quenching technique. A good review discussing the preparation of amorphous materials is given in reference [22].

1.2.1 Melt quenching

Many materials can be prepared in bulk glassy form by rapid cooling of the melt below a temperature at which the viscosity of the liquid is so great that the atoms cannot arrange themselves into a crystalline array. Sometimes it is sufficient to drop an ampoule containing the molten material into cold water but for some materials higher quenching rates are required. The technique of splat cooling, for example, involves squirting of a jet of the molten glass on to the edge of a rapidly rotating wheel (cooling rate $\sim 10^8 \text{ K s}^{-1}$ [20]). For some semiconductors, e.g. Si, Ge, and indeed GaAs, even

the highest rate of quenching is insufficient to produce bulk glasses [21] and deposition from the vapour phase is necessary.

Elliott [22] pointed out that the commonly accepted definition of glass, namely the amorphous product produced by the rapid quenching of a melt, is not very precise. Instead he suggested that the term be restricted to those materials that exhibit a glass transition temperature. Glassy materials, therefore, need not to be prepared by quenching from the melt; all glasses are amorphous but not all amorphous solids are necessarily glasses.

1.2.2 Thermal evaporation

Thermal evaporation is perhaps the simplest of all deposition methods and is widely used for amorphous film preparation. It is normally carried out in a vacuum of better than 10^{-6} Torr. The material to be deposited is usually heated by an electric boat filament (e.g. tungsten or molybdenum) or by electron-beam bombardment. In thermal evaporation, the material to be deposited is first transformed by evaporation or sublimation into the gaseous state, which is then deposited on to a substrate. This is sometimes cooled so that the atoms (molecules) are frozen into the random positions at which they arrive and crystallization is avoided.

The purity and the morphology of films prepared by this technique can be influenced by residual gas pressure, the temperature of the substrate and the evaporation rate. This means that reproducible properties of the films can only be obtained if these parameters are kept constant. Multicomponent materials such as alloys and compounds present difficulties because the components, having different saturated vapour pressures, will evaporate at different rates, so that the composition of the film will differ from that of the source

material. Usage of several independently heated crucibles or flash evaporation can sometimes overcome this problem. Flash evaporation is well suited for multicomponent compounds or mixtures. It involves instant evaporation of the material which is dropped in a steady stream onto the hot surface of the source. The material is normally in the form of powder which is dispensed from a reservoir using mechanical or ultrasonic vibration.

The flash-evaporation technique has been used to produce a-GaAs thin films [23]. Perhaps the disadvantage of this technique is the difficulty of incorporating reactive gases such as hydrogen directly into the evaporated film.

1.2.3 Glow-discharge decomposition

Another technique which can produce thin amorphous films is glow-discharge decomposition. In this technique, a radio-frequency (r.f.) discharge (of e.g. 13.56 MHz) is created in a low-pressure gas, usually ~ 0.1 Torr, to create a plasma. The difference between r.f sputtering (see sec. 1.2.4) and this technique is that in the former, ions from the plasma bombard the target causing ejection of material and subsequently deposition of the film on a substrate, while in the glow-discharge technique, chemical decomposition of the gas itself take place. The most attractive advantage of the glow-discharge method, at least when applied to a-Si, is that the density of states in the gap is lower than that of evaporated films [24] as shown in Fig. 1.1. Moreover, a better reproducibility of the film's characteristics can be obtained. Amorphous films of Si and Ge can readily be prepared from their hydrides SiH_4 and GeH_4 . Amorphous GaAs films have also been produced by the glow-discharge process [25] using a mixture of arsine (AsH_3) and trimethylgallium ($\text{Ga}(\text{CH}_3)_3$).

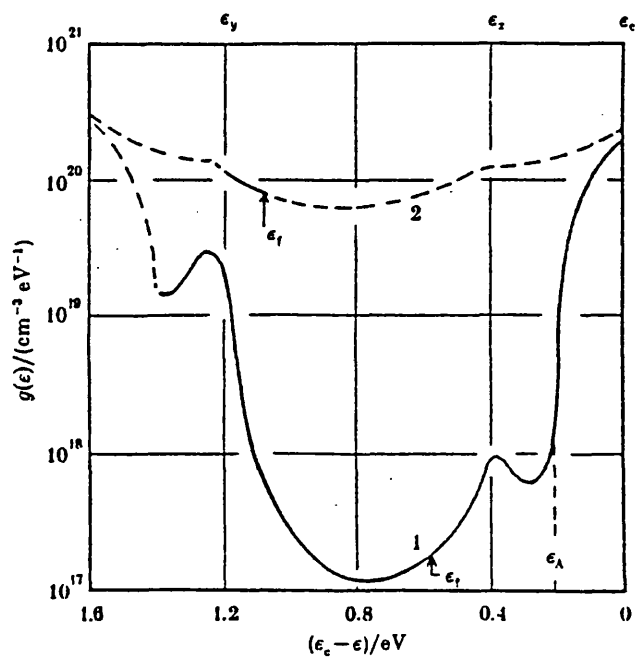


Fig. 1.1 Experimental curves of densities of state within the gap, deduced from field-effect measurements. Curve 1, for glow-discharge specimen deposited at 270 °C. Curve 2, for an evaporated specimen deposited on a room-temperature substrate [24].

1.2.4 Radio-frequency sputtering

In this technique, the target is usually placed on a lower electrode, which is powered with an r.f source at 13.56 MHz. The substrate is fixed on the upper electrode. Electrons leave the argon plasma, which is struck between the electrodes, to reach the target causing it to become negatively biased. This attracts heavy, positively charged argon ions towards the target causing ejection of either atoms or clusters of atoms and subsequent deposition of a film on the substrate.

As this technique was employed to prepare samples for this study, it will be described in more detail in the experimental chapter.

1.3 DIFFERENCES BETWEEN III-V AND GROUP-IV AMORPHOUS SEMICONDUCTORS

Amorphous semiconductor materials, especially a-Si, have been the subject of intense research due to their technological importance. Although crystalline III-V semiconductors have already been used in various device applications (e.g., light-emitting diodes, semiconductor lasers etc.), the corresponding amorphous III-V materials might also be expected to be important in various types of future optoelectronics and thin-film devices.

We shall choose a-GaAs and a-Si as representatives of III-V and group-IV materials respectively.

Although all the tetrahedrally coordinated semiconductors possess very similar structures and electronic properties [8], there are a few but significant differences between the elements and compounds. Both Si and GaAs have tetrahedrally coordinated crystal lattices consisting of six-membered rings of bonds. While a-Si is known to be topologically disordered

and contain odd-numbered rings, a-GaAs is also tetrahedrally coordinated and odd numbered rings would automatically involve like-atom bonds [9]. The atomic coordinations in amorphous semiconductors generally obey the 8-N rule. This rule states that an atom's coordination is given by 8-N, where N is the valence number, but by N if $N < 4$ [10,11]. Ga and As have three and five valence electrons respectively, and so would be expected to be trivalent, each obeying the 8-N rule. However, in order to account for the tetrahedral bonding in GaAs, this rule requires a formal charge transfer to provide $\text{Ga}^- \text{As}^+$, so that each site now possesses four electrons (one per sp^3 hybrid) [11]. During bonding, further charge transfer occurs which produces slightly negative As sites.

The nature of the defects is also expected to be different. In a-Si, the major defect is the dangling bond of the trivalent site, denoted by Si_3 . Dangling bonds in a-Si create a continuous density of states across its gap with very high concentration. Thus, pure a-Si is a poor electronic material, whereas the incorporation of hydrogen (a-Si:H) causes the defect density to decrease (to $\sim 10^{15} - 10^{17} \text{ cm}^{-3}$). Hydrogenation converts the dangling bonds into Si-H bonds, whose states lie deep in the valence band leaving a small residual density of dangling bonds in the gap. On the other hand, a-GaAs ideally contains only Ga-As bonds, with Ga and As dangling bonds (Ga_3 and As_3) as the simplest defects. In addition, however, there are like-atom bonds or wrong bonds, viz Ga-Ga and As-As [12]. The As_{Ga} antisite (As atoms at Ga sites) consists of four As-As wrong bonds and is expected to produce a state around mid-gap [13]. Theoretically, dangling and isolated wrong bonds give states around the band edges, while clusters of wrong bonds are the most probable cause of mid-gap states in a-GaAs [13]. Thus, a much lower density of states at the Fermi level E_F is expected for a-GaAs compared to a-Si, as found experimentally [14-17]. However,

hydrogenation of a-GaAs and other III-V compounds does not seem to be as effective as in a-Si in reducing the gap state density [18,19].

Another difference between a-Si and a-GaAs is that, in the former, the optical gap increases in going from the crystalline to the amorphous phase, whereas it decreases for the latter. This is possibly associated with fact that the smallest gap in c-Si is indirect while in c-GaAs it is direct. Relaxation of the k-selection rule in amorphous semiconductors, has a more pronounced effect in indirect-gap materials.

The most important difference to date between the two materials is that, while a-Si:H can be doped, doping has not been observed in a-GaAs:H. This is possibly due to the fact that stoichiometric films of a-GaAs:H with optimum preparation conditions cannot be achieved easily and moreover the dopants are strongly compensated [13].

1.4 PREVIOUS WORK ON AMORPHOUS III-Vs

In this section we review previous work on amorphous III-V compounds which relates to their structure and to their optical and electrical properties.

A comprehensive study of amorphous III-V semiconductor films began only after 1970 when Stuke [27], Eckenbach et al [28] and Stuke and Zimmerer [29], measured the fundamental electrical and optical properties of flash-evaporated InSb, GaSb, GaAs and GaP. They found that the optical properties of the amorphous compounds showed marked differences to those of their crystalline counterparts. The E_2 peak in the ϵ_2 (imaginary part of the dielectric constant) spectrum of the crystal is absent for the amorphous form as shown in Fig. 1.2. The ϵ_2 spectrum has its maximum near the E_1 peak of the

crystal spectrum and its centre of mass is shifted to a lower energy. In general, the optical constants of amorphous III-V compounds behave similarly to those of a-Si and Ge.

Shevchik and Paul [8] measured the radial distribution functions (RDF) of a-III-V and a-Ge films. Their similarity suggests that any model for the structure of a-Ge may also be applicable to the a-III-V compounds. An early model for the a-Ge structure is Polk's continuous random network (CRN) model [30]. Such a network contains an appreciable fraction of five-membered rings which, if applied to III-Vs, implies bonds between like atoms. On the other hand, photoemission experiments performed by Shevchick et al [31,32] on a-GaAs, GaP, GaSb, InP, InAs, InSb and AlSb, have shown that the core-level spectra of these compounds are as sharp as those of the corresponding crystalline forms (see Fig. 1.3), suggesting that the concentration of wrong bonds is not as high as expected from the Polk model. Only a small bump was observed in the spectra of some compounds, just below the second peak (mixed s and p character) in the valence band states, which was attributed to the presence of wrong bonds. This suggest that the Polk model, as proposed for a-Ge and Si, is probably not applicable to the amorphous III-V compounds. Connell and Temkin [33] have constructed a random network model containing only even-membered rings which also provided a fair fit to the RDF of a-Ge. Such a model might be more appropriate for amorphous III-V compounds.

A theoretical approach, based on density of states (DOS) computations using a simple tight-binding model and the empirical pseudopotential method, was considered by Joannopoulos and Cohen [34,35]. They investigated the effects of two types of disorder on the electronic density of states of stoichiometric III-V compounds. The first type of disorder related to bond-length and bond-angle distortions in a randomly connected network with only unlike-atom bonds. The

second type of disorder includes the above along with the occurrence of like-atom bonds. Their results show that the effects of bond length and angle variations alone are quite small and insignificant compared to those arising from the presence of wrong bonds. The s-like region of the DOS is very sensitive to the various clustering configurations that the like-atom bonds can form. The p-like region of the DOS is also very sensitive to the clustering configurations of the like atoms; it broadens and can be divided into three p-like regions (I, II, and III) as shown in Fig. 1.4. For GaAs, the regions I and III represent anion-anion (As-As) and cation-cation (Ga-Ga) bonding states respectively, while region II represents the cation-anion (Ga-As) bonding states, and is therefore the only region of the DOS that retains its character under this type of disorder. On the other hand, from their charge density calculations, Joannopoulos and Cohen[34] found that the top of the valence band represents Ga-Ga bonding-like states. In addition, the bottom of the conduction band has some antibonding states of As s-like character. Therefore, they predicted a shift in the energy of these regions depending on the Ga-Ga and As-As nearest-neighbour distances. A 10% decrease in the Ga-Ga nearest-neighbour distance and a 3% increase in the As-As bonding distance yielded a bandgap which decreased to only 0.1 eV.

Pollak [53] showed the influence of large numbers of like-atom bonds on the photoemission spectra of ZrS_3 and Zr_3Se_3 ; in particular, the splitting of the s-like valence bands. He then compared these effects with the available photoemission results of III-V compounds. He strongly criticized the suggestion of the presence of substantial amounts of covalent like-atom bonds but pointed out that the results were insufficient to prove the absence of 5 to 10% like-atom bonds in amorphous III-V semiconductors.

It is well known that the optical gaps in a-GaAs and GaP

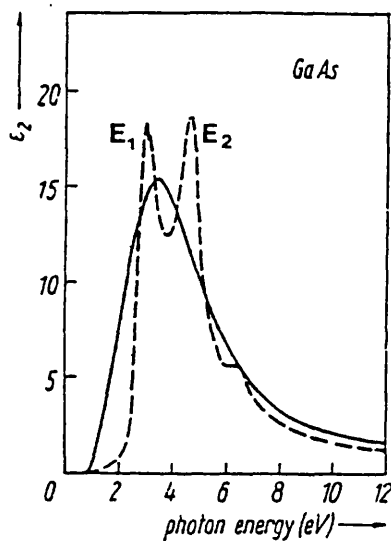


Fig. 1.2 ϵ_2 -spectra of amorphous (solid curve) and crystalline (dashed curves) GaAs [29].

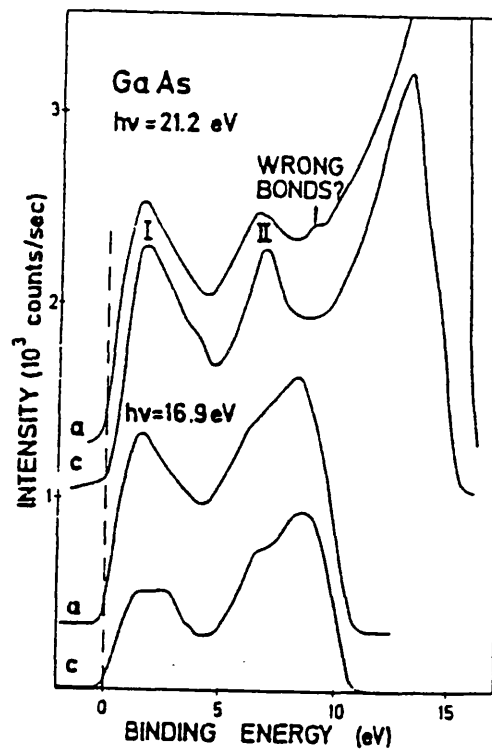


Fig. 1.3 The electron distribution curves (EDCs) for amorphous and crystalline GaAs obtained with photons of $h\nu=21.2$ and 16.9 eV [31].

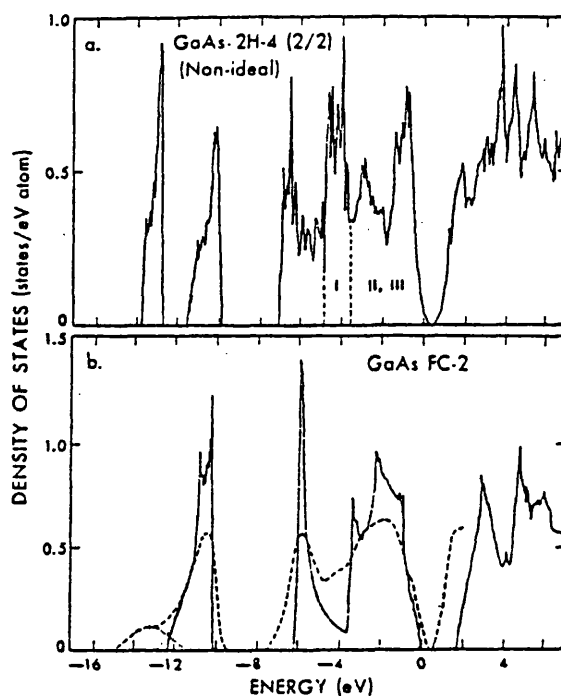


Fig. 1.4 Density of states of GaAs in the (a) modified 2H-4 (2/2) and (b) FC-2 structures using the EPM. The modified 2H-4 structure was obtained from the ideal 2H-4 structure by taking a 10% decrease in Ga-Ga bonding distances and a 3% increase in the As-As bonding distances. this resulted in a merging of regions II and III and the formation of a non-zero gap. The dashed curve in (b) represents the consequences of the second type of disorder (discussed in the text) for a-III-V compound with 10% like-atom bonds taking GaAs as a prototype.

are smaller than in their crystal counterparts (our results show a gap of approximately 1.0 eV for a-GaAs, while for c-GaAs the reported value is 1.42 eV). The region of the density of states spectrum most sensitive to the wrong bonds is quite possibly that in the vicinity of the energy gap [34,35]. The presence of wrong bonds, is therefore an essential issue for amorphous III-V compounds. If these compounds are chemically ordered (i.e. no wrong bonds), then the nearest-neighbour spacing occurring at the III or V atoms should be identical [14]. If the above spacings are significantly different, this suggests the presence of chemical disorder. Since diffraction methods give only average information on the environment of both constituents, more specific experiments are needed to resolve the issue of possible chemical disorder.

Extended X-ray absorption fine structure (EXAFS) experiments should in principle be able to sample the local environment of each type of atom in a compound. Such experiments have been performed on sputtered amorphous GaAs films by Del Cueto and Shevchik [36]. The first-nearest-neighbour distribution centred around the As atoms was found to peak at a distance greater by 0.04 Å than that of crystalline GaAs, while the first-nearest-neighbour distribution centred around the Ga atoms peaked at the same distance as in the crystal to within 0.015 Å. This result was interpreted as evidence for the presence of wrong bonds. However, contrary EXAFS results have been obtained by Theye et al [37]. Their experiments were performed on flash-evaporated a-GaAs and a-GaP films at the K edge of Ga and As for GaAs and of Ga for GaP, using crystals as reference materials. In the case of a-GaAs, they found that the mean first-nearest-neighbour distance was the same around each type of atom (Ga and As) within experimental uncertainty and was larger by only 0.01 Å than the crystalline distance. These

results are therefore not in accord with those found for sputtered a-GaAs [36]. The authors therefore interpreted their results in favour of chemical ordering in this compound and suggested that if wrong bonds exist, they should be in very small proportion. If stoichiometry was really achieved in both studies, this discrepancy could reveal important structural differences between the two kinds of samples due to their different method of preparation, for example clustering of some of the As atoms in the case of sputtered a-GaAs. In the case of a-GaP [37], EXAFS results indicated the presence of Ga-Ga wrong bonds, with the bond length slightly larger than Ga-P normal bonds.

We mentioned earlier in this section that dangling and wrong bonds in amorphous III-V compounds introduce states in the pseudogap as well as at the band edges. These states should certainly lead to significant optical absorption tails, modification of the optical gap and the electrical properties. These effects may depend on the sample preparation condition, heat treatments and also the composition of the film (a-GaAs films are always slightly As-rich). Several investigations on a-GaAs, GaP, and GaSb were carried out by Theye's group [14,38,39]. The optical results show that the ϵ_2 spectra of a-GaAs was similar to that previously reported [29]. Annealing shifted the ϵ_2 curves towards higher energies; this was accompanied by a decrease of the refractive index n (at 0.5 eV) and an increase of the optical gap from about 1.0 to 1.15 eV, along with a reduction in the tailing of the absorption edge. The optical properties of a-GaAs films were not found to be very sensitive to the substrate temperature during deposition. On the other hand, the d.c electrical conductivity of these films was found to undergo an abrupt decrease when annealed to room temperature (the films were deposited at low temperature). Below room temperature the conductivity followed Mott's variable-range-hopping law ($\sigma = \sigma_0 \exp(-T_0/T)^{-1/4}$)

suggesting that conduction takes place in localized states at the Fermi level. For films containing relatively large contents of As ($x=0.6$), an insignificant change in the optical properties was observed; for example the optical gap increased only from 1.0 to 1.05 eV. Similar results were obtained by Paul et al. [18] for As-rich sputtered a-GaAs.

X-ray photoelectron spectroscopy (XPS) experiments have revealed the presence of isolated wrong bonds in As-rich films [40], suggesting that the excess As atoms are incorporated at random. Since the flash-evaporated stoichiometric a-GaAs films are believed to be essentially chemically ordered, the defects in these films were taken to be dangling bonds [39].

It should be mentioned here that the absorption edge of a-GaAs can also be shifted towards higher energies by hydrogen incorporation [18]. This behaviour was also observed in our a-GaAs:H films (see chapter 4). However, the effect of hydrogen on the optical properties of a-GaAs was found to be much stronger than the annealing effect mentioned above. In a-GaAs, hydrogen was found to bond preferentially to Ga in the form of Ga-H-Ga bridges, and monovalently to As in the form of As-H [41]. (In the present work, hydrogen bridges were detected in infrared measurements, while As-H bonds could not be detected). Photoemission measurements [42] show that hydrogen does not produce a large erosion of the valence band edge in a-GaAs:H as in a-Si:H. This is because the valence band edge is largely As p-like and the hydrogen bonds preferentially to Ga [13]. The conduction band consists of Ga s states and the formation of Ga-H-Ga bridges raises these states. This could account for the fact that the absorption edge shifts towards higher energies and the optical gap widens.

Recent calculations by O'Reilly and Robertson [13] of the DOS of a-GaAs using the tight-binding recursion method showed that, unlike a-Si, the valence and conduction band edges are

hardly shifted compared with those of c-GaAs. However, experimental data on the movement of the band edges is rather contradictory. Photoemission [40,42] measurements suggest that the valence band edge of GaAs does not move when disordered, while phosphorus K_{β} X-ray emission spectra suggests that the valence band edges of a-GaP [43] and a-InP [44] have both receded. Meanwhile, X-ray absorption showed that the conduction band edges of a-GaP and a-InP have not moved. Thus these experiments suggest that the gap is either unchanged or increased in the amorphous phase. In contrast, all the measurements (including ours) of the optical gap find a decrease relative to that in the crystal. For example, the 1.42 eV gap of c-GaAs shrinks to 1.1-1.2 eV in annealed a-GaAs [14,15,45] and to 0.9-1.0 eV in unannealed a-GaAs [18 and present work], the 1.33 eV gap of InP shrinks to approximately 1.2 eV in a-InP [16] and the 2.26 eV gap of c-GaP shrinks to 1.2-1.55 eV in a-GaP [14]. The lower optical gap in a-GaAs compared with c-GaAs has been attributed partially to tailing and Ga-Ga wrong bonds [46].

In a-GaAs, O'Reilly and Robertson [13] found that both unrelaxed Ga_3 and As_3 dangling bonds with tetrahedral bond angles of 109° give gap states just below the conduction band edge E_c and above the valence band edge E_v respectively. This causes a charge transfer from Ga_3 to As_3 which drives a relaxation of bond angles towards their chemically preferred values of 120° for Ga_3 and 97° for As_3 and this expels both states from the gap (Ga_3 to the conduction band and As_3 to the valence band). This means that chemically ordered a-GaAs would have no gap states [12].

Wrong bonds also give states around the band edges [13], the As-As σ^* -level lying below E_c and the Ga-Ga σ -level lying just below E_v . Antisites (consisting of a tetravalent site surrounded by four wrong bonds) are calculated to produce gap states. The anion (As) antisite gives deep gap states in

a-GaAs at approximately 0.65 eV, while the cation antisite (Ga) gives gap states just above the valence band [13,47].

As isolated dangling bonds and wrong bonds are calculated to introduce only band edge states, one might expect a lower density of states at the Fermi level $N(E_F)$ in a-III-V compounds than in a-Si, as indeed found experimentally. E_F usually lies near midgap. As we mentioned earlier, at low temperatures the conductivity is characterized by variable-range-hopping conduction in most of the amorphous compounds (GaAs, GaP, GaSb, AlSb and InSb) [14,17], which gradually changes to intrinsic conduction upon annealing of the material. Then, conduction takes place by thermally assisted tunnelling of the charge carriers in localized states at the band edges rather than at the Fermi level [15,16]. These results suggest an upper limit for $N(E_F)$ of the order of $10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$ for most compounds.

The localized gap states responsible for variable-range hopping and the spin concentration determined by electron spin resonance (ESR) measurements, were assumed by Hauser et al to be associated with the dangling bonds in a-III-V compounds [48]. The ESR measurements were performed on a-GaAs films using different preparation technique [49-51]. The stoichiometric flash-evaporated a-GaAs films [49] gave a paramagnetic signal with a g-value of 2.06 ± 0.02 and a spin concentration of the order of 10^{18} cm^{-3} . This spectrum coincides closely with that of unhydrogenated Ar-sputtered a-GaAs [50]. Hoheisel et al [50] argued that these defect must be related to group-V atoms and tentatively attributed them to As dangling bonds. Bardeleben et al [49] agree with this but they have shown that the defects are not necessarily associated with an As excess, since they could not be detected in As-rich a-GaAs. This was explained in terms of a possible rearrangement of the excess As to three-fold coordination. However, O'Reilly and Robertson [13] argued against such an

identification, and suggested that the paramagnetic states near midgap should be assigned to clusters of wrong bonds. Such defects were observed in a-GaAs films prepared by molecular beam epitaxy (MBE) [51] and the As_{Ga} antisite was found from ESR in a concentration of approximately $3 \times 10^{17} \text{ cm}^{-3}$.

More recently, Mosseri and Gaspard [52] have calculated the effect of wrong bonds on the density of states using an approximation similar to that of O'Reilly and Robertson [13] with a structural model that closely resembles that of Connell and Temkin [33]. They obtained results in good agreement with the previous ones [13,34] except for the ionic gap whose filling with states was not reported. Very recently, Agrawal et al [47] have studied the electronic structure of simple defects and their complexes in a-GaAs using a cluster Bethe lattice (CBL) method. The results obtained for dangling and wrong bonds are in good agreement with those of O'Reilly and Robertson [13] as shown in Fig. 1.5.

1.5 OBJECTIVES OF THE PRESENT STUDY

Amorphous Si and Ge may be considered as first-generation amorphous semiconductors and have been extensively studied. There is now a fair understanding of their fundamental physical properties; they have many application and devices made from them are available on the market.

Amorphous III-V compounds might be considered as potentially attractive materials for commercial applications also, although it is clear that the high mobilities which characterize certain crystalline III-Vs are unlikely to be realized in the amorphous form. Nevertheless it would seem foolhardy to dismiss future application on this basis alone. The search for new amorphous semiconductors with different band gaps and density of states distributions, particularly as

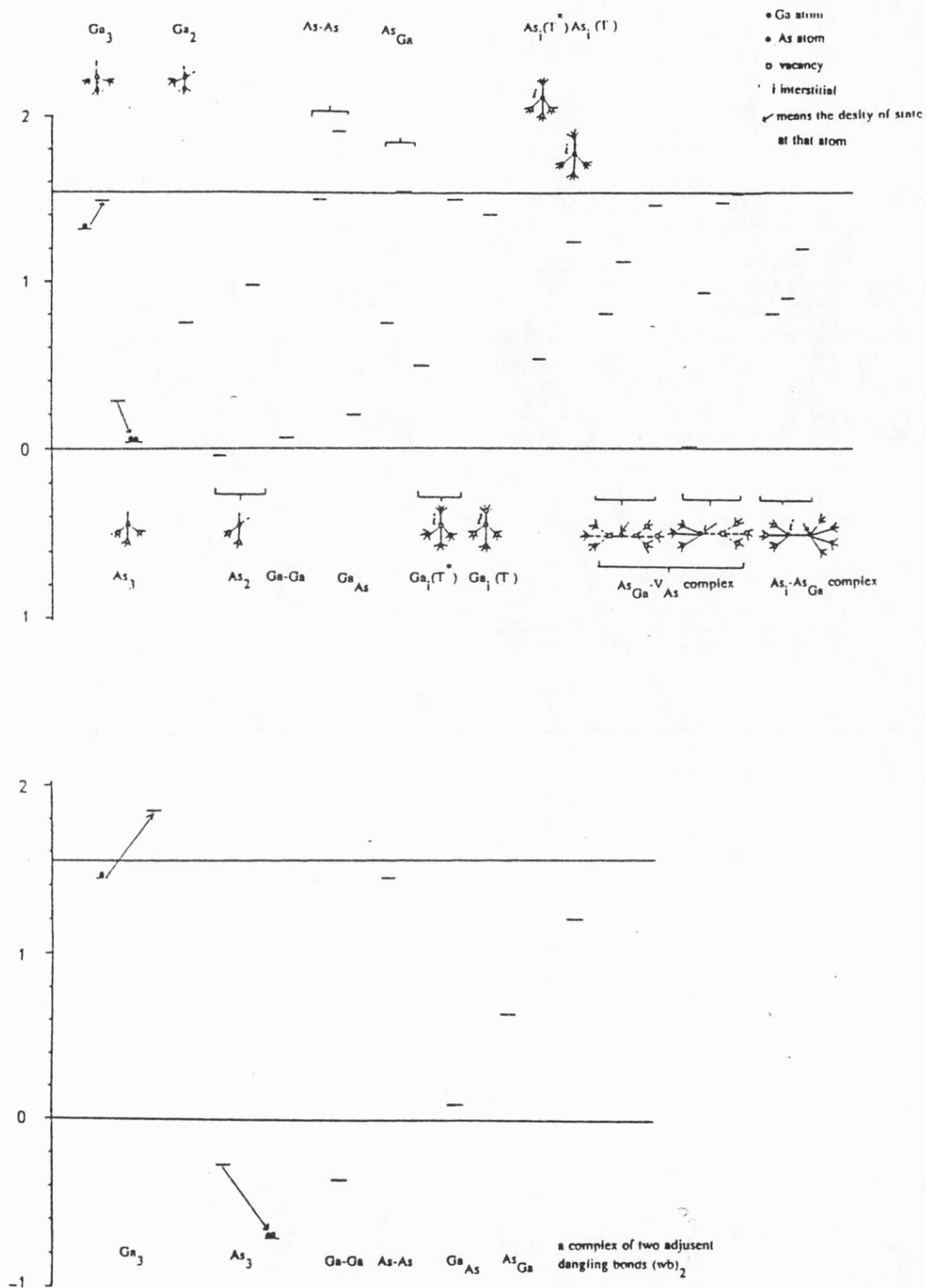


Fig.1.5 Levels in the gap and band edges for various defects in a-GaAs as calculated by (a) O'Reilly and Robertson [13] and Agrawal et al [47].

the limitations of a-Si (e.g. instability) become apparent, is a foregone conclusion.

However, the principal aims of this study are of more fundamental nature. Binary and ternary systems offer the challenge of understanding materials that are more complex than the elemental semiconductors; the nature and the role of defects in III-Vs is likely to be very different, as is the effect of hydrogenation. A beginning to this understanding is made in the work described in this thesis. In particular a-GaAs and related compounds have been prepared and their electrical, optical and structural properties studied with a view to correlating these and describing them with theoretical concepts.

The organization of the thesis is as follows: Chapter one presented a general introduction to amorphous semiconductors, outlining the experimental technique used for their preparation. Differences between the III-V and Group-IV amorphous semiconductors are emphasised and previous work on amorphous III-Vs is reviewed. Chapter two introduces the theoretical background and principles of the techniques used for evaluation of the optical and electrical parameters. Chapter three describes the equipment employed for the preparation and characterization of the films used in the present study. The experimental results and discussion are presented in Chapter four. Chapter five is devoted to a description of an EXAFS study of a-GaAsP; the theoretical background, experimental details, data analysis, and experimental results are included. The final Chapter of this thesis summarizes the main findings of this work.

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CHAPTER TWO

THEORETICAL BACKGROUND AND PRINCIPLES OF TECHNIQUES USED

2.1 DENSITY OF STATES DISTRIBUTION IN AMORPHOUS SEMICONDUCTORS

The electronic properties of amorphous semiconductors are strongly influenced by the distribution in energy of the electronic states.

It is well known that in crystalline semiconductors the energy bands are well defined and separated by a range of energies in which $N(E) = 0$ ($N(E)$ is the number of electronic states per unit volume for a unit energy range at energy E). The band edges of the conduction band and valence band are denoted by E_c and E_v respectively and $E_c - E_v$ is called a band gap or energy gap as shown in Fig. 2.1a. In non-crystalline semiconductors, although long-range-order (LRO) is absent (as we mentioned in section 1.1), short-range-order (SRO) is essentially preserved and this often results in an overall electronic structure which is similar to that of the equivalent crystal. However, due to disorder, certain modifications to the crystalline band structure do occur; in particular the abrupt band edges of the crystal are replaced by broadened tails of states extending in to the band gap (see Fig. 2.1b-d), their origin being a consequence of the disordered structure.

The tail states play a significant role in carrier transport because they control the carrier mobility. At E_c , the nature of the electron wavefunction changes. Above E_c , the electron wavefunction extends throughout the structure and electrons behave similarly to those in the crystalline phase, albeit with a short mean free path. Below E_c however, the carriers become localized, which means that their wavefunctions are now confined to a small region in the structure. On the other hand, there occurs a rapid decrease in the mobility as the energy crosses E_c [1]. At zero temperature, only

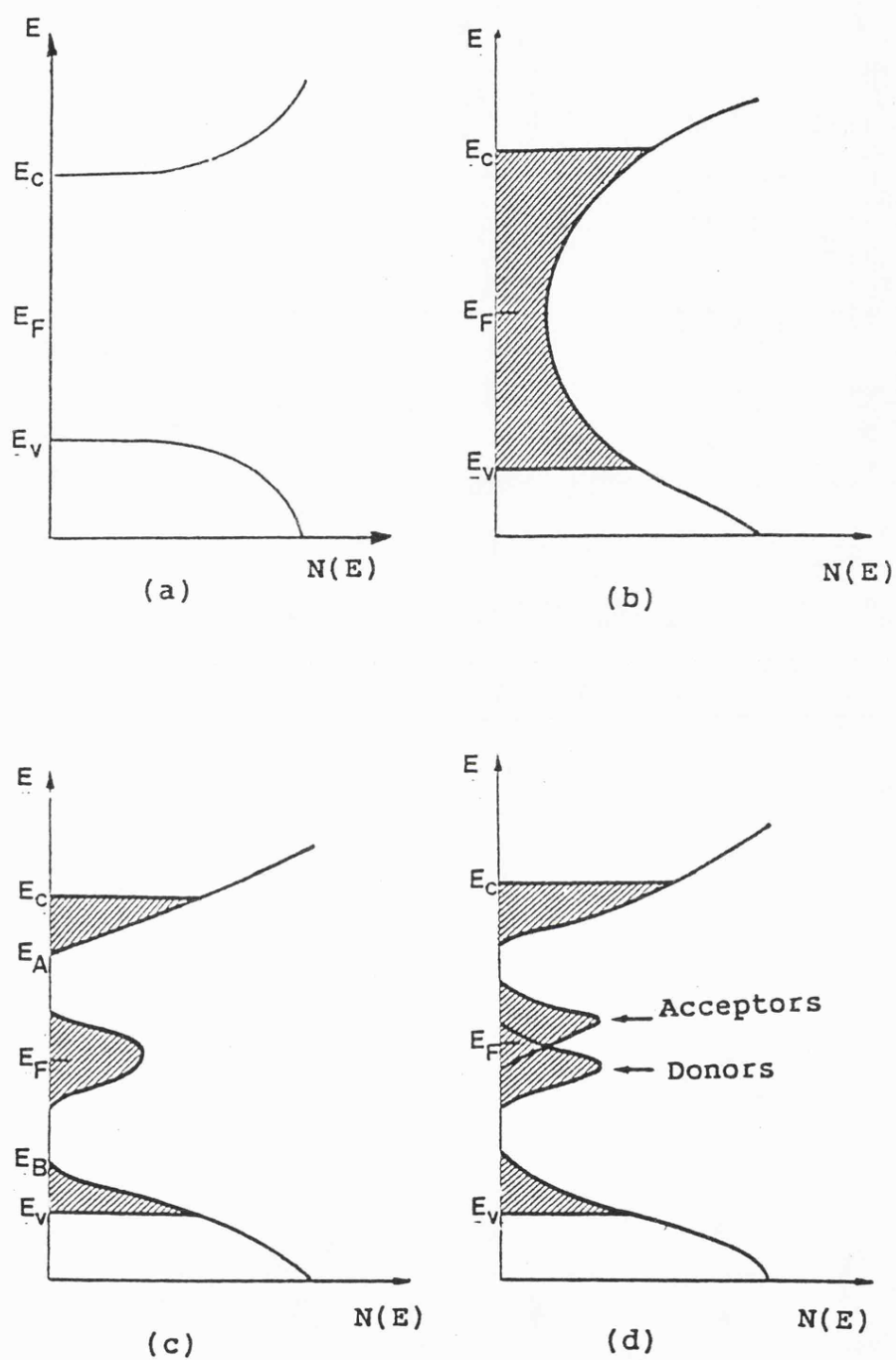


Fig. 2.1 Various models for the density of states (DOS) in (a) a crystalline semiconductor and (b-d) an amorphous semiconductor. Localized states are shown shaded. (b) proposed by Cohen et al [2]; (c) Davis-Mott model [3]; (d) Mott-model [4]. In an amorphous semiconductor $E_C - E_V$ is known as the mobility gap.

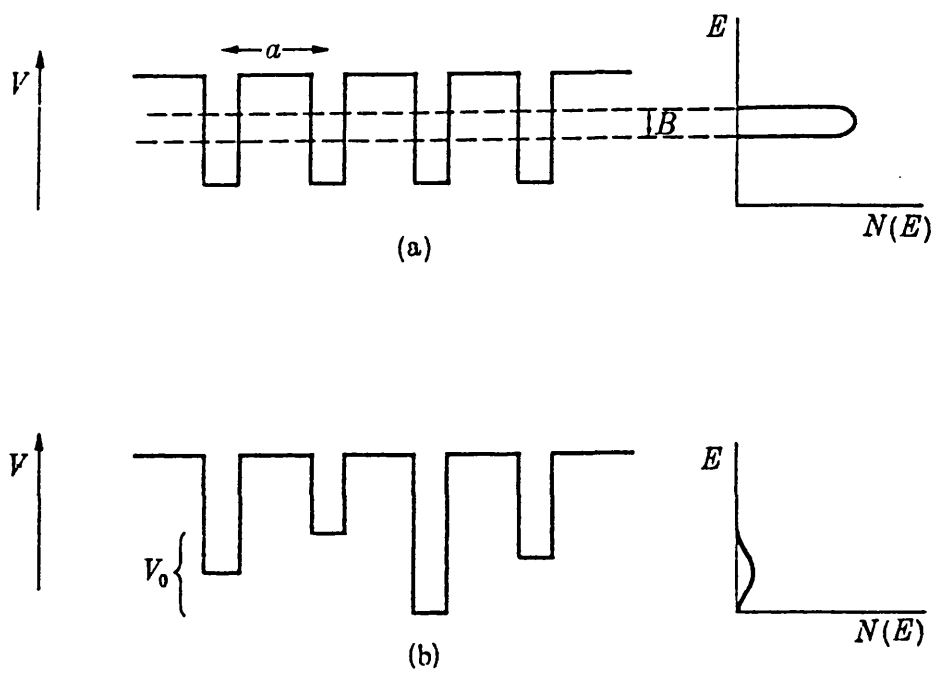


Fig. 2.2 (a) Potential wells for a crystalline lattice. (b) The same with a random potential energy at each well, as in Anderson [5]. The DOS $N(E)$ is also shown (after [1]).

electrons above E_c are mobile and contribute to electrical conductivity. Carriers below E_c are mobile only at finite temperatures. The same applies to the localized tail states for holes above E_v . This is the essence of the standard model of amorphous semiconductors proposed by Mott and Davis [1].

Electronic states deep within the band gap (deep states) arise from departures to the ideal network, such as dangling bonds (DBs) in the case of a-Si. These defects determine many electronic properties by controlling trapping, recombination and carrier lifetimes.

Several models have been proposed to describe the distribution of the electronic states in amorphous materials as illustrated in Fig. 2.1b-d. The common feature of these models is the band edges E_c and E_v defined so that states above E_c and below E_v are extended and those located between E_c and E_v are localized. Also the models show the Fermi level pinned in the middle of the gap by defect states. However, in a-III-V materials the distribution of the density of states in the gap is different from that of amorphous group-IV materials (see chapter 1). The dangling bonds, which form the deep states in the gap of group-IV materials, lie near the band edges in a-III-V materials. However, clusters of wrong bonds are expected to form deep states. Therefore, models used for group-IV semiconductors have to be slightly modified when applied to a-III-V semiconductors.

Understanding the concept of localization and of the behaviour of electrons in non-crystalline materials came after Anderson [5]. In his model, as illustrated in Fig. 2.2, Anderson showed that, for a great enough degree of disorder, all the states in an allowed band would become localized; in other words, when V_o/B (where B is the undistorted band width and V_o is the disorder potential) exceeds a critical value, the probability for an electron to diffuse away from a particular site is zero. The critical ratio V_o/B for complete localization through the band has been estimated to be 5 [5]. Edwards and Thouless [6] gave 2 and Elyutin et al [7]

gave 1.7.

If the parameter V_o/B is not great enough to give localization throughout the band, it was pointed out by Mott [8] that states near the extremities of the conduction and valence band (the band tails) would be localized and that the localized and extended (non-localized) states would be separated by energies E_c and E_v known as a "mobility edges".

2.2 TEMPERATURE DEPENDENCE OF THE D.C CONDUCTIVITY

Amorphous semiconductors show several transport mechanisms not normally found in the crystalline phase. These mechanisms will be discussed in the light of the models described in section 2.1 for the density of states and the mobility edges.

2.2.1 Extended-state conduction

At high temperatures the conductivity is dominated by carriers excited beyond the mobility edge into extended states. The conductivity σ (for electrons) is the product of the carrier density n , the electronic charge e and the carrier mobility μ

$$\sigma = ne\mu \quad 2.1$$

The carrier density n is given by the product of the density of states $N(E)$ and the probability of occupying the state at energy E , $f(E)$ integrated (for electrons) from E_c to infinity. Thus the carrier density above E_c is given by

$$n = \int N(E) f(E) dE \quad 2.2$$

The conductivity can then be expressed in terms of the density of states, the mobility, and the occupancy of the states as

$$\sigma = \int N(E) f(E) e\mu(E) dE \quad 2.3$$

where

$$f(E) = [1 + \exp(E - E_F)/kT]^{-1} \quad 2.4$$

is the Fermi-Dirac distribution function, k is the Boltzmann constant, T is the absolute temperature, and E_F is the Fermi level. The probability of the states at energy not being occupied by an electron is $f'(E) = 1 - f(E)$. If $(E_C - E_F) \gg kT$, and $N(E)$ does not vary too much in the neighbourhood of E_C , then

$$n = N(E) kT \exp[-(E_C - E_F)/kT] \quad 2.5$$

The extended-state conductivity above E_C can be written as

$$\sigma = N(E) kT e \mu \exp[-(E_C - E_F)/kT] \quad 2.6$$

if μ is taken to be independent of energy close to E_C .

i.e.

$$\sigma = \sigma_0 \exp[-(E_C - E_F)/kT] \quad 2.7$$

where the pre-exponential term has been written as σ_0 . A plot of $\ln \sigma$ versus $1/T$ yields a straight line with slope $-(E_C - E_F)/k$ and the intercept on the $\ln \sigma$ axis at $1/T=0$ will provide the constant σ_0 . σ_0 has been given by Mott [9] as

$$\sigma_0 \approx 0.03 e^2 / \hbar L_i \quad 2.8$$

where L_i is the inelastic diffusion length. The value of σ_0 is not strongly dependent on the material and for most amorphous semiconductors it lies in the range $10^2 - 10^4 \Omega^{-1} \text{ cm}^{-1}$. Equation 2.7 was used to calculate the activation energy of the conductivity in the present work when extended-state conduction was believed to occur.

One feature of the conductivity not accounted for by equation 2.7 is the variation of the band gap with temperature. If $E_C - E_F$ is a linear function of T over the temperature range measured, then

$$E_C - E_F = (E_C - E_F)_0 - \gamma T \quad 2.9$$

and the slope of $\ln \sigma$ versus $1/T$ plot will be $-(E_C - E_F)_0/k$, giving the activation energy extrapolated to $T=0$ and an intercept on the $\ln \sigma$ axis of $\sigma_0 \exp(\gamma/k)$.

2.2.2 Conduction in localized tail states

As the temperature is lowered, the number of carriers thermally activated to the mobility edge E_C will be reduced and the contribution to the total conductivity of the electrons in the extended states will diminish. Conduction by carriers excited into the localized states at the band edges will then become of increasing importance. Since all the states at the band edge are localized, conduction will be via a hopping mechanism requiring thermal activation. Then

$$\sigma = \sigma_1 \exp[-(E_A - E_F + W_1)/kT] \quad 2.10$$

where W_1 is the activation energy for hopping and E_A is the energy at the band edge if the form of the DOS is as shown in Fig. 2.1c. σ_1 is expected to be much lower than σ_0 because of the drop of the effective density of states and the carrier mobility near E_A compared with E_C .

2.2.3 Conduction in localized states at the Fermi level

As the temperature is lowered further, a temperature will exist below which the conduction path will switch from that of hopping in the band tails to hopping near the Fermi level if $N(E_F)$ is

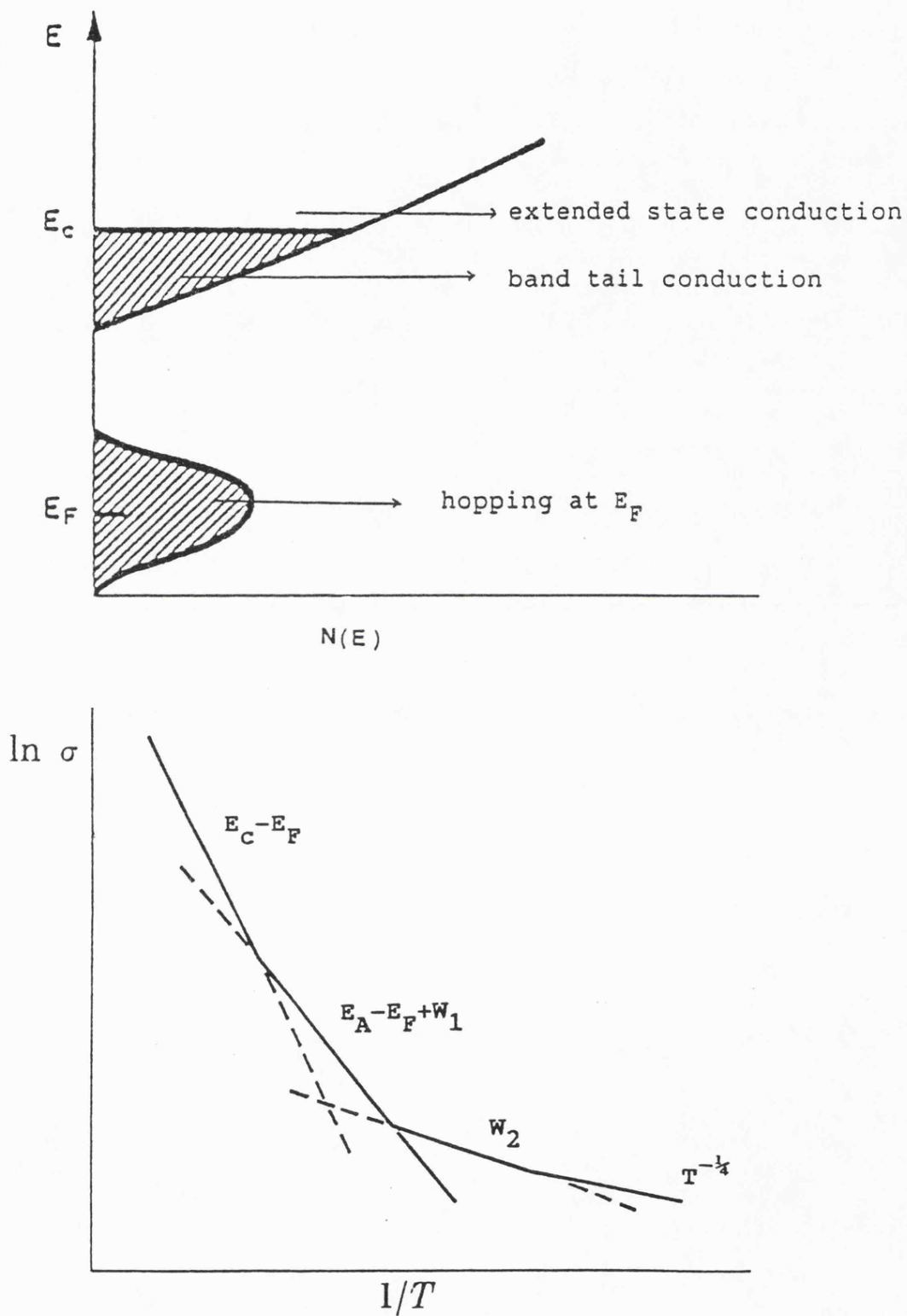


Fig. 2.3 Illustration of (a) the three main conduction mechanisms expected in an amorphous semiconductor, (b) the temperature dependence of conductivity along with the associated activation energies for the various regimes (after [1]).

finite. This is the processes in which an electron in an occupied states with energy below E_F gains energy from a phonon which enables it to move a nearby state above E_F . Then σ will be of the form

$$\sigma = \sigma_2 \exp(-W_2/kT) \quad 2.11$$

where W_2 is the hopping energy. This will be of the order of the half the width of the band of states, again if the form of the density of states is as shown in Fig. 2.1c. σ_2 is expected to be lower than σ_1 .

At even lower temperatures, it may become energetically more favourable for the carriers to tunnel to a more distant site in order to find a final state closer in energy to the initial site. Then conduction occurs close to the Fermi level by so-called variable-range-hopping (VRH). Under these circumstances, Mott [10] has shown that σ is of the form

$$\sigma = \sigma_3 \exp(-T_0/T)^{1/4} \quad 2.12$$

where

$$T_0 = [18\alpha^3/kN(E_F)] \quad 2.13$$

Here α is the decay constant for the localized electron wavefunction. This relation is known as Mott's $T^{-1/4}$ law, from which $N(E_F)$, the density of states at the Fermi level, can be calculated.

The possible conduction mechanisms discussed in the text are illustrated in Fig. 2.3a and the manner in which σ is expected to vary with temperature is shown in a schematic plot of $\ln\sigma$ versus $1/T$ in Fig 2.3b.

2.2.4 Recent ideas on the nature of the mobility edge

Early considerations of the behaviour of the mobility at the mobility edge (say E_c) have recently been revised following

theoretical and experimental investigations of transport near E_c . Initially it was thought that the mean free path of electrons just above E_c was as small as possible—namely an average interatomic spacing—the so-called Ioffe-Regel limit. This led to the suggestion that there was a discontinuous drop in the mobility on passing through E_c .

It is now clear that this concept (strongly linked to the existence of Mott's minimum metallic conductivity $\sigma_{\min}$) needs modification because L_i in equation 2.8 can be several times larger than the interatomic spacing and, in principle, σ_0 can take on values from $\sigma_{\min}$ down to zero. Furthermore at high temperatures, "phonon delocalization" [19] can shift E_c downwards.

For the purpose of this thesis, these considerations will not affect the interpretation of our results.

2.3 OPTICAL PROPERTIES

Optical measurements constitute one of the most important means of determining the band structures of semiconductors. Optically-induced electronic transitions can occur between different bands, which leads to a determination of the optical band gap E_0 . The optical absorption coefficient α depends on both the valence and conduction band density of states and the transition probabilities or matrix elements.

In crystalline semiconductors there are two type of transitions that can occur between valence and conduction bands; direct and indirect. In the former the optically-induced transitions connect those energy levels of the same momentum, while, in the latter, the transition occurs between states of different k . For indirect transitions, phonons must be involved (absorbed or emitted) in order to conserve momentum. Such transitions are therefore generally weak and are only observed at energies when direct

transitions are forbidden. In an amorphous semiconductor, momentum is not a good quantum number and the requirement of k-conservation is relaxed. This allows transitions to occur between any two states for which energy conservation applies.

In most crystalline semiconductors, the absorption coefficient rises fairly rapidly near E_0 , i.e. they exhibit sharp absorption edges within a relatively small energy range near the optical gap. On the other hand, the fundamental absorption edge of amorphous semiconductors is found to be much broader due to the disorder-induced broadening of the valence and conduction bands and also because of the breakdown of the optical selection rules that control interband transitions in crystals.

The relationship between the absorption coefficient and the density of states of both valence and conduction bands can be expressed (assuming the matrix elements and the refractive index n_0 to be independent of energy) as [see 1],

$$\alpha(\omega) = 8\pi^4 e^2 \hbar a / c m_e^2 n_0 \int N_V(E) N_C(E + \hbar\omega) dE / \hbar\omega \quad 2.14$$

where a is the average lattice spacing. The integration is carried out over pairs of states in the valence and conduction bands separated by $\hbar\omega$. The other terms in 2.14 have their usual meanings.

The optical parameter of most interest is the band gap E_0 . This is not defined precisely in an amorphous semiconductors because of the presence of the band tails. A simple model was assumed by Tauc et al [11] and Davis and Mott [3]. They assumed that the density of states at the band edges increases as power laws of energy, i.e.

$$N_C(E) = \text{const.} (E - E_A)^P \quad 2.15a$$

$$N_V(E) = \text{const.} (E_B - E)^Q \quad 2.15b$$

Then the absorption near the gap is given by

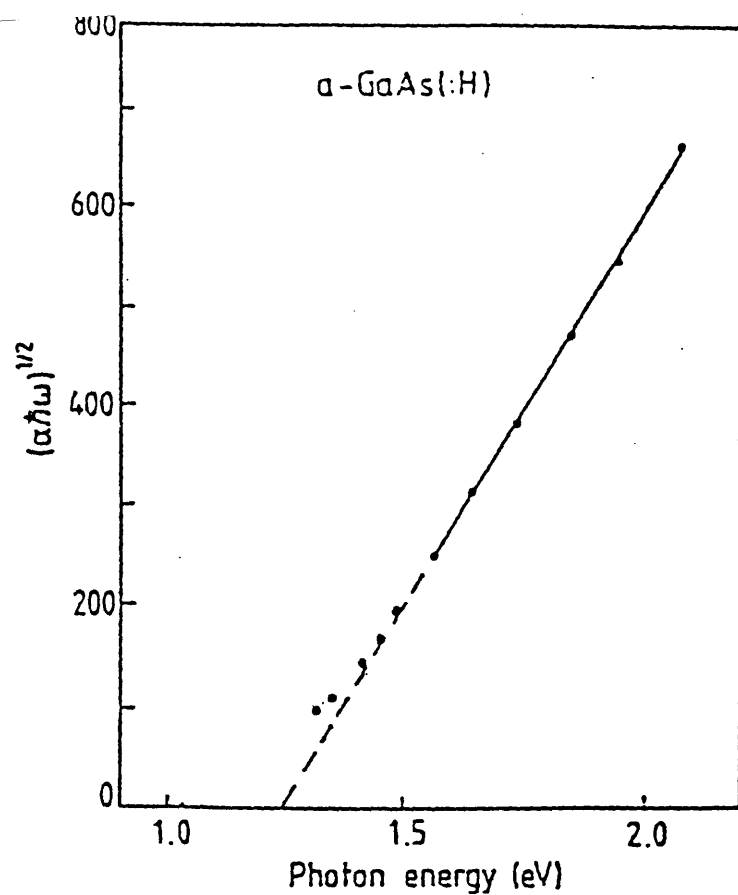


Fig. 2.4 The absorption coefficient plotted in the form of equation 2.17 giving an extrapolated band gap of 1.25 eV for $a\text{-GaAs}:\text{H}$ (after [20]).

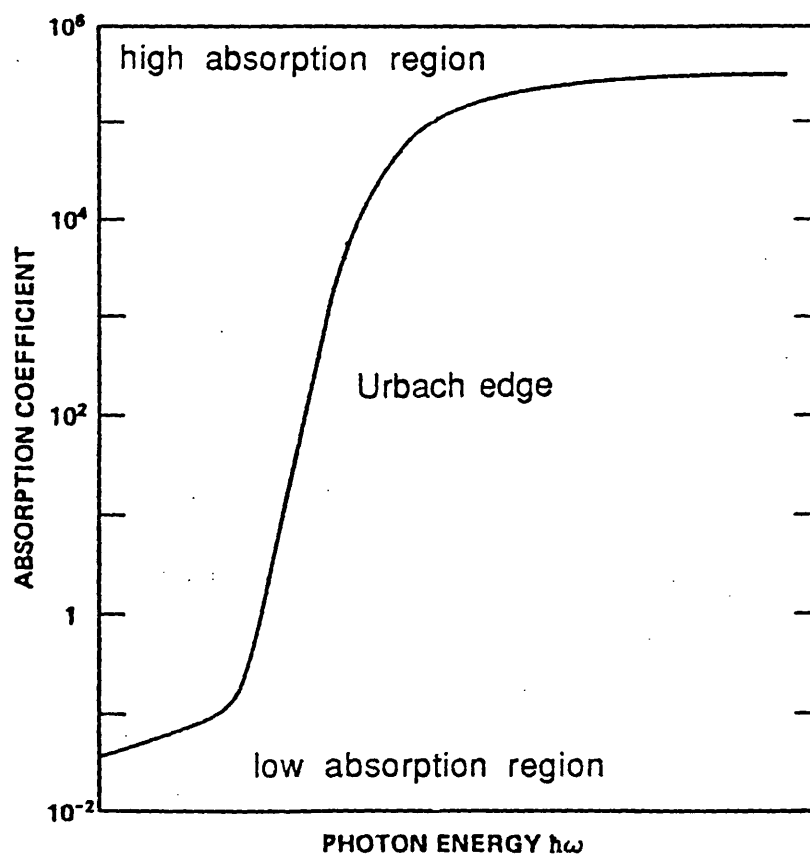


Fig. 2.5 Schematic representation of the absorption edge of amorphous semiconductors.

$$\alpha(\omega)\hbar\omega = \text{const.}(\hbar\omega-E_0)^{p+q+1} \quad 2.16$$

For parabolic band edges, $p=q=\frac{1}{2}$ and

$$[\alpha(\omega)\hbar\omega]^{\frac{1}{2}} = \text{const.}(\hbar\omega-E_0) \quad 2.17$$

This relation provides a simple procedure to extract E_0 from $\alpha(\omega)$ measurements as shown in Fig. 2.4. This form of absorption is observed for many amorphous semiconductors. However, there is a possibility of optical transitions between say states at the valence band mobility edge and the localized conduction band tail [1]. It should be mentioned here that the magnitude of the absorption due to the latter process is likely to be considerably smaller than that for the first process (extended-extended transitions) due to the lower density of states in the tail state regions.

Alternatively the optical gap in amorphous semiconductors can be defined as the photon energy corresponding to an optical absorption coefficient of 10^4 cm^{-1} (E_{O4}); sometimes it is defined at $\alpha = 10^3 \text{ cm}^{-1}$ (E_{O3}). The E_{O4} definition of the optical gap was first suggested by Stuke [12]. Generally speaking, it does not differ greatly from E_0 determined by 2.17.

In the present work the optical band gap defined using equation 2.17, has been used.

2.3.1 The Urbach edge

In the last section we considered the optical transitions that occur in a range of energies corresponding to the band gap energy (inter-band transitions) for which the optical absorption coefficient $\alpha \geq 10^4 \text{ cm}^{-1}$. If only these mechanisms were operative, one would expect a sharp absorption edge for absorption coefficients less than 10^4 cm^{-1} . Instead, what is found experimentally for most amorphous semiconductors is an edge which

tails to low energies as shown schematically in Fig. 2.5. The absorption coefficient in this region is found to obey an exponential dependence on photon energy [1]

$$\alpha(\omega) = \alpha_0 \exp [(\hbar\omega - E_0)/\Gamma] \quad 2.18$$

where α_0 is a constant and Γ^{-1} is the slope of a plot of $\ln\alpha(\omega)$ versus $\hbar\omega$. The slope is often interpreted as a measure of the width of the tails, generally the valence band tail in a-Si:H, of the localized states in the gap region. The exponential portion is called the Urbach edge after its first observation in alkali halide crystals [13]. Despite the generality of the above law, its precise origin is not certain. For amorphous semiconductors it is believed that it reflects the shape of the band tails, because the slope $1/\Gamma$ varies with the structural disorder [14]. A review of other theoretical models put forward for the Urbach edge may be found in reference 1.

At even lower values of the absorption coefficient (say $\alpha \leq 10 \text{ cm}^{-1}$), another type of optical transition is observed in some amorphous semiconductors. This is believed to be associated with transitions into (or from) defect states in the gap from (or into) the valence and/or conduction band. Its observation is normally beyond the capability of conventional transmission or reflection methods used for higher values of the absorption. Photothermal deflection spectroscopy (PDS) has been shown to be a sufficiently sensitive technique to observe it [15]. The weak absorption tail shown in Fig. 2.5 has not yet been observed in a-III-V semiconductors. This is probably because the dangling bonds in these materials lie near the band edges (see ch.1) unlike in a-Si for which they lie deep in the mid-gap.

2.3.2 Infrared (IR) spectroscopy

The optical properties of crystalline and amorphous

semiconductors in the IR region of the spectrum (5000 cm^{-1} - 400 cm^{-1}) are dominated by excitation of vibrational modes. Modes are said to be IR-active if there is a change in dipole moment associated with the vibration. The vibrational behaviour of amorphous material is similar to that of the corresponding crystal, except that selection rules for transitions are relaxed, and sharp features in the density of vibrational modes become broadened in the amorphous case. This suggests that it is short-range order which determines the essential features of the vibrational properties.

Infrared techniques yield direct information about the type and the number of the various bonds present. This can be obtained from the positions and areas of peaks in the IR transmission spectrum.

Infrared spectroscopy has been used in detailed studies of hydrogen-containing elemental tetrahedral amorphous semiconductors (e.g. a-Si:H, a-Ge:H) and a-III-V compounds (e.g. a-GaAs:H, a-GaP:H). Fig. 2.6 shows the IR transmission spectrum of a-GaAs:H. The two strong and broad bands at 1460 and 530 cm^{-1} are the most distinguishable peaks in the spectrum and have been assigned as Ga-H-Ga bridge stretching and wagging modes respectively [16]. The smaller peaks are due to different types of hydrogen bonding, for example Ga-H and As-H. It is clear then that IR measurements provide a quick and useful method for obtaining information about the type and concentration of different chemical bonds in the sample.

In the present work both IR and EXAFS have been used to investigate the atomic structure of a-GaAs and its related compounds. However, IR spectroscopy was the only technique available for investigating the presence of hydrogen and for studying its evolution of from films annealed at different temperatures.

2.4 EVALUATION OF THE OPTICAL ABSORPTION COEFFICIENT

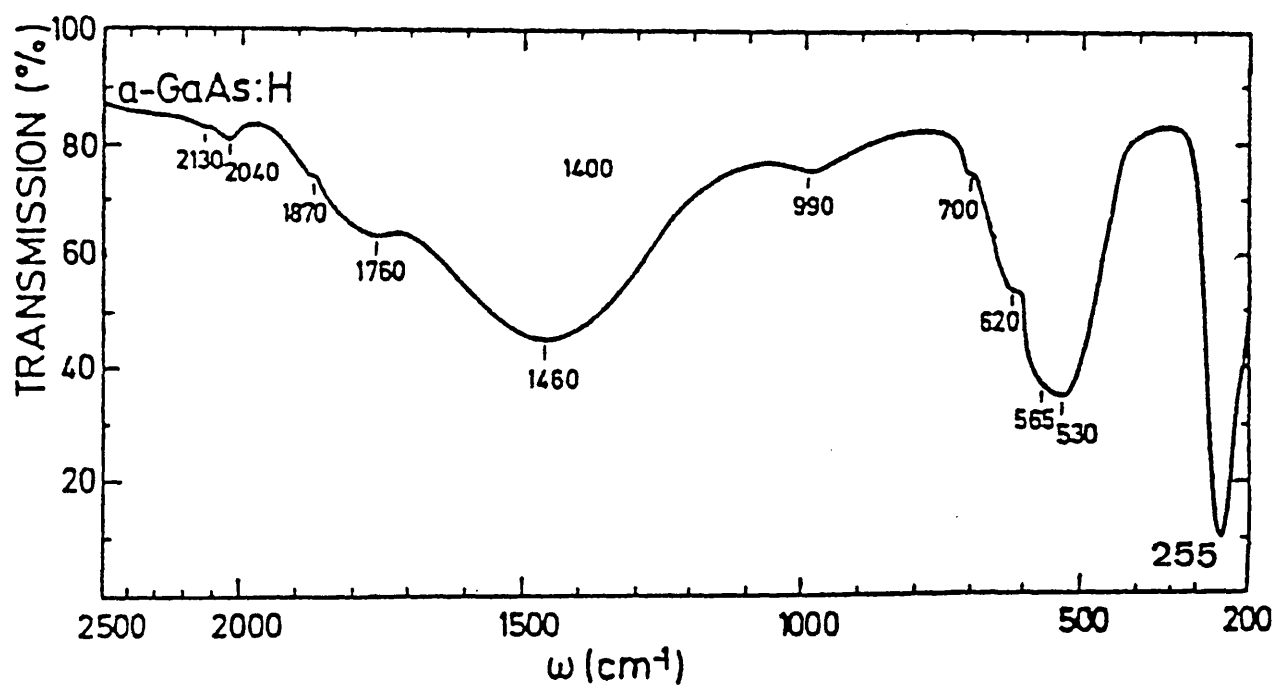


Fig. 2.6 Infrared transmission spectra of a-GaAs:H (after [16]).

The absorption coefficient was determined from measurements of transmittance T and reflectance R , for wavelengths ranging between 400 and 2500 nm, using a double-beam Perkin Elmer 330 spectrophotometer (see section 3.5). The absorption coefficient of a film with thickness d was obtained from the expression [17]

$$T = (1-R_1)(1-R_2)(1-R_3)\exp(-\alpha d) / (1-R_2R_3)\{1 - [R_1R_2 + R_1R_3(1-R_2)^2]\exp(-\alpha d)\} \quad 2.19$$

where R_1, R_2, R_3 are the reflectivities of the air-film, film-substrate, and substrate-air interfaces respectively. In those spectral regions where multiple reflections lead to interference fringes (see Fig. 2.7), we approximated T by the average between the maxima and minima in the transmission spectrum. When αd is small ($\ll 1$) the imaginary part of the refractive index is negligible and

$$R_1 = (n - n_a)^2 / (n + n_a)^2 \quad 2.20a$$

$$R_2 = (n - n_s)^2 / (n + n_s)^2 \quad 2.20b$$

$$R_3 = (n_s - n_a)^2 / (n_s + n_a)^2 \quad 2.20c$$

where n_a is the refractive index of air ($n_a=1$), n_s is the refractive index of the substrate, and n is the refractive index of the film. n was obtained using the method explained in section 3.4.2a Equation 2.19 was used for the low-absorption region. For the high-absorption region, when the fringes in transmittance and reflectance become broad and eventually disappear, the following approximate expression was used [18]

$$T = (1 - R_m)\exp(-\alpha d) \quad 2.21$$

where $T = I_T/I_0$ is the transmittance, $R_m = I_R/I_0$ is the measured

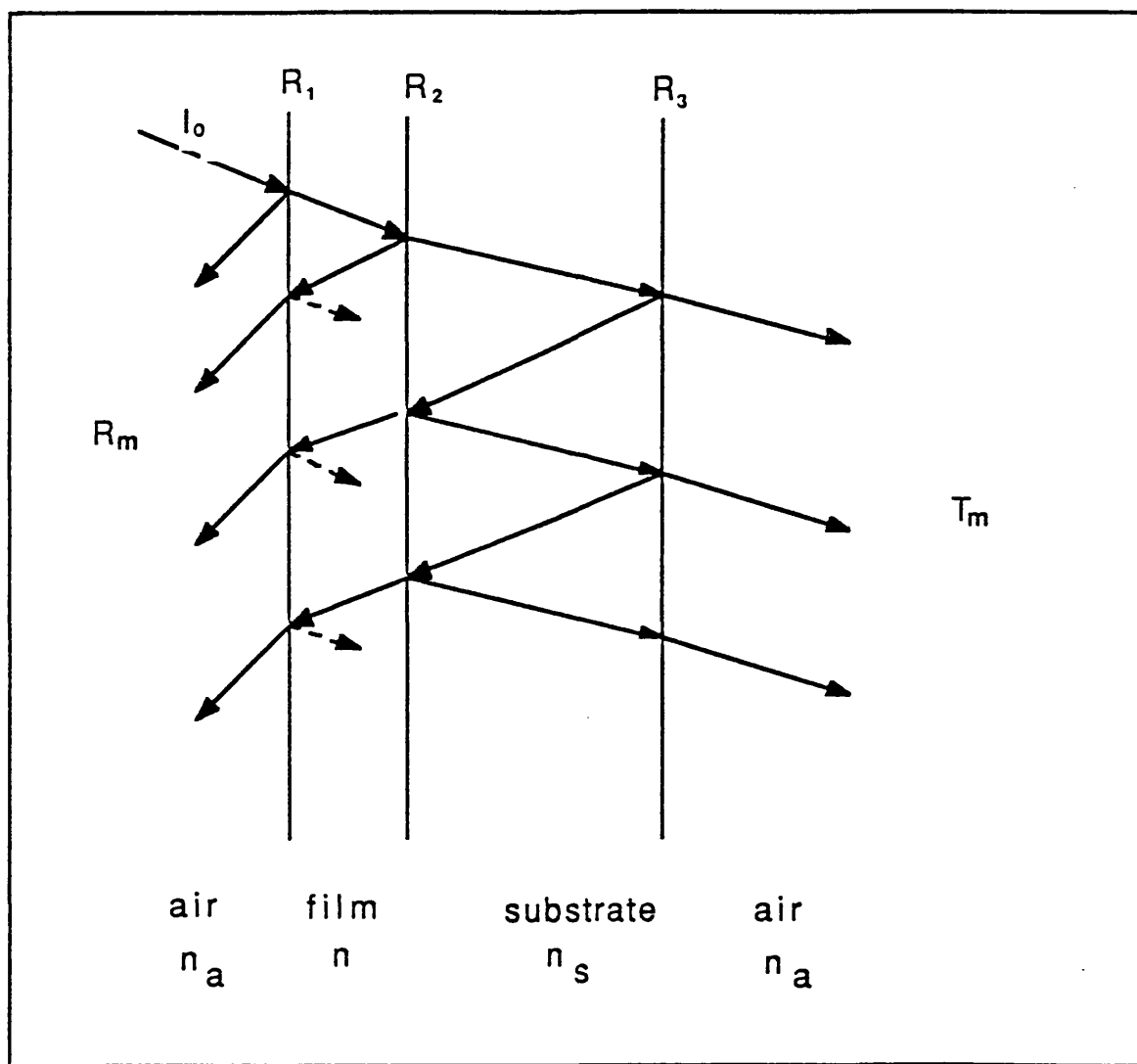


Fig. 2.7 Shows multiple reflections and transmissions by a thin film.

reflectance, I_T and I_R are the total transmitted and reflected intensities and I_0 is the incident beam intensity. The absorption coefficient as a function of energy for the low-absorption and high-absorption regions overlapped and matched well using the two expressions.

2.5 A CHECK ON THE ACCURACY OF R AND T BY AVERAGING THE MAXIMA AND MINIMA OF THE INTERFERENCE FRINGES

As mentioned in the last section, interference fringes appear in the low-absorption region of the T and R spectra. When this happens an envelope was drawn embracing the minima and maxima, and this was then carefully averaged. Some error might be expected using this method because of inaccuracies in the averaging. Therefore, it was important to check on the accuracy of R_{average} from the spectra and $R_{\text{meas.}}$ using the expression [see 18]

$$R_{\text{meas.}} = R_1 + [R_2(1-R_1)^2 e^{-2\alpha d}] / [1 - R_1 R_2 e^{-2\alpha d}] + [R_2(1-R_1)^2 (1-R_2)^2 e^{-2\alpha d}] / [(1-R_2 R_3)(1-R_1 R_2 e^{-2\alpha d})] \quad 2.24$$

R_1, R_2, R_3 were defined in equation 2.19. These parameters were calculated from the Fresnel formulas using the known refractive index of air ($n_a=1$) and of the substrate (Corning 7059 glass $n_s=1.53$) and the values of the refractive indices of our films n (see section 3.4.2a). By substituting them in equation 2.24

$$R_1 = c R_{\text{meas.}} \quad 2.25$$

where c is the reflectance correction factor. For example, if we use a value of the refractive index n in the low-absorption region of one of our a-GaAs:H films (say at 1200 nm), n was found to be 3.6, $R_1=0.31947$, $R_2=0.163$, and R_3 is known=0.044. Substituting these values in equation 2.24 we find that $R_{\text{meas.}} = 0.414$, while R_{average} from the spectra at the same wavelength is =0.405. It can

be seen that the error is about 2%. Another wavelength was chosen in the high-absorption region ($\lambda=600$ nm). $R_{\text{meas.}}$ was 0.498 and R_{average} was 0.511 which is higher by about 2%. Transmission spectra were also checked using the same wavelengths as before and, using equation 2.19, we found similar results with about 2% error. From these simple calculations we can conclude that the method of averaging R and T is quite accurate if care is taken when averaging.

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CHAPTER THREE

EXPERIMENTAL METHODS AND TECHNIQUES

3.1 SPUTTERING SYSTEM

3.1.1 General description

All the films studied in the present work were prepared using a Nordiko NM - 2000 - T8 sputtering system; its schematic diagram is shown in Fig. 3.1.

The vacuum chamber, 22" in diameter and 15.8" high, contains a multi-electrode turret with an evaporation source and two sputtering electrodes; one of the latter is for high-rate magnetron sputtering and the second is for conventional sputtering. A particular electrode can be selected by rotating the turret. Throughout this work, the conventional sputtering electrode was used.

The substrates were clamped on to an 8" diameter copper platen using a stainless-steel contact mask. The platen was locked into the substrate electrode by means of special key wrench. Thin copper gaskets were inserted between the platen and the electrode to improve the thermal contact.

The substrate temperature, monitored using two chromel-alumel (type K) thermocouples, could be varied by means of a heating element located within the mounting column. Stabilization of the substrate temperature was achieved using a Eurotherm temperature controller. One thermocouple was located on top of the substrate heater outside the chamber; the second was inside the chamber, inserted into a drilled hole in the side of the substrate platen, and electrically insulated from the platen by a quartz sleeve.

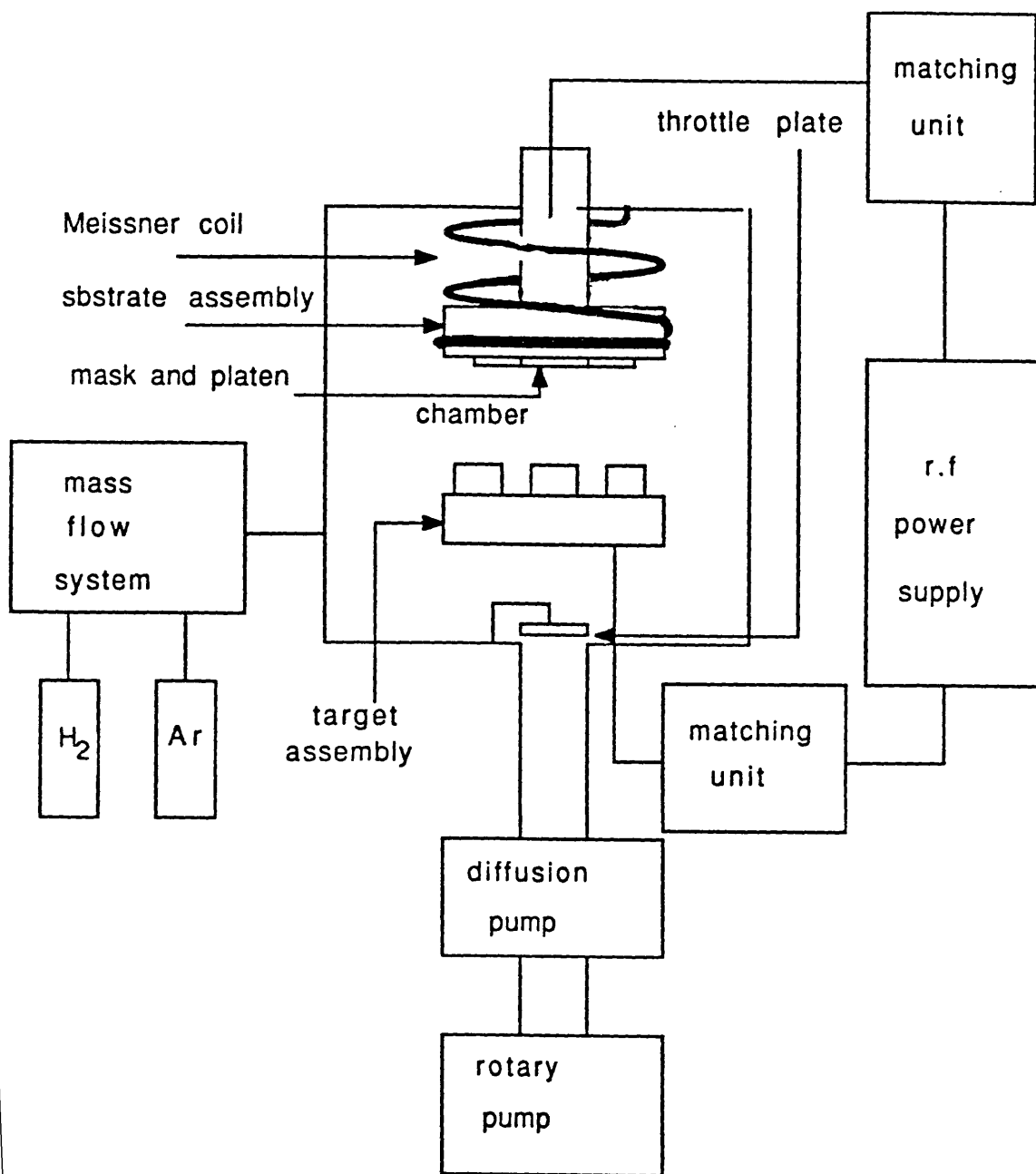


Fig. 3.1 Schematic diagram of the sputtering system

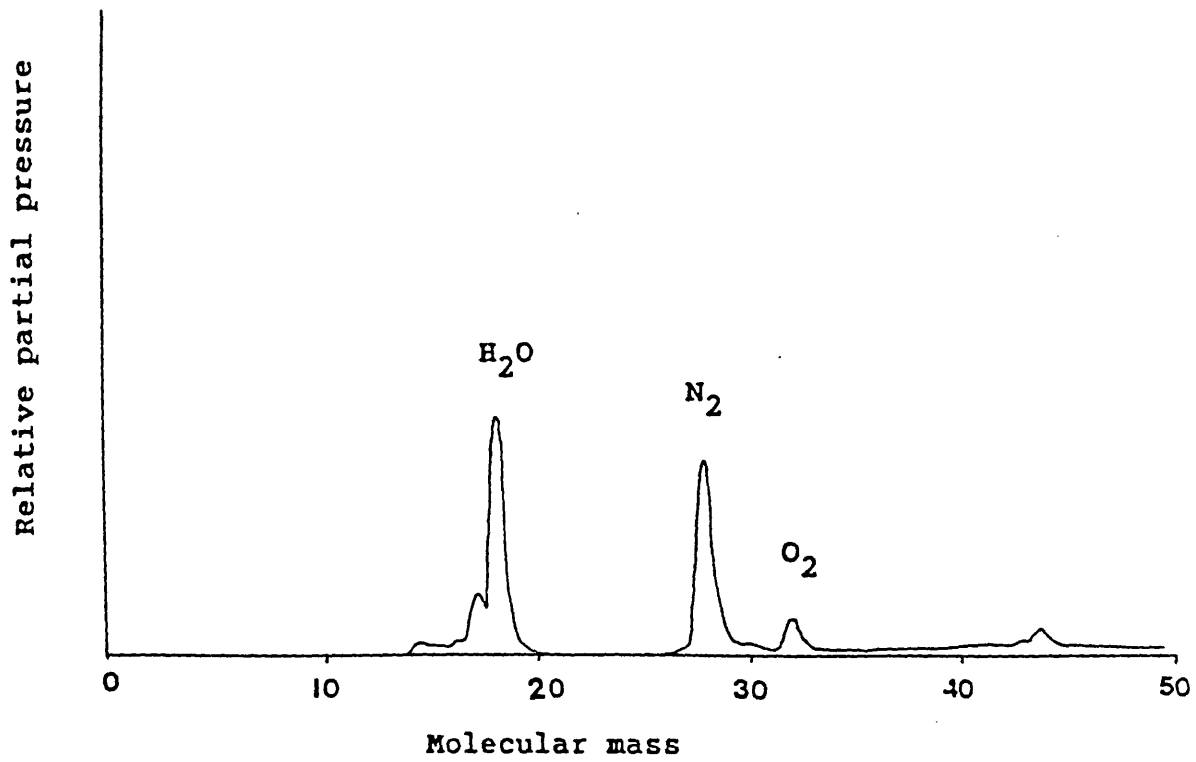


Fig. 3.2 Typical spectra of the residual gases in the vacuum chamber.

A rotating substrate holder (built in the Physics Department at Leicester University) was used to prepare some of the a-GaAlAs films. The rotating substrate can be used to prepare multilayer films (by using two different target materials simultaneously), but in this work was used to improve the thickness uniformity of the films.

The chamber was pumped by a Varian VHS - 6 inch diffusion pump, with a liquid-nitrogen cold trap and a continuous-flow water baffle to prevent the diffusion pump oil from reaching the chamber. The diffusion pump was backed by a Leybold - Hereaus D30A direct-drive rotary pump to maintain the backing pressure at a level considerably below the critical backing pressure of the diffusion pump. The above combination of pumps enabled the chamber to be pumped down to a pressure $< 6 \times 10^{-7}$ Torr. By flowing liquid nitrogen through a copper Meissner coil located around the substrate, the pressure could be reduced to $< 2 \times 10^{-7}$ Torr.

A residual gas analyser (mass spectrometer) was installed in the chamber, and enabled accurate checking of contamination in the chamber prior to sputtering. The main sources of contamination in the chamber were found to be water vapour and nitrogen. A typical trace showing the main residual gasses is shown in Fig. 3.2.

The flow of sputtering gases (argon and hydrogen) into the chamber, was controlled by a Vacuum General 78-7 flow-ratio and pressure control system. The total sputtering pressure was measured by means of a sputtering pressure gauge. The throttle plate was kept almost closed to reduce the pumping speed during sputtering.

The r.f power was provided by a 1.25 kW, 13.56 MHz crystal-controlled r.f generator. The output impedance of the power supply was designed to be 50 ohms. If the co-axial cable carrying the output from the power supply

were simply connected to the electrode (target or substrate), a gross impedance mismatch would cause practically all of the power to be reflected back to the power supply and very little r.f power would be available for sputtering. This problem is overcome by use of a matching unit positioned between the end of the co-axial cable and the electrode system.

3.1.2 Radio-frequency (r.f.) sputtering

Sputtering is a thin-film deposition technique in which material is ejected from the target by ion bombardment from the plasma.

The simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, this d.c sputtering can only be used for low-resistance targets, such as metals on which charge does not accumulate, cutting-off the discharge. A more common technique for insulators is to apply a radio frequency field (13.5 MHz in the case of the present work) to the target. The sputtering gas (normally argon) is introduced into the chamber, typically at a pressure of 10^{-3} - 10^{-2} Torr. The application of an r.f voltage to the target causes the striking of the plasma. During each negative half-cycle the ion current will flow towards the target. Similarly, an electron current flows towards the target during the positive half-cycle. However, since the mobility of the electrons is higher than that of ions, more electrons are attracted to the target in their respective half-cycles resulting in the build-up of a negative bias after some time. The negative bias causes

ions to be attracted to the target; the resulting bombardment removes atoms or groups of atoms from the target by momentum transfer. The ejected atoms reach the substrate and are frozen in the random position at which they arrive, thus producing an amorphous film. At elevated substrate temperatures a certain amount of structural relaxation can take place, resulting in less disordered films.

Other gases (e.g. hydrogen) can be introduced into the chamber during sputtering. If these additional gases are incorporated into the sputtered film, the technique is known as reactive sputtering. Hydrogenation by this method of sputtering has been applied successfully to prepare a-Si:H, a-Ge:H and a-GaAs:H (see section 1.4 ch. 1). Since the target surface and the substrate are both in direct contact with the plasma, film growth would be expected to be influenced by several processes which may occur following ion impact. These phenomena can occur at the target, in the plasma and at the substrate. A review on the effect of these phenomena on film growth is given in references [1] and [2].

3.1.3 Sample preparation conditions

Three different sets of a-GaAs films and two sets of ternary a-GaAlAs and GaAsP alloys were prepared and investigated in the present work.

Amorphous GaAs films were prepared by radio-frequency sputtering using a 2 inch diameter single-crystal GaAs target in an argon atmosphere for unhydrogenated films and an argon/hydrogen atmosphere for hydrogenated films. The relative flow rates of the two

gases, and hence their partial pressures, were adjusted to vary the content of hydrogen in the film. The base pressure was $< 2 \times 10^{-7}$ Torr. The residual gas analyser confirmed a low level of any appreciable contaminants such as CO_2 , H_2O and hydrocarbons in the chamber. The films were deposited simultaneously on to various ultrasonically cleaned substrates (using acetone and methanol). The substrates used for electrical and optical work were 7059 Corning glass slides (high-resistivity barium-alumino-silicate alkali-free glasses). Highly polished c-Si substrates were used for infrared measurements and aluminium (or glass) for composition measurements. Specimens for transmission electron microscope (TEM) measurements were deposited on mica, the latter for checking the amorphicity of the films.

Typical deposition conditions were as follows:

Power	70-80 W
Target bias	0.3-0.4 kV
Total sputtering pressure	5-6 mTorr
Target to substrate separation	5.5 cm

The substrates were held at about 20°C by water cooling for "room-temperature" deposition. Throughout the investigation of the deposition conditions the argon flow rate was fixed at 30 scc/min. Certain deposition parameters were varied in order to investigate their influence on the optical, electrical and structural properties of the films. These were :

1. The hydrogen content, defined as the ratio of the hydrogen flow rate to the total hydrogen and argon flow rates. This was varied from 0-50%.
2. The As content; altered by varying the number of As pieces added to the GaAs target.
3. The substrate temperature; varied by heating the substrate to the required temperature using a heater and

temperature controller.

Ternary compounds a-GaAlAs and a-GaAsP were prepared in a similar way to a-GaAs. The aluminium and phosphorus contents of the films were altered by varying the number of Al and P chips added to the GaAs target.

The target was pre-sputtered for about one hour with a shutter covering the substrates in order to remove adsorbed impurities from the surface of the target. After cleaning the target in this way, the substrate shutter was rotated out of the way so that deposition could commence. A small shutter was positioned over the mica substrate(used for the TEM measurements) after about 1.5 to 2 hours depending on the sputtering gas mixture (the typical thickness required for TEM measurements is ~ 400 Å), so that further sputtered material did not reach the mica while deposition continued on the other substrates. After the required deposition time, the chamber was repumped to $< 2 \times 10^{-7}$ Torr and left at this pressure for several hours to ensure that all gases were pumped away before opening the chamber and removing the samples.

3.2 ELECTRON MICROSCOPY

Evidence for the amorphous structure of the deposited films was obtained using a JOEL Jem 100CX transmission electron microscope (housed in the Medical Science Department at Leicester University). The films for the experiments were deposited on mica (see section 3.1.3) to a thickness of about 400 Å and floated off the substrate in distilled water. The pieces of film were then gently lifted out of the water onto a standard copper electron microscope grid. All GaAs samples examined were

amorphous while those of GaAlAs were amorphous up to about 30 at% Al but polycrystalline above this concentration. The TEM photographs will be shown later (chapter 4). An additional check on the amorphous nature of the films was provided by EXAFS data (see chapter 5) which confirmed that all films on which such measurements were carried out were amorphous.

3.3 COMPOSITION DETERMINATION

The composition of the samples was determined by energy dispersive X-ray analysis using a D.S. 130 scanning electron microscope (SEM) (again in the Medical Science Department at Leicester University). Figs. 3.3 a-c shows typical X-ray emission spectra for GaAs, GaAlAs and GaAsP respectively. The films were slightly As rich. Fig. 3.4 gives the composition of the GaAlAs films. The tie lines of $(\text{GaAs})_{1-x}\text{Al}_x$ and $(\text{Ga}_{1-x}\text{Al}_x)\text{As}$ are also shown. A few % of argon was detected in most of the samples. Hydrogen cannot be detected by this technique. These measurements also confirmed the homogeneity of the films since the composition varied little in different areas of the same sample.

3.4 DETERMINATION OF FILM THICKNESS AND REFRACTIVE INDEX

Knowledge of the thickness is essential when determining properties such as optical absorption coefficient or electrical conductivity. For this reason,

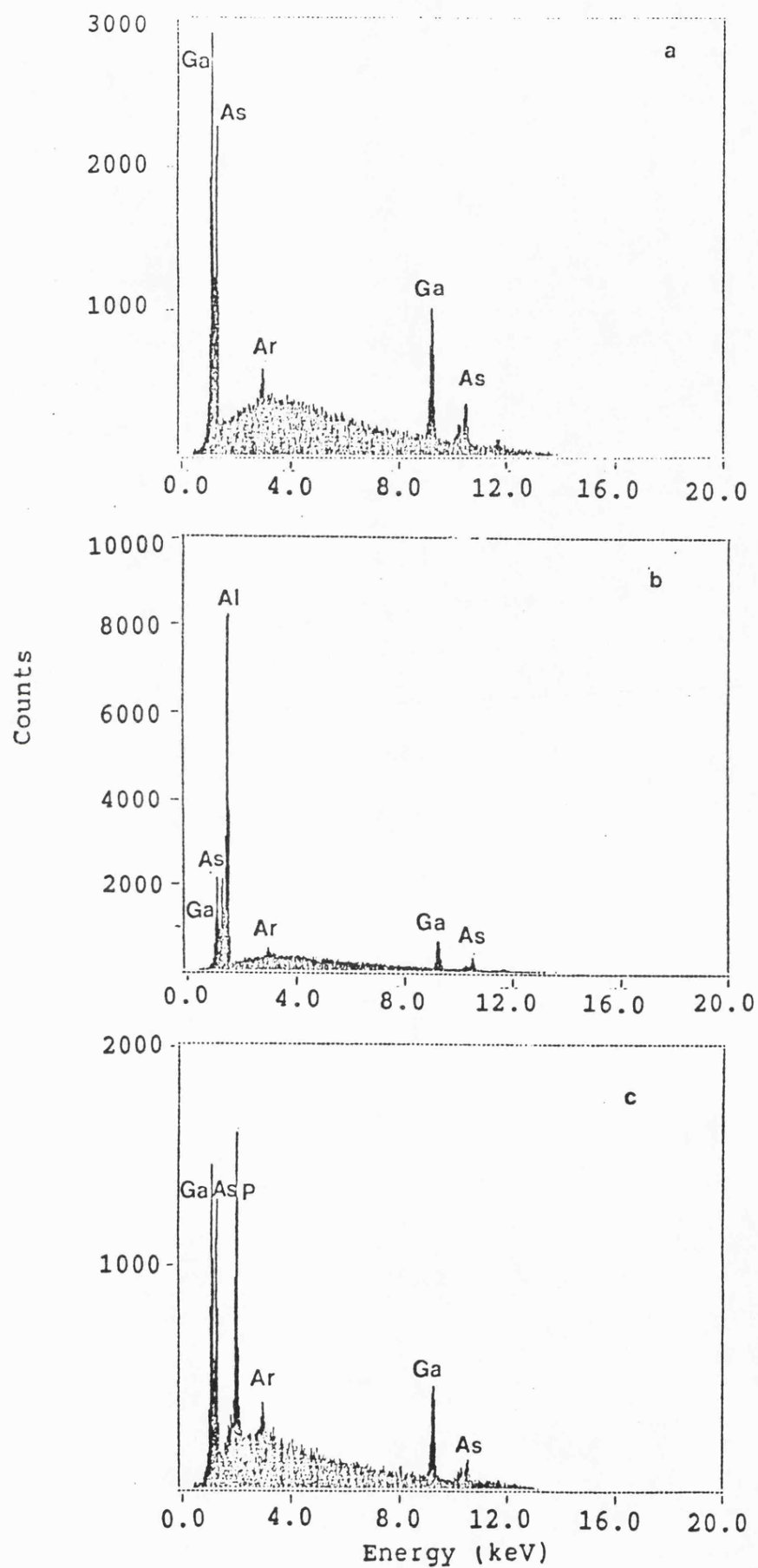


Fig. 3.3 X-ray emission spectra of (a) GaAs (b) a-GaAlAs a-GaAsP samples.

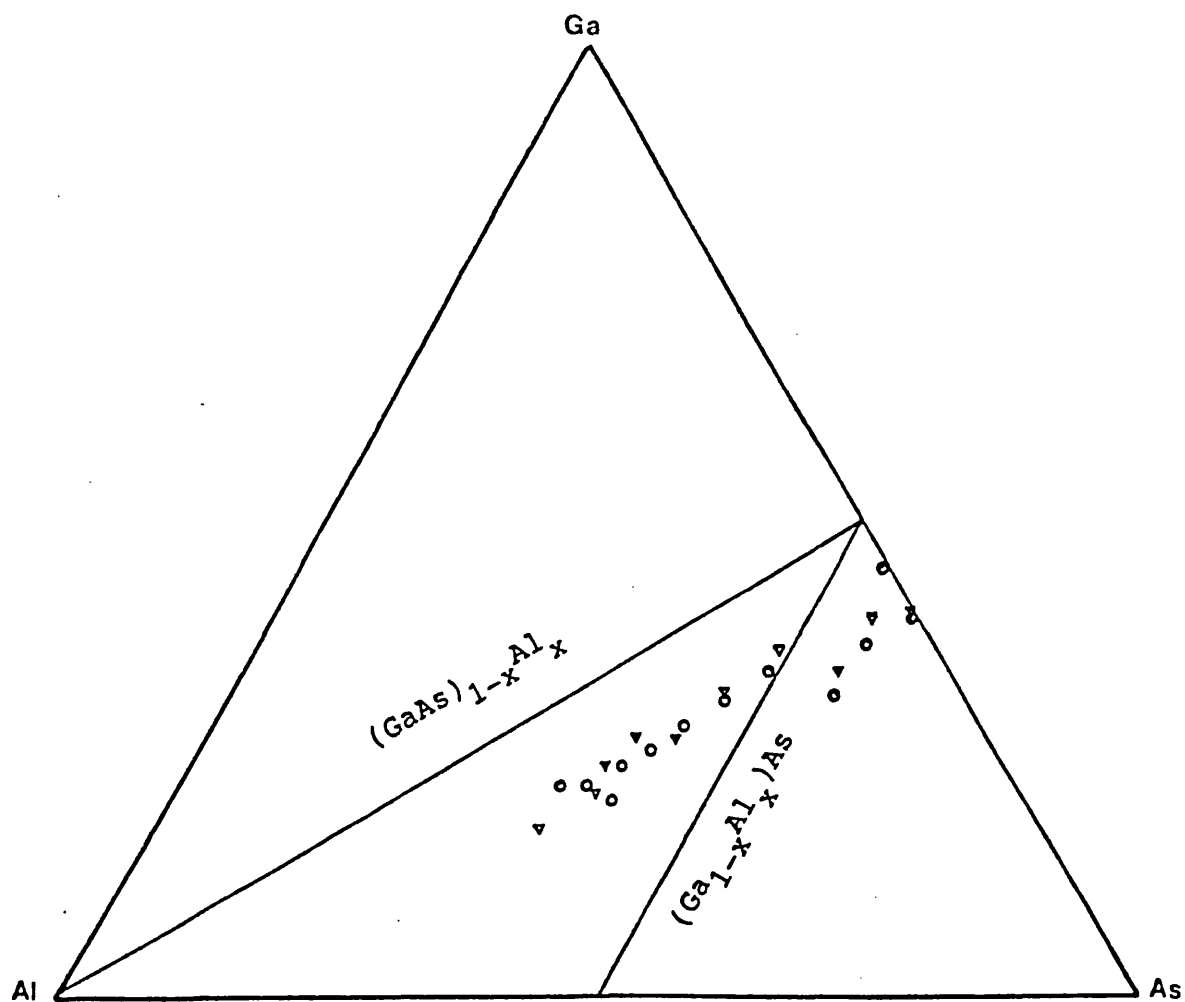


Fig. 3.4 Composition of GaAlAs samples
 (° hydrogenated; Δ unhydrogenated films).

different methods should be used to determine the thickness of the film in order to obtain reliable and accurate values. In the present work, film thicknesses were measured with a stylus instrument as well as by optical methods.

3.4.1 Stylus method

Stylus instruments consist essentially of a fine tip or stylus which rest on the surface of interest and is translated uniformly across it. The vertical movement of the tip, caused by irregularities on the surface or the edge of the film, is converted to an electrical signal which is then amplified and recorded.

A computerized Talysurf instrument was used to measure film thicknesses (in the Engineering department at Leicester University). The tip was positioned manually on the surface of the film and then moved across edges and/or grooves produced in the central region of the film by a sharp tool. Since some of the film surfaces lacked uniformity, several edges and grooves were scanned in order to obtain the best measure of the film thickness. Some film thicknesses were measured using a Sloan Dektak as a further check, at Dundee and Cardiff Universities and later with an instrument in the Physics Department at Leicester. Reasonable agreement was obtained with different instruments.

3.4.2 Optical method

This method of measuring the film thickness is based on interference effects in thin films. and is described by Cisneros et al [3]. It permits calculation of the refractive index n and the thickness h using the interference region of experimental curves of the optical reflectance and transmittance over a range of wavelengths. The method is outlined below.

(a) Determination of refractive index

If multiple reflection occurs in the film, the reflectance and transmittance show oscillatory variations with wavelength as shown in Fig. 3.5. The refractive index at different wavelengths can be determined from the values of the wavelengths at which maxima and minima of transmission and reflection occur. The conditions for occurrence of extremum values for reflectance are [4]

$$4nh = m\lambda_m [1 + \{ (\delta_{af} - \delta_{fs}) / \pi m \}] \dots\dots\dots 1$$

where n is the refractive index of the film, h is the geometrical thickness, m is a fringe order and λ_m is the wavelength corresponding to an extremum of order m . Odd values of m give maxima in R , while even values yield minima. δ_{af} and δ_{fs} are phase angles corresponding to reflections at the air-film and film-substrate interfaces respectively and are given by

$$\delta_{af} = \tan^{-1} [2k / (n^2 - 1 - k^2)] \dots\dots\dots 2a$$

$$\delta_{fs} = \tan^{-1} [2n_1 k / (n^2 - n_1^2 + k^2)] \dots\dots\dots 2b$$

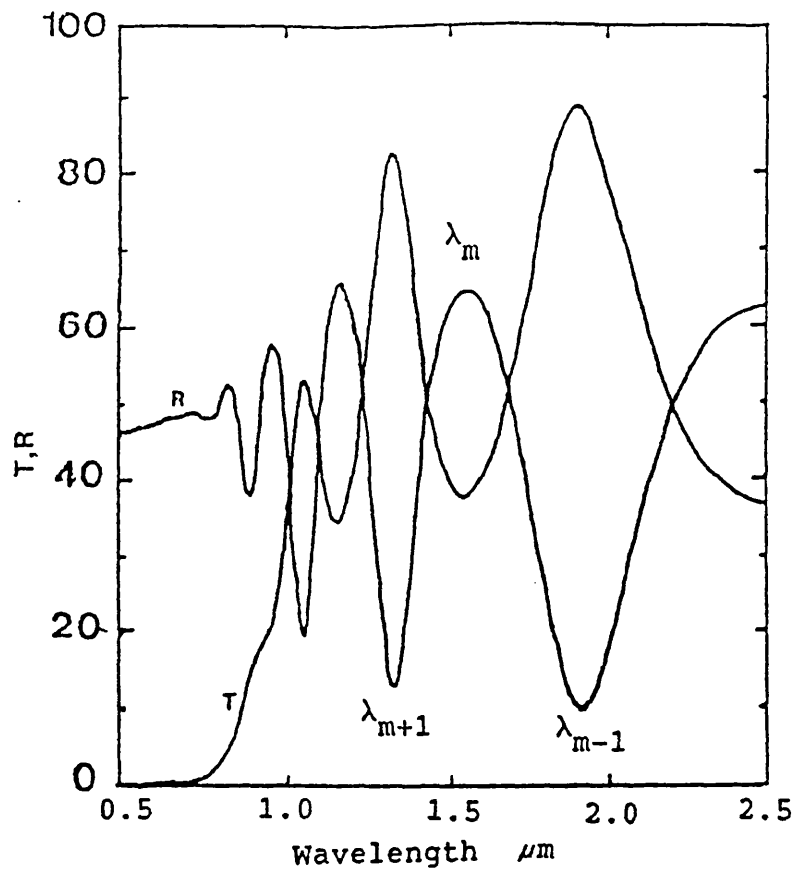


Fig. 3.5 Transmission and reflectivity versus wavelength for a-GaAs:H film.

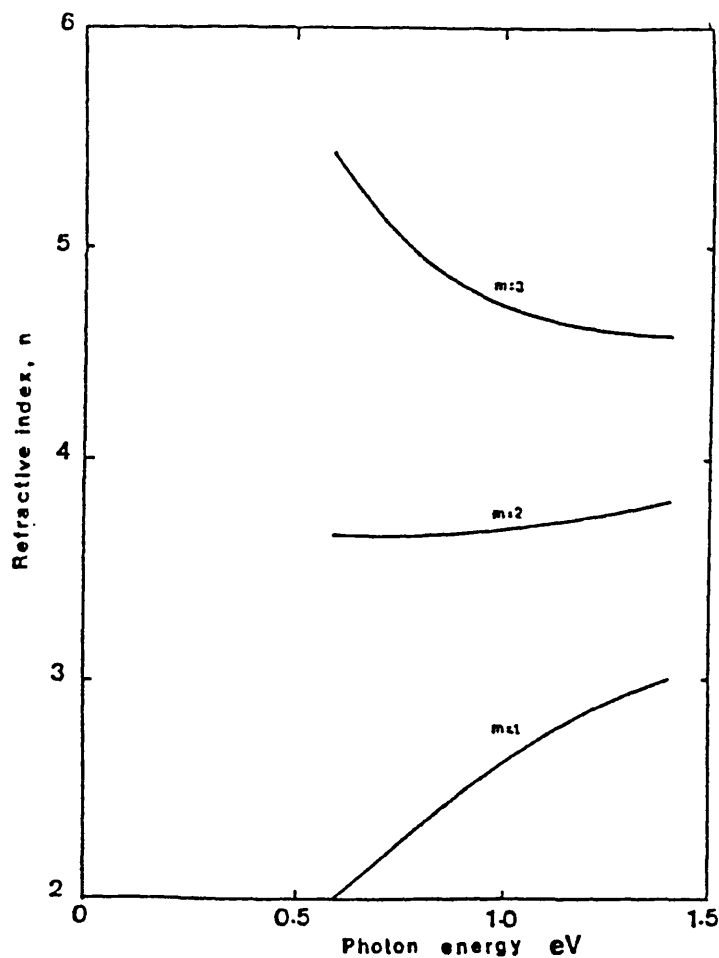


Fig. 3.6 Dispersion of refractive index with photon energy. Unreasonable values for n are obtained when the wrong value for m is chosen, as in the case above when $m=1$ and 3 . Note that m should approach a constant value as the photon energy $\rightarrow 0$.

where n_1 is the refractive index of the substrate. For a transparent or nearly transparent film and substrate (little or no absorption) δ_{af} and δ_{fs} may be neglected as k will be nearly zero. Thus equation 1 simplifies to

$$4nh = m\lambda_m \dots\dots\dots 3$$

$d_m = nh = m\lambda_m/4$ is called the optical thickness.

This equation can be used to determine the refractive index provided m is unambiguously known and h measured using some other method (see 3.4.1). But how h can be determined using this method?. In this case n should be obtained using an alternative method.

When there is experimental evidence that the film is transparent (i.e. when $R + T = 1$), the reflectivity at the extrema of the interference fringes is given by [3]

$$R_{\text{even}} = [(1 - n_1) / (1 + n_1)]^2 \dots\dots\dots 4a$$

$$R_{\text{odd}} = [(n_1^2 - n^2) / (n_1^2 + n^2)]^2 \dots\dots\dots 4b$$

where even and odd correspond to the order m of the fringes and n_1 is the refractive index of the substrate. For transparent films odd integers correspond to maxima when $R_{\text{max}} > R_{\text{sub}}$ and to minima when $R_{\text{min}} < R_{\text{sub}}$. For Corning glass (used as a substrate for the optical work on our films), $n_1 = 1.53$ and $R_{\text{even}} = 0.044$. From Fig. 3.6 we see that R_{max} and R_{min} are both greater than this value; hence $R_{\text{odd}} = R_{\text{max}}$ i.e.

$$R_{\text{max}}^{1/2} = \pm (n_1^2 - n^2) / (n_1^2 + n^2) \dots\dots\dots 5$$

The positive roots of this equation are

$$n' = [n_1 (1 - R_{\max}^{1/2}) / (1 + R_{\max}^{1/2})]^{1/2} \dots 6a$$

$$\text{and } n'' = n_1 / n' \dots\dots\dots 6b$$

The two roots give quite different values so that it is usually clear which is the correct one. The refractive index can also be calculated from reflectance maxima (nh is an odd multiple of $\lambda/4$) providing $n > n_1$ and $2\pi kh/\lambda < 0.05$ by [5],

$$n = [n_1 \{ (1 + R^{1/2}) / (1 - R^{1/2}) \}]^{1/2} \dots\dots\dots 7$$

(b) Determination of the order of the fringes m and the optical thickness d_m

If the value of the refractive index does not change rapidly from one extrema to the next, we have from equation 3

$$d_{m-1} \approx d_m \approx d_{m+1} \dots\dots\dots 8a$$

or

$$(m-1)\lambda_{m-1} \approx m\lambda_m \approx (m+1)\lambda_{m+1} \dots\dots\dots 8b$$

Consequently, the following alternative formulas for m are obtained:

$$m = \lambda_{m-1} / (\lambda_{m-1} - \lambda_m) \dots\dots\dots 9a$$

$$m = \lambda_{m+1} / (\lambda_m - \lambda_{m+1}) \dots\dots\dots 9b$$

$$m = (\lambda_{m-1} + \lambda_{m+1}) / (\lambda_{m-1} - \lambda_{m+1}) \dots\dots\dots 9c$$

where $\lambda_{m+1} > \lambda_m > \lambda_{m-1}$ (see Fig. 3.5). Equation 9a-c

will give an approximate values for the fringe order m assuming that the films are transparent or nearly transparent.

Another method used for determination of m is simply to guess at a value of m and to calculate n versus λ . In this method two adjacent maxima should be considered; then n can be calculated at each maxima wavelength using

$$n = m\lambda/2h \dots\dots\dots 10$$

A set of curves can be drawn using different values for the order m . Incorrect values for m lead to unreasonable values for n as shown in Fig. 3.6. Thus, knowing m , d_m can be calculated at each maxima and minima and, since n is already known from 3.4.2.1, h can be calculated from $h = d_m/n$.

The results obtained by the stylus method were in good agreement with those from optical measurements.

3.5 OPTICAL MEASUREMENTS

3.5.1 Visible - ultraviolet region

Room-temperature transmittance T and reflectance R measurements over a wavelength range of 2500 nm - 187 nm (0.5 - 6.5 eV) were carried out on a Perkin Elmer 330 double-beam spectrophotometer. The reflectance measurements were made using a specular reflection attachment. To determine absolute values, the reflectance of a standard aluminium mirror was measured.

The transmittance and reflectance of the sample was measured at liquid-nitrogen and room temperatures using an Oxford instruments cryostat. A cryostat sample holder was

made especially to enable these measurements to be recorded with the sample at an ambient pressure of $\sim 10^{-3}$ Torr.

3.5.2 The infrared region

Infrared transmission spectra from 4000 cm^{-1} to 200 cm^{-1} (0.5 eV to 0.05 eV) were measured using a Perkin Elmer model 580B double-beam spectrophotometer with a highly polished crystalline silicon substrate in the reference beam. (Specimens for i.r. measurements were deposited onto c-Si as mentioned in section 3.1.3). To prevent adsorption of water vapour and carbon dioxide, a model CD3 air dryer was used to purge the air flowing around the sample compartment. Pure-oxygen free nitrogen gas was also used to purge the sample compartment. This reduced the concentration of the water vapour to a very low level.

3.6 ELECTRICAL TRANSPORT MEASUREMENTS

The electrical dark d.c conductivity measurements were performed using either a four-or two-probe technique along with a Coutant 0 - 50 d.c stabilized power supply, a Keithley 616 electrometer and a Keithley 181 digital nanovoltmeter. Gold or aluminium electrodes, 1.2 cm long and 4 mm apart, were evaporated onto the surface of the specimen through a metal mask in a co-planar configuration. Electrical contact to the specimen was made by attaching a fine copper wire to the electrodes with a

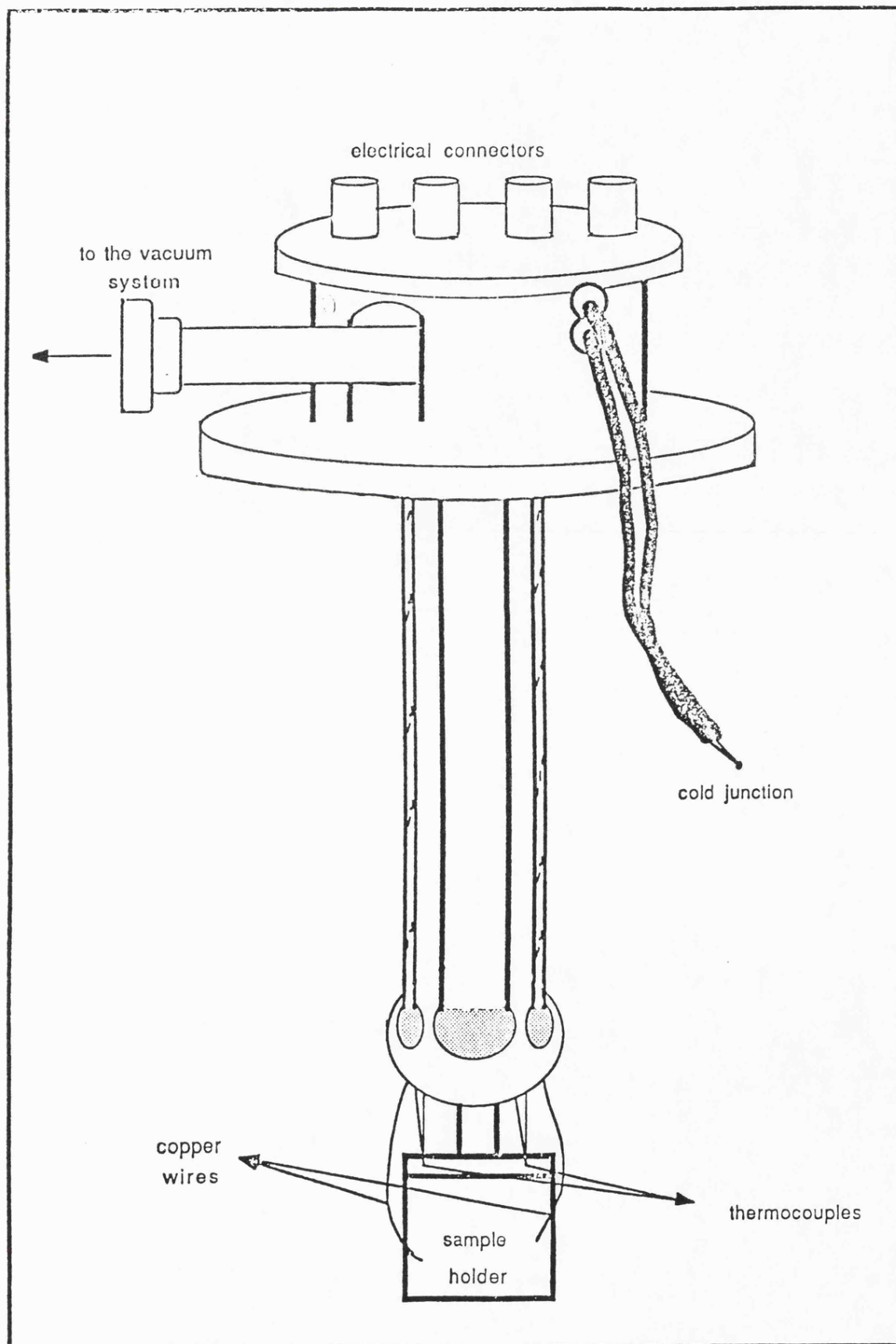


Fig. 3.7 Schematic diagram of the high-temperature cryostat

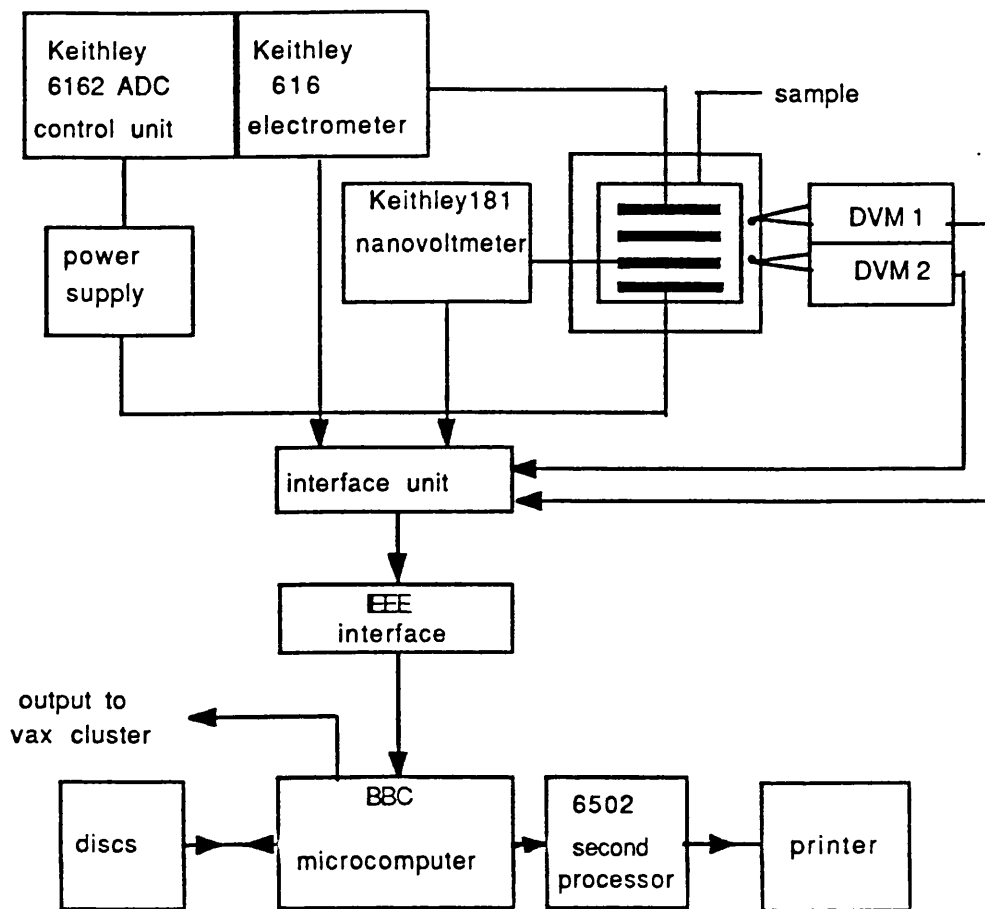


Fig. 3.8 Circuit diagram used for the conductivity measurements

silver-loaded electrically conducting paste (silver dag). This had to be left for a few hours to dry. The measurements were carried out over the temperature range of 77 - 550 K using two different cryostats.

3.6.1 Conductivity measurements between 77 K and room temperature

Measurements below room temperature were carried out using an Oxford Instruments CF100 continuous-flow helium cryostat. The sample was mounted on a cold finger, which in turn fitted into the cryostat chamber. The cryostat was evacuated to below 10^{-5} Torr using a diffusion pump with a liquid-nitrogen cold trap, backed by a rotary pump.

The temperature was measured using a cryogenic linear temperature sensor (CLTS) and controlled by an Oxford Instruments precision temperature controller. The measurements were taken manually. The electrometer was always switched on for a few hours before any measurements were taken in order to ensure its stability. The temperature was slowly reduced in steps from room temperature down to liquid-nitrogen temperature. After changing the temperature , the current flowing in the specimen took several minutes to stabilize. To ensure that this did not introduce a systematic error into the measurements, the current was monitored at regular intervals until no further increase or decrease was found to occur. As the temperature was again raised to room temperature, the current readings were taken at the same or different temperatures to those on the cooling cycle in order to check for absence of hysteresis and thermal stability.

3.6.2 High-temperature conductivity measurements

The equipment used for these measurements was essentially the same as that described above except that the sample was mounted in a cryostat (shown schematically in Fig 3.7) which was fitted into a Delta Design environmental temperature control cabinet. This was capable of controlling the temperature to within $\pm 0.5^{\circ}\text{C}$ of the required temperature and was achieved by using an internal heater and a flow of liquid nitrogen from a pressurized dewar into the chamber. A temperature range of 120 to 550 K was available.

The temperature was measured using two copper-constantan thermocouples (type T) attached to a blank area of the substrate with silver dag paste and monitored by means of two voltmeters accurate to $\pm 0.2 \mu\text{m}$.

The measurements could be made manually or with the aid of a BBC microcomputer. A circuit diagram for these measurements is shown in Fig. 3.8.

The cryostat was evacuated to $\sim 10^{-6}$ Torr (using the same vacuum system described in 3.6.1. The chamber was flushed with helium several times, being repumped in between and then filled with an overpressure ($\sim 2 - 3$ psi) of helium.

3.7 REFERENCES

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CHAPTER FOUR

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 a-GaAs(:H)

4.1.1 OPTICAL PROPERTIES

(a) Refractive index

The index of refraction n was obtained from analysis of the minima and maxima of interference fringes in the reflection spectra (see section 3.4.2).

Fig. 4.1 presents the refractive index as a function of photon energy for differently hydrogenated samples. The refractive index at 0.5 eV for the unhydrogenated a-GaAs film is about 3.7. This can be compared with the refractive index obtained by Gheorghiu and Theye [1] for stoichiometric films deposited at a low temperature (100 K) for which n was about 3.8. (Note that our films are slightly As rich - see figure 3.4). In Fig. 4.1 and subsequent figures, "increasing hydrogen content" refers to an increasing flow rate of hydrogen relative to argon through the chamber during sputtering; the actual hydrogen content in the films is not known but it is clear from infrared spectra (section 4.1.4) that the hydrogen content increases with increasing hydrogen flow rate. For the purpose of comparison, the refractive index of high-purity c-GaAs is also included in the figure [2]. We can observe that at a fixed photon energy the refractive index of the amorphous films decreases with increasing hydrogen content. These results are qualitatively in a good agreement with those obtained by Flohr and Helbig [7], although they obtained their refractive indices by a different technique (photoacoustic spectroscopy) and their samples were prepared by

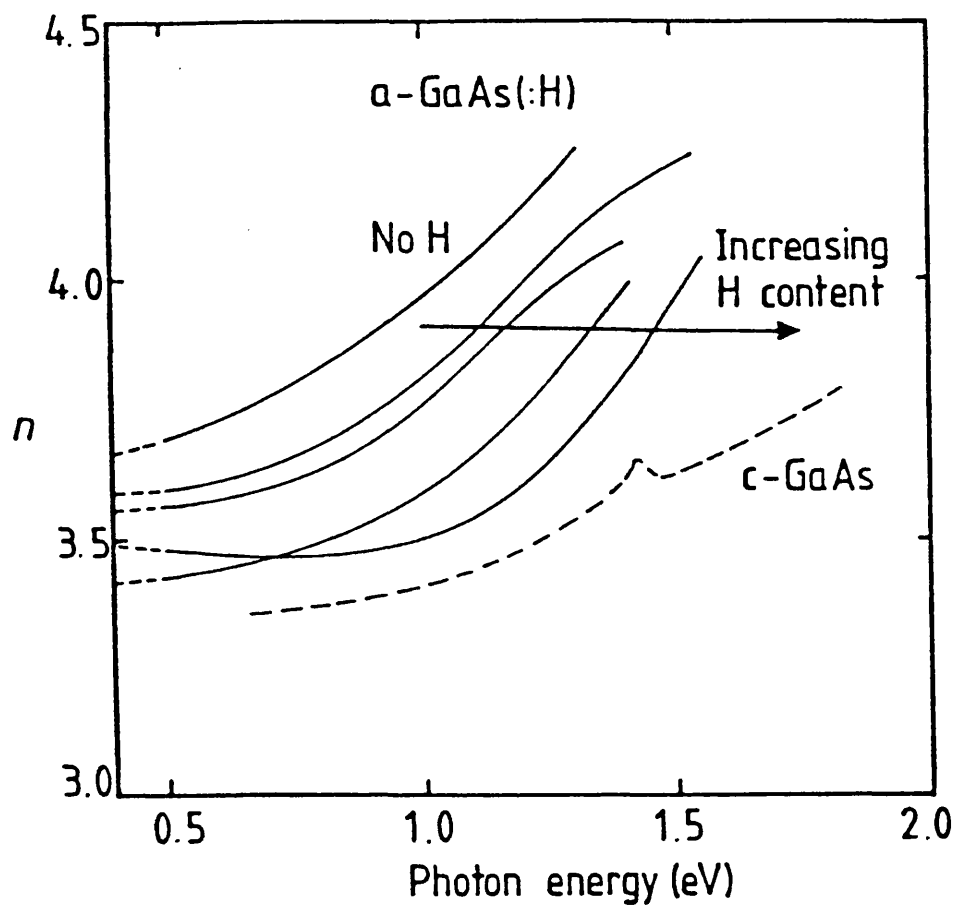


Fig. 4.1 Refractive index versus photon energy for various $a\text{-GaAs} (: \text{H})$ films

glow-discharge deposition. In contrast to c-GaAs, the refractive index of a-GaAs does not show any peak at the band edge energy where the absorption coefficient changes rapidly.

The decrease of the refractive index with hydrogen may be interpreted using an equation relating the refractive index at zero energy $n(0)$ to the Penn gap E_g [3,4] by

$$n(0)^2 = 1 + 2/3 (\hbar\omega_p/E_g)^2 \quad 4.1$$

where $\hbar\omega_p$ is the plasma frequency of the valence electrons, related to the density ρ of the material by [5]

$$\omega_{pa}^2 = \omega_{pc}^2 (\rho_a/\rho_c) \quad 4.2$$

where the subscripts a and c refer to the amorphous and crystalline states respectively. E_g represents the average separation of the valence and conduction bands (and is therefore greater than the optical gap E_o) and gives a measure of the bond strength. Thus for $n(0)$ to be reduced, one has to increase the average E_g or bond strength and/or decrease the density of the material. It was found that hydrogenated material has a lower density than unhydrogenated one [6]. In addition to this, incorporation of hydrogen into the film may allow stronger bonding and a probable increase of E_g . These two factors may play a role in reducing the refractive index of a-GaAs:H.

(b) Optical absorption edge and the band gap

The absorption coefficient α of a-GaAs(:H) was determined from relations 2.19 and 2.21 (see section 2.4). Fig. 4.2 shows the absorption coefficient of a-GaAs(:H) as a function of photon energy for films with different hydrogen content. For comparison, the absorption curve for c-GaAs is included [8].

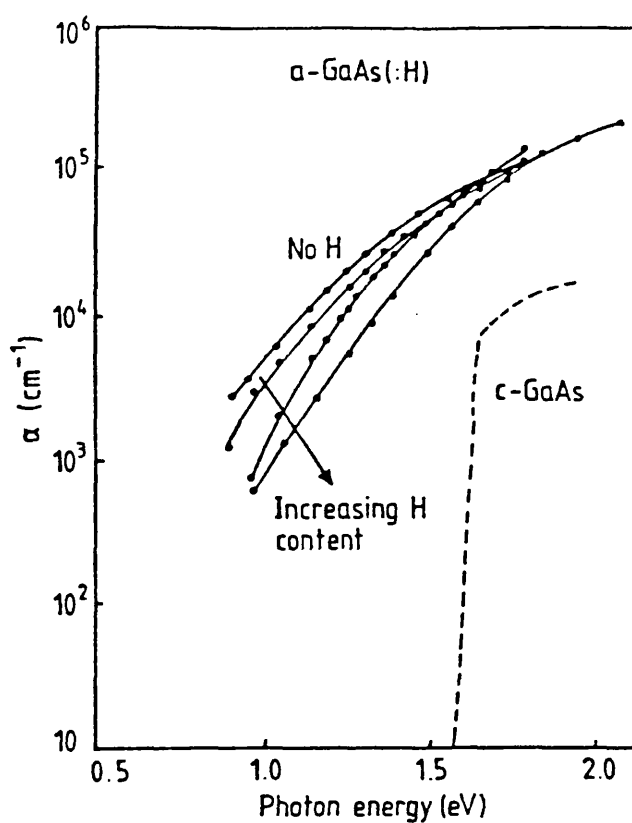


Fig. 4.2 Absorption coefficient α versus photon energy for a-GaAs prepared with different $\text{H}_2/\text{H}_2+\text{Ar}$ flow rate ratios.

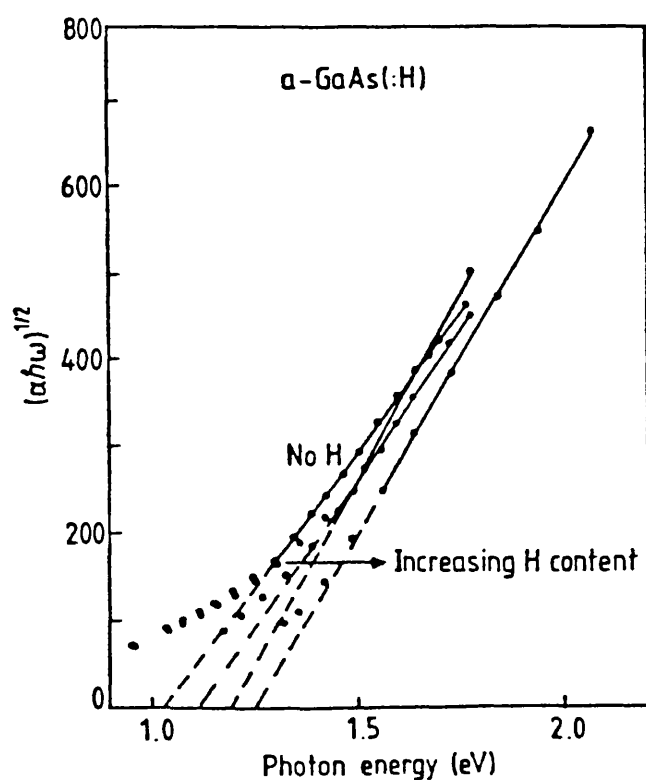


Fig. 4.3 Tauc plot for a-GaAs(:H) films as a function of photon energy for various $\text{H}_2/\text{H}_2+\text{Ar}$ flow rate ratios.

The first clear features in this plot are that the absorption coefficient of a-GaAs at a given photon energy is higher and the absorption edge is broader than that of their crystalline counterparts. The latter behaviour is general to all amorphous semiconductor and is arises from the existence of density-of-states tails to the conduction and valence band edges. The absorption coefficient has an exponential dependence on $\hbar\omega$ below $\alpha \sim 10^4 \text{ cm}^{-1}$, while above this it is usually found that

$$(\alpha \hbar\omega)^{\frac{1}{2}} = \text{const.} (\hbar\omega - E_0) \quad 4.4$$

which defines an optical gap E_0 (Tauc gap).

The Tauc plots obtained from the experimental data in Fig. 4.2 are displayed in Fig. 4.3. The optical gap of the unhydrogenated a-GaAs film shown in Fig. 4.3 is of the order of 1.0 eV. This compares favourably with values (1.0–1.1 eV) obtained by others for films prepared by different methods [1,9–14]. Our films are slightly As-rich (see Fig. 3.4), but results [9] on films containing an excess of As show that the optical gap is not too sensitive to composition variation near stoichiometry. (Our own results for $\text{a-Ga}_{1-x}\text{As}_x$, to be discussed later, show similar behaviour.)

It is evident that with increasing hydrogen content the absorption edge in these films shifts towards higher energies and E_0 increases, becoming closer to that for c-GaAs (see also Fig.4.5). Similar behaviour for a-GaAs(:H) films prepared in our laboratory has been observed using Photothermal Deflection Spectroscopy (PDS) technique (the measurements were made by M.L.Theye at Universite Pierre et Marie Curie in Paris). Typical absorption spectra for differently hydrogenated a-GaAs samples is shown in Fig. 4.4 [45]. It can be seen that the absorption spectra extend to below 10^2 cm^{-1} . It is known that the slope of $\log \alpha$ versus $\hbar\omega$ plots provide information about

Optical Absorption Coefficient α (cm^{-1})

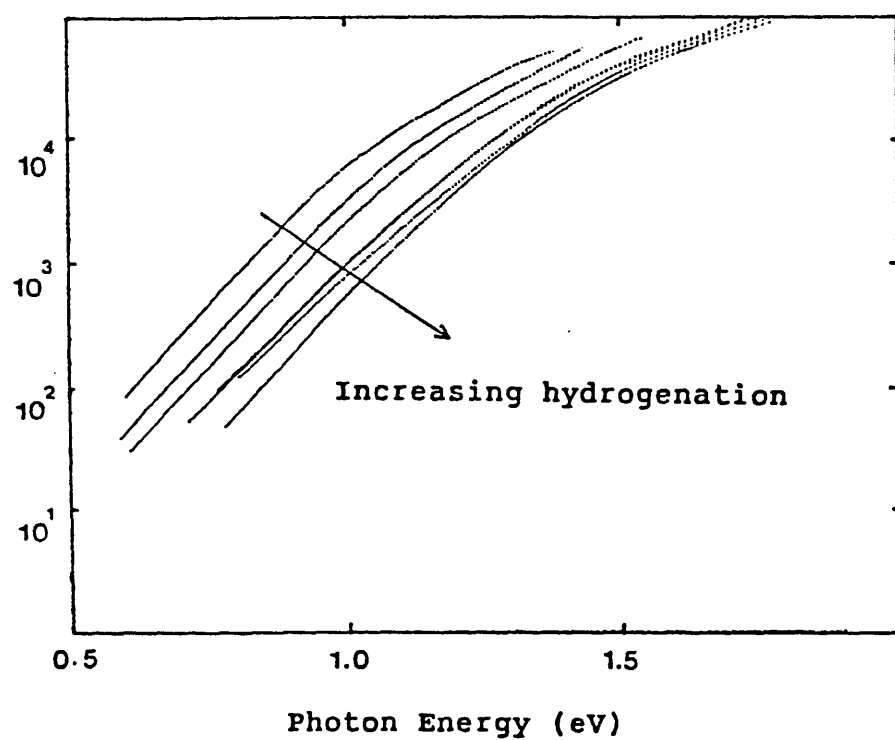


Fig. 4.4 Optical absorption edges of a-GaAs(:H).

the band tails in the gap. PDS absorption spectra shows that the absorption edge shifts towards higher energies with increasing hydrogen, but there is no essential sharpening of the absorption upon hydrogenation of these films. A similar shift and accompanying sharpening of the absorption edge is observed for a-Si:H. The generally accepted reasons for the effect of hydrogen in increasing and sharpening the gap in amorphous silicon are (i) a recession of the top of the valence band by replacement of weak Si-Si bonds with stronger Si-H bonds and (ii) the removal of mid-gap dangling-bond states by hydrogen bonding to threefold coordinated (Si_3) silicon atoms [15].

In GaAs, Ga and As dangling bonds (Ga_3 and As_3) are expected in the amorphous phase. Robertson [16] has calculated that the unrelaxed Ga_3 level lies just below the conduction band edge while the As_3 lies near the valence band. Hydrogen incorporation probably satisfies some of these dangling bonds, eliminating the associated states from the gap. Wrong bonds (i.e. Ga-Ga and As-As) also give states around the band edges [16]. As we have seen in section 1.4, Ga-Ga bonds may be expected to introduce p-like states into the high-energy region of the valence band [17]. Therefore, one can argue that hydrogen incorporated in the a-GaAs network breaks these bonds and forms a hydrogen bridge. However, photoemission measurements on a-GaAs:H carried out by Karcher et al [26], did not show an erosion in the top of the valence band when hydrogen was incorporated in the film. This therefore led them to suggest that the increase in the optical gap of a-GaAs:H film is due to a corresponding recession of the conduction band edge. If this is so, then the Ga-H-Ga bridges are possibly related to Ga dangling bonds below the conduction band edge. Our infrared measurements on the same samples confirm the presence of Ga-H-Ga bonds in the hydrogenated samples (see Fig. 4.9), and we suggest that this could account

for the fact that the absorption edge shifts towards higher energies.

4.1.2 INFLUENCE OF HYDROGEN ON DEPOSITION RATE

The thickness of differently hydrogenated a-GaAs samples was measured using various methods (see section 3.4). Fig. 4.5 shows the deposition rate as a function of H_2/H_2+Ar flow rate ratio, as well as the variation of optical gap. It can be seen from the figure that the deposition rate decreases rapidly when the H_2/H_2+Ar ratio changes from 0% to 20 %. This suggests that adding hydrogen to the argon plasma (at constant pressure) reduces the number of ionized argon atoms, which are mainly responsible for the sputtering process. The hydrogen ionization potential is lower than that of argon [11] but the mass is too low for effective sputtering. Above 20 %, the deposition rate is approximately constant and reactive sputtering may become important.

4.1.3 TEMPERATURE DEPENDENCE OF DARK D.C. CONDUCTIVITY

Electrical conductivity measurements on a-GaAs(:H) were carried out between 77 and 550 K (see section 3.6). The temperature dependence of the conductivity, σ , of films prepared with various hydrogen concentrations is illustrated in Fig. 4.6. for temperatures below room temperature. With increasing hydrogen content, the conductivity decreases and the activation energy E_a increases. Conductivity measurements on the same films above room temperature showed an activated behaviour characteristic of band-like conduction in extended states, and are shown in Fig. 4.7. Activation energies, calculated over the temperature range 300-360 K, are approximately equal to half the optical gap, suggesting a Fermi level pinned near mid-gap(Fig.4.5a).

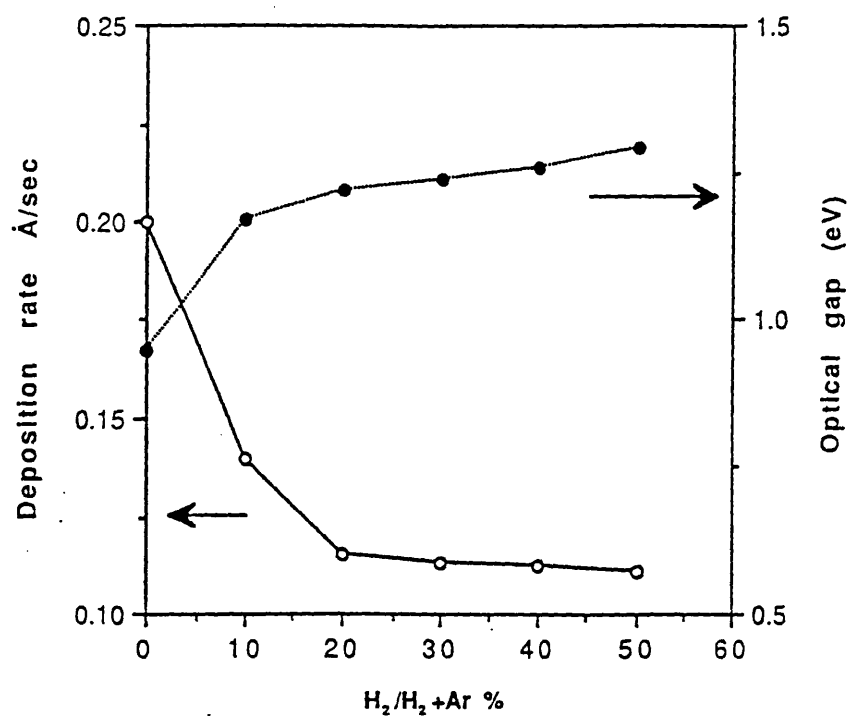


Fig. 4.5a The influence of hydrogen content on deposition rate and optical gap of a-GaAs(H)

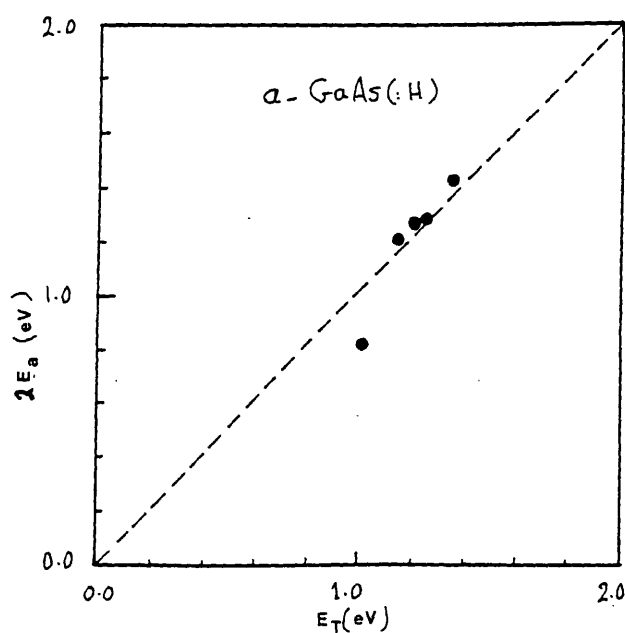


Fig. 4.5b Variation of $2E_a$ versus E_T for a-GaAs(H).

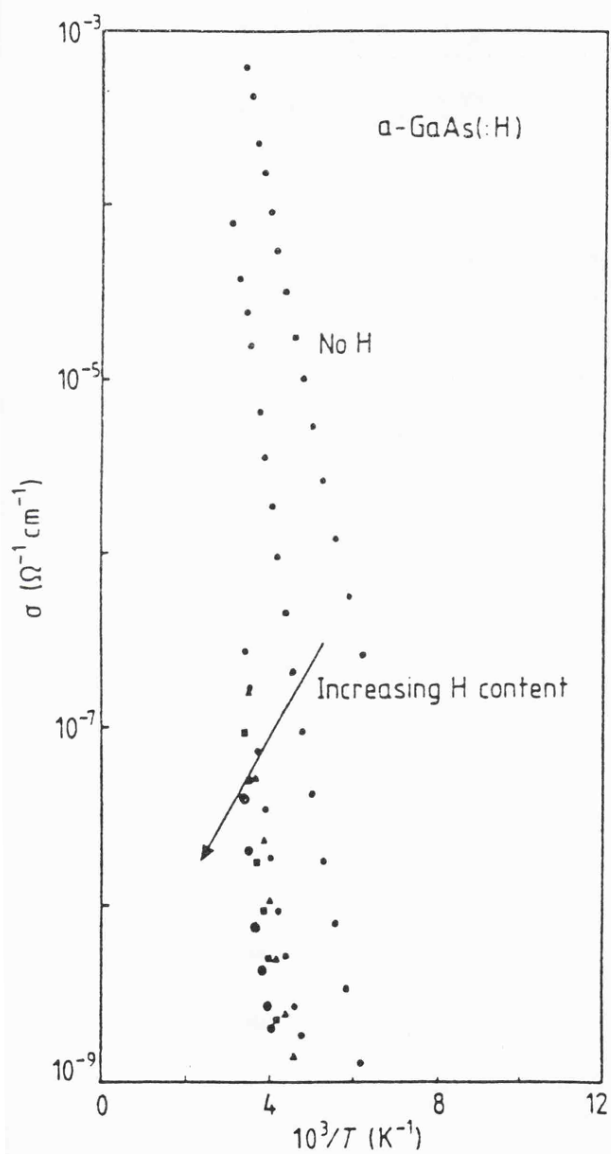


Fig. 4.6 Log σ versus $1/T$ for several a-GaAs(:H) films below room temperature.

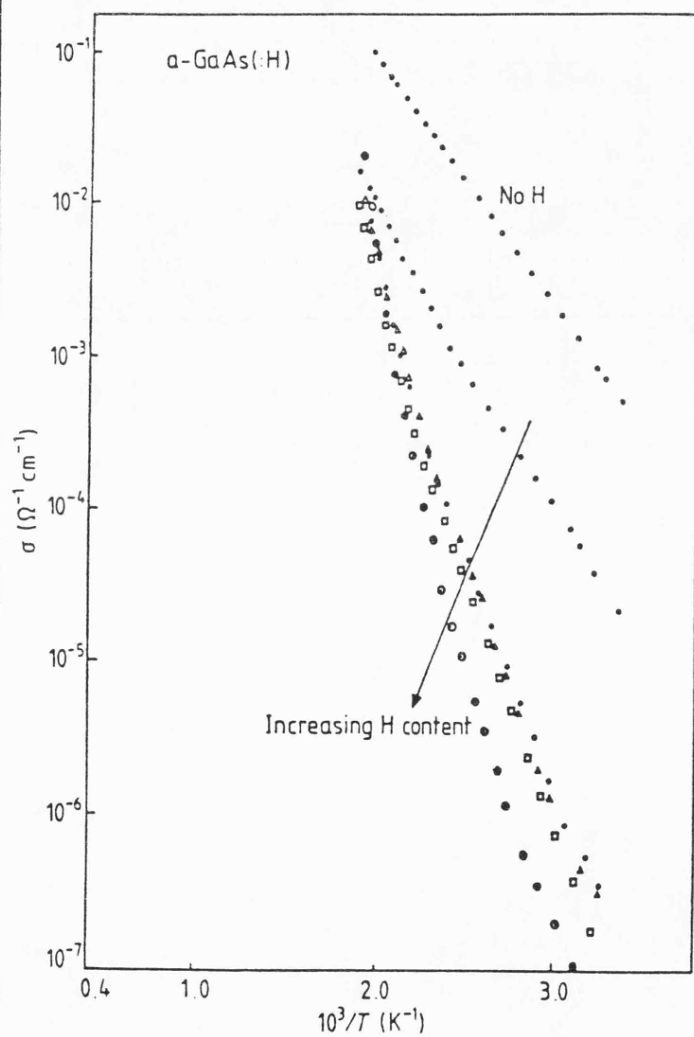


Fig. 4.7 Log σ versus $1/T$ for several a-GaAs(:H) films above room temperature.

It can be seen in figure 4.7 that, for hydrogenated a-GaAs, the conductivity curves bend upwards above 430 K. This seems likely to be associated with evolution of hydrogen from the samples at higher temperatures [18]. In order to investigate hydrogen evolution, we measured the conductivity of a hydrogenated sample as a function of annealing in vacuum for periods of one hour at several temperatures T_a . It was found that (i) the conductivity at room temperature increased and (ii) the activation energy decreased as shown in Fig. 4.8, the curves approaching that for unhydrogenated a-GaAs (also shown in the figure). Table 1 summarises the effect of annealing on σ and E_a at different annealing temperatures.

These observations were supported by infrared measurements carried out on a film deposited under exactly the same conditions (in the same run) on a c-Si substrate. The film was annealed at identical temperatures as those in the conductivity measurements. It was found that a broad band at 1460 cm^{-1} , which is believed to be a hydrogenic mode (Ga-H-Ga bridge - see next section), flattened out. This is attributed to the evolution of incorporated hydrogen in the film, with a consequent rearrangement of the network.

Table 1.

Annealing T_a (K)	295	380	480	530
$\sigma_{RT} (\Omega^{-1} \text{cm}^{-1})$	3.8×10^{-8}	9.0×10^{-8}	1.7×10^{-6}	1.0×10^{-5}
E_a (eV)	0.61	0.58	0.50	0.43

4.1.4 INFRARED MEASUREMENTS OF a-GaAs(:H)

Fig. 4.9 shows infrared transmission spectra for a set of a-GaAs(:H) films prepared at room temperature. Three strong

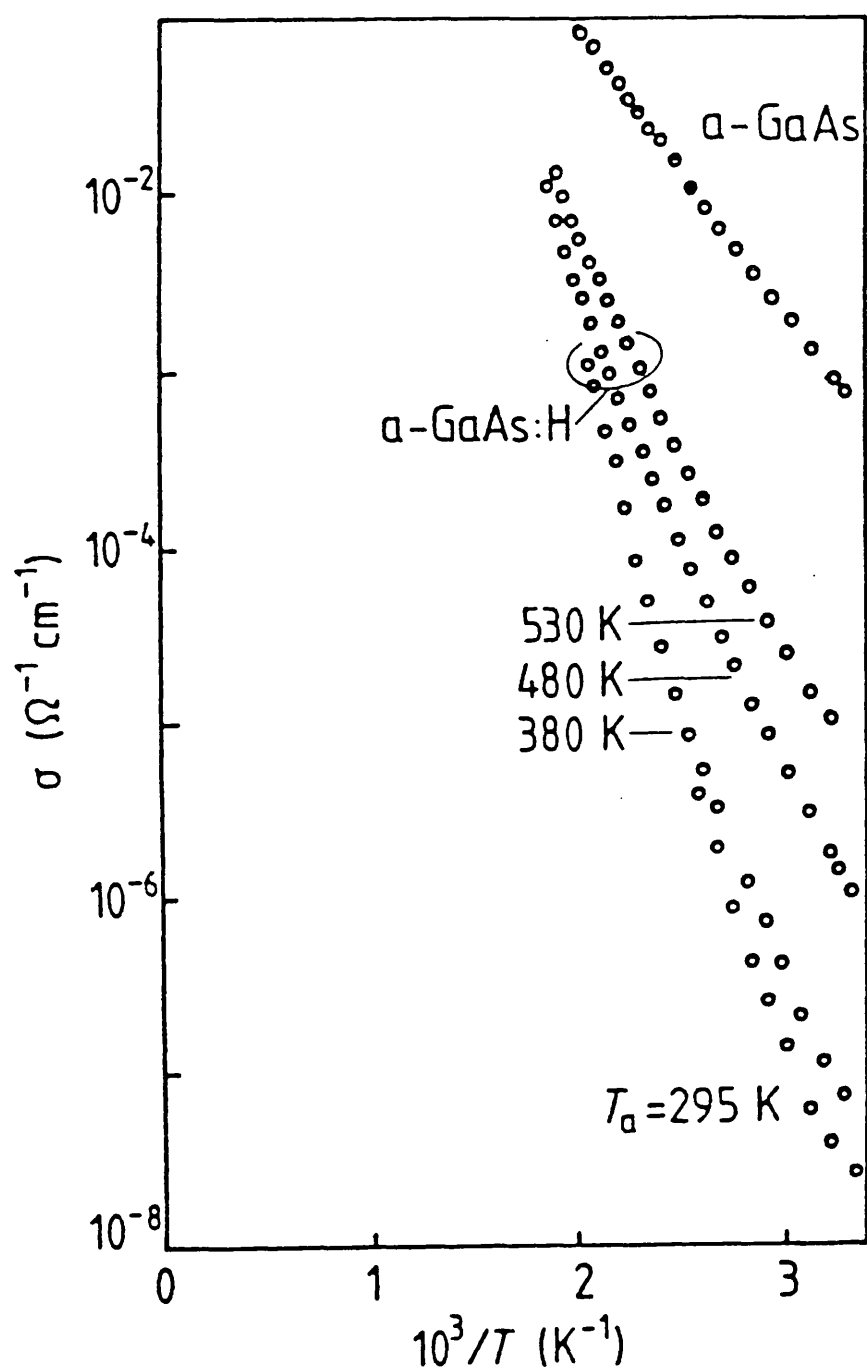


Fig. 4.8 Log σ versus $1/T$ for an a-GaAs:H film annealed at different temperatures T_a . The curve marked a-GaAs is for a film containing no hydrogen. Anneal time 1 hour at each anneal temperature.

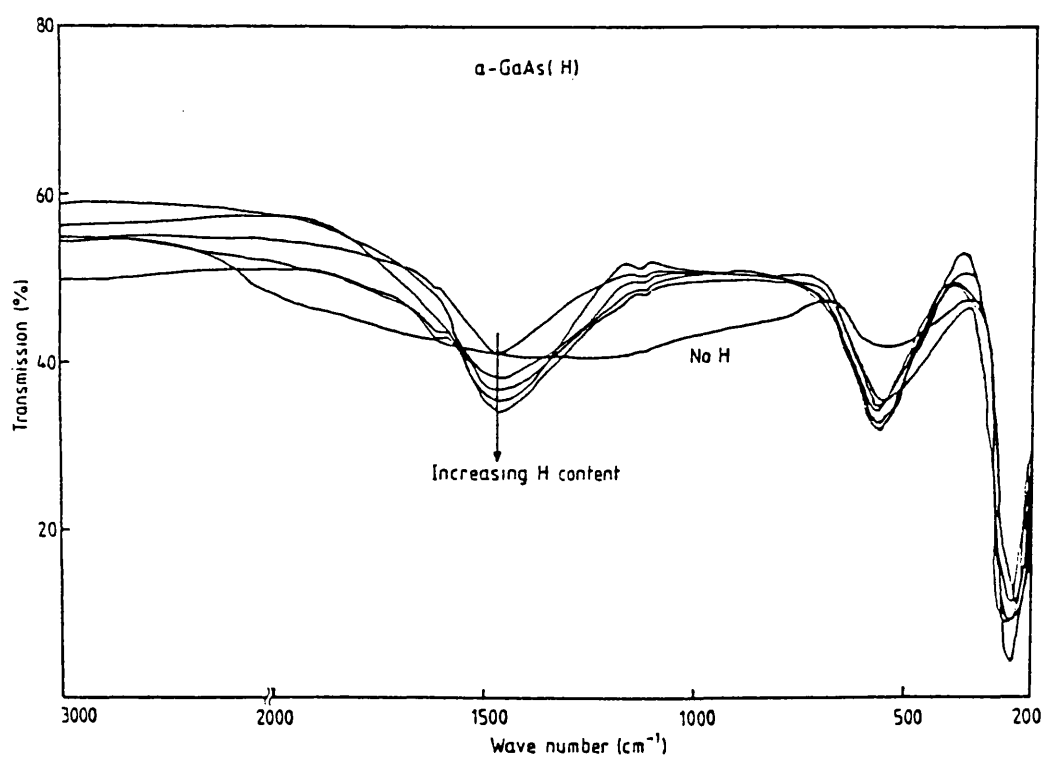


Fig. 4.9 Infrared transmission spectra of a-GaAs(:H) films prepared with different H/H+Ar flow rate ratios.

absorption bands were observed at 1460 cm^{-1} , 530 cm^{-1} and 250 cm^{-1} . Paul et al [18] have pointed out that the two strong broad bands at 1460 and 530 cm^{-1} are hydrogenic modes. Wang [19] assigned them to bridging Ga-H-Ga stretching and wagging modes respectively. The intensity of these bands increases with increasing $\text{H}_2/\text{H}_2+\text{Ar}$ flow rate ratio and therefore we conclude that the hydrogen content in the film increases with the $\text{H}_2/\text{H}_2+\text{Ar}$ ratio. Bridging hydrogen has been found in a number of aluminium compounds (as Al-H-Al) such as $\text{Al}(\text{BH}_4)_2\text{H}$ and $\text{Al}(\text{BH}_4)\text{H}_2$ [20], and in the present work in a-GaAlAs [21] (to be discussed later). Also, it has been detected in boron hydrides (B_2H_6) (as B-H-B) [22]. Recent electronic structure calculations by O'Reilly and Robertson [23] support this assignment and suggest that hydrogen occurs as single $\equiv\text{GaHGa}\equiv$ rather than double $=\text{GaH}_2\text{Ga}=$ bridges, and that the peak position is relatively insensitive to the bridging angle. The peak at 250 cm^{-1} can be assigned to the TO mode [18,19,24]. The TO normal mode of c-GaAs is at 268 cm^{-1} [30].

4.2 a-GaAs(:H) PREPARED AS A FUNCTION OF SUBSTRATE TEMPERATURE (T_s)

4.2.1 SAMPLE CHARACTERIZATION

The effect of preparation conditions of the properties of a-Si and a-Ge have been extensively studied in the past. It was found that the substrate temperature is one of the important parameters which influences the structural, optical and electrical properties. Therefore, it seemed of interest to perform this kind of study on a-GaAs(:H) and investigate the influence of T_s on films properties.

Generally, a-GaAs studies have been limited to deposition at low temperatures [12,25,26]. Paul et al [12] reported that the r.f sputtering of a-GaAs has to be carried at $T_s \leq 4^\circ\text{C}$ in order to avoid crystallization. However, Matsumoto et al [27] found that the amorphous character of molecular-beam-deposited GaAs could be retained up to 190°C . In this study, we have investigated the substrate temperature dependence of the structural, optical and electrical properties for hydrogenated and unhydrogenated a-GaAs films.

Hydrogenated and unhydrogenated a-GaAs films were deposited at various substrate temperatures between room temperature and 130°C using the same preparation conditions described in section 3.1.3. The thicknesses of the films ranged from 1800 to 2800 Å. Energy-dispersive X-ray analysis measurements were carried out on the films to determine their composition. No essential change in composition compared to the a-GaAs(:H) films prepared at room temperature was found (see section 4.1).

The amorphicity of the samples was checked by TEM. Diffraction pattern diagrams shown in plates 4.1 and 4.2 for unhydrogenated and hydrogenated a-GaAs did not show evidence for the presence of crystalline structure throughout the

Plate 4.1 Transmission electron diffraction pattern for
a-GaAs prepared at T_s (a) 59 °C (b) 81 °C (c) 102 °C.

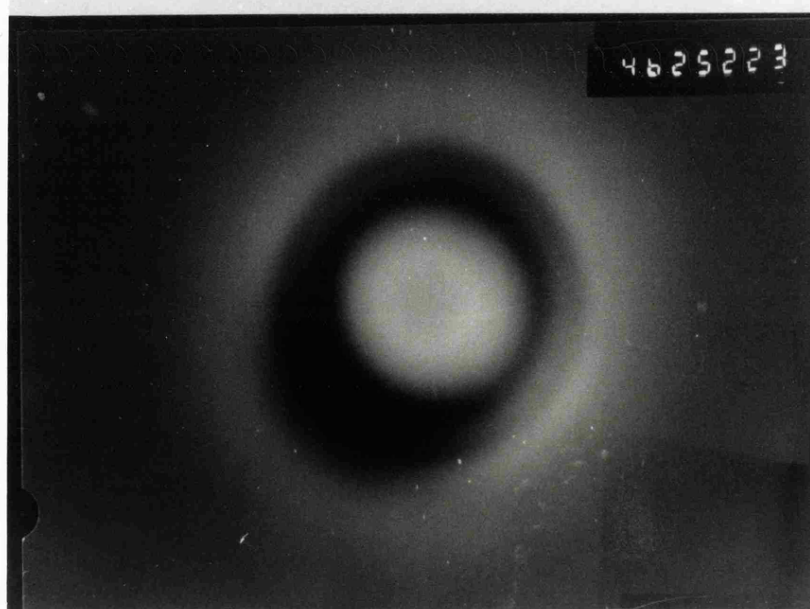
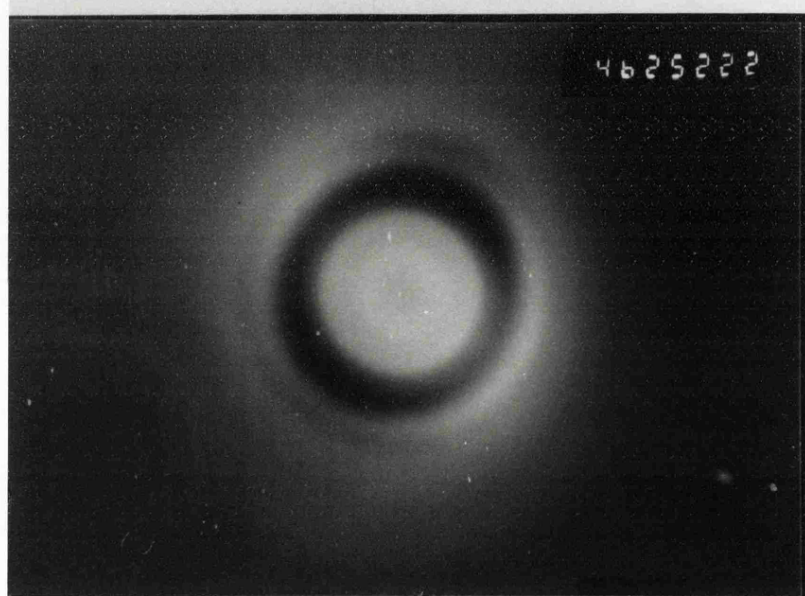
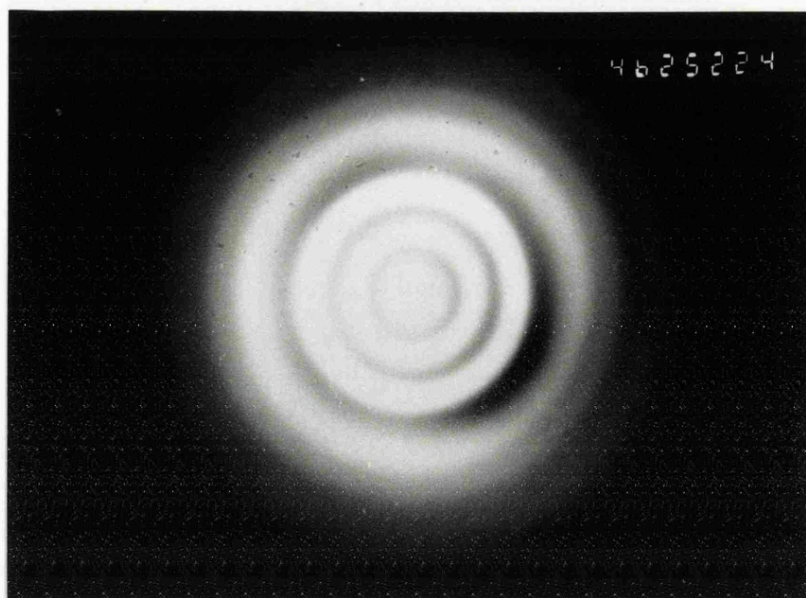
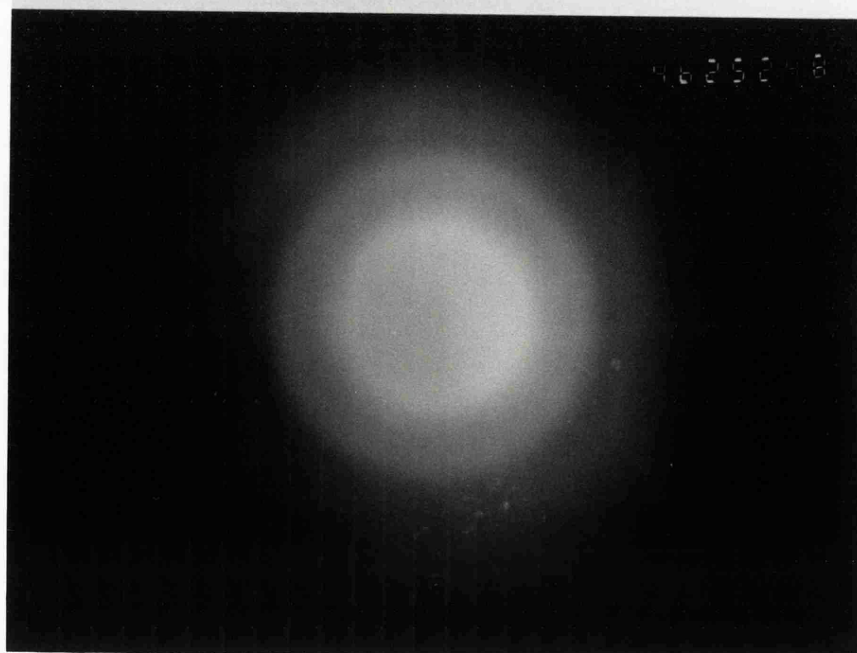
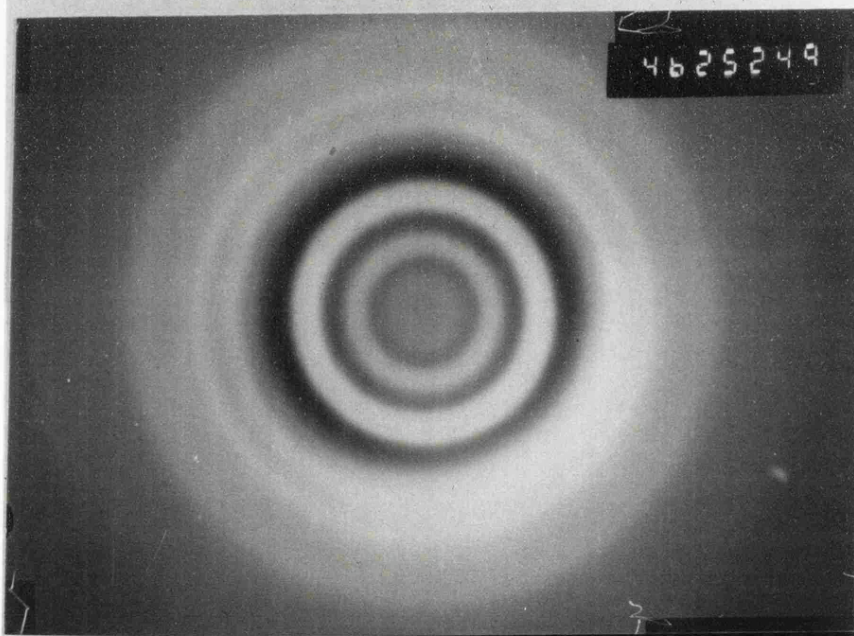
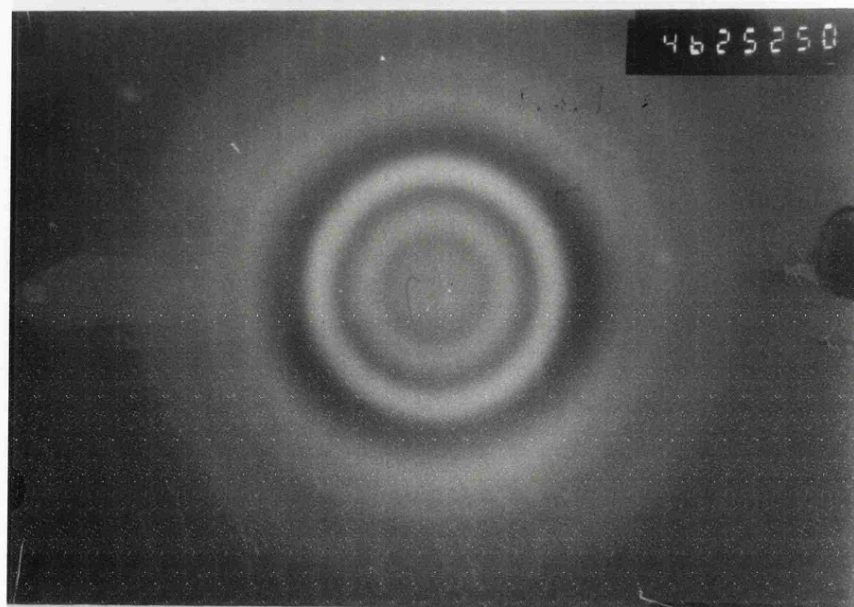


Plate 4.2 Transmission electron diffraction pattern for
a-GaAs:H prepared at T_s (a) 64 °C (b) 93 °C (c) 118 °C.



temperature range of investigation. However, infrared transmission spectra (Fig. 4.16) show that the TO mode for a-GaAs films prepared at $T_s=59,81$ and 102°C shifts from $\sim 250\text{ cm}^{-1}$ to a slightly higher value (TO for c-GaAs is $\sim 270\text{ cm}^{-1}$) with increasing sharpening, although for the film prepared at $T_s=131^\circ\text{C}$ the peak shifts back towards the amorphous position. On the other hand, for the infrared spectra of a-GaAs:H, the TO mode peak remains fairly broad without shifting except for the film which was prepared at $T_s = 118^\circ\text{C}$ (see Fig. 4.16).

4.2.2 OPTICAL PROPERTIES

The optical spectra are shown as a function of substrate temperature in Fig. 4.10a. The optical band gap E_o for a-GaAs(:H) prepared at different substrate temperatures was determined from the Tauc law (equation 2.17) and is displayed in Fig. 4.10b as a function of substrate temperature. It can be seen that the optical gap of unhydrogenated a-GaAs increases with increasing T_s up to about 100°C , then decreases for the film deposited at 131°C . If we assume that these films are still amorphous (and they are in fact according to TEM within its scale range), this increase in optical gap may be attributed to an improvement in film quality (reduction in band tail widths, defect density), and the optimum T_s for these improvements might be around 100°C .

For a-GaAs:H films (the $\text{H}_2/\text{H}_2+\text{Ar}$ flow rate ratio was 20%) the optical gap (shown in Fig. 4.10b) shows an expected increase compared to the corresponding unhydrogenated a-GaAs. With increasing substrate temperature, E_o remains roughly constant up to about 90°C , then increases quite rapidly. This behaviour suggest that the substrate temperature has little effect on the optical properties of a-GaAs:H. The sudden increase of E_o for T_s above about 90°C seems to be consistent with the infrared results and may be attributed to a better

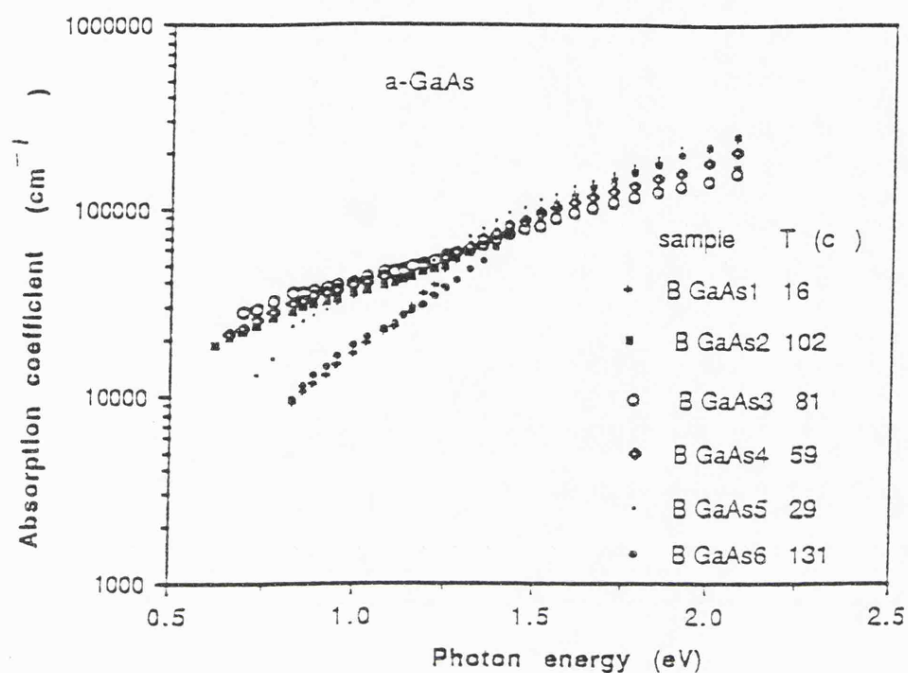


Fig. 4.10a Absorption coefficient α versus photon-energy for a-GaAs prepared at different substrate temperatures (T_s).

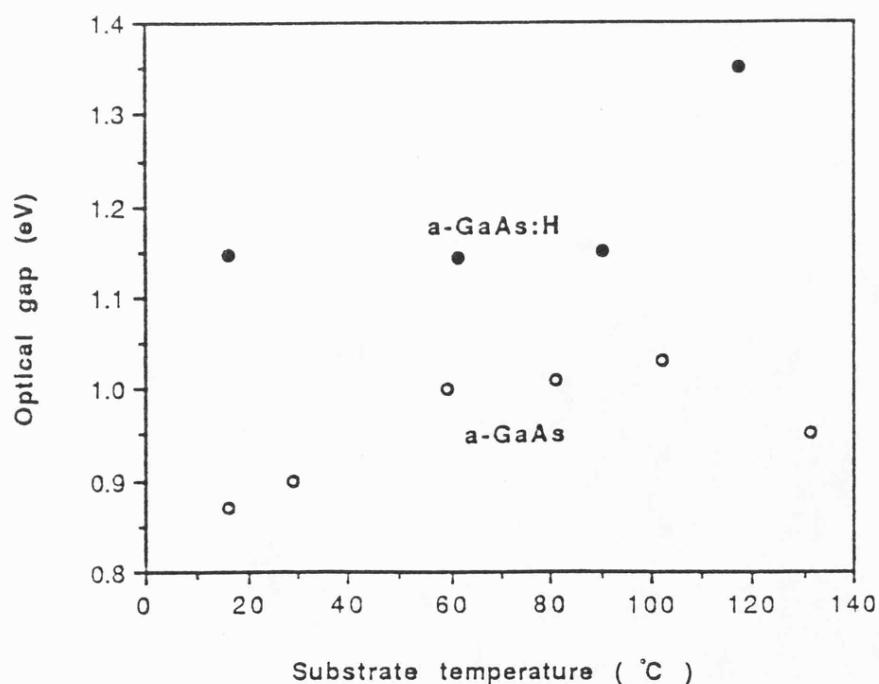


Fig. 4.5b Variation of $2E_a$ versus E_T for a-GaAs(:H).

ordered amorphous film. However, this behaviour was not expected because the hydrogen from the film prepared at $T_s = 118^\circ\text{C}$ has almost entirely evolved (see infrared spectra in Fig. 4.17 in which all the hydrogen mode peaks flatten for this sample) which should cause the gap to reduce in the film prepared at room temperature, but it seems that the effect of T_s dominated on that of hydrogen and more ordered film is produced. This can be seen from TO mode for this sample which shifts towards the crystalline value (i.e. $\sim 270\text{ cm}^{-1}$) as mentioned in the preceeding section.

4.2.3 TEMPERATURE DEPENDENCE OF DARK D.C. CONDUCTIVITY

The temperature dependence of the conductivity σ of a-GaAs films prepared at various substrate temperatures is shown in Fig. 4.11.

The first feature that may noticed in Fig. 4.11 is that the conductivity of the films is not singly activated over the whole temperature range investigated. Below room temperature, the conductivity curves exhibit a slight change in slope and follow Mott's variable range hopping law $\sigma = \sigma_0 \exp(-T_0/T)^{1/4}$, suggesting that conduction take place in localized states at the Fermi level. This behaviour has been seen in most amorphous III-V compounds (see ref. 14 and 17, chapter 1). It can also be observed that there is a marked increase in conductivity and decrease of activation energy for the films prepared at $T_s = 59, 81$ and 102°C .

The room-temperature conductivity ($\sigma_{r.t.}$) of a-GaAs deposited at room temperature is of the order of 10^{-4} - $10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. This value is quite similar to that obtained by Paul et al [12] for films prepared by r.f. sputtering and by Gheorghiu and Theye for the off-stoichiometry films prepared by flash evaporation [32], but is higher than $\sigma_{r.t.}$ of As-rich sample prepared by molecular beam deposition [27] (10^{-5} - $10^{-4}\ \Omega^{-1}\text{cm}^{-1}$).

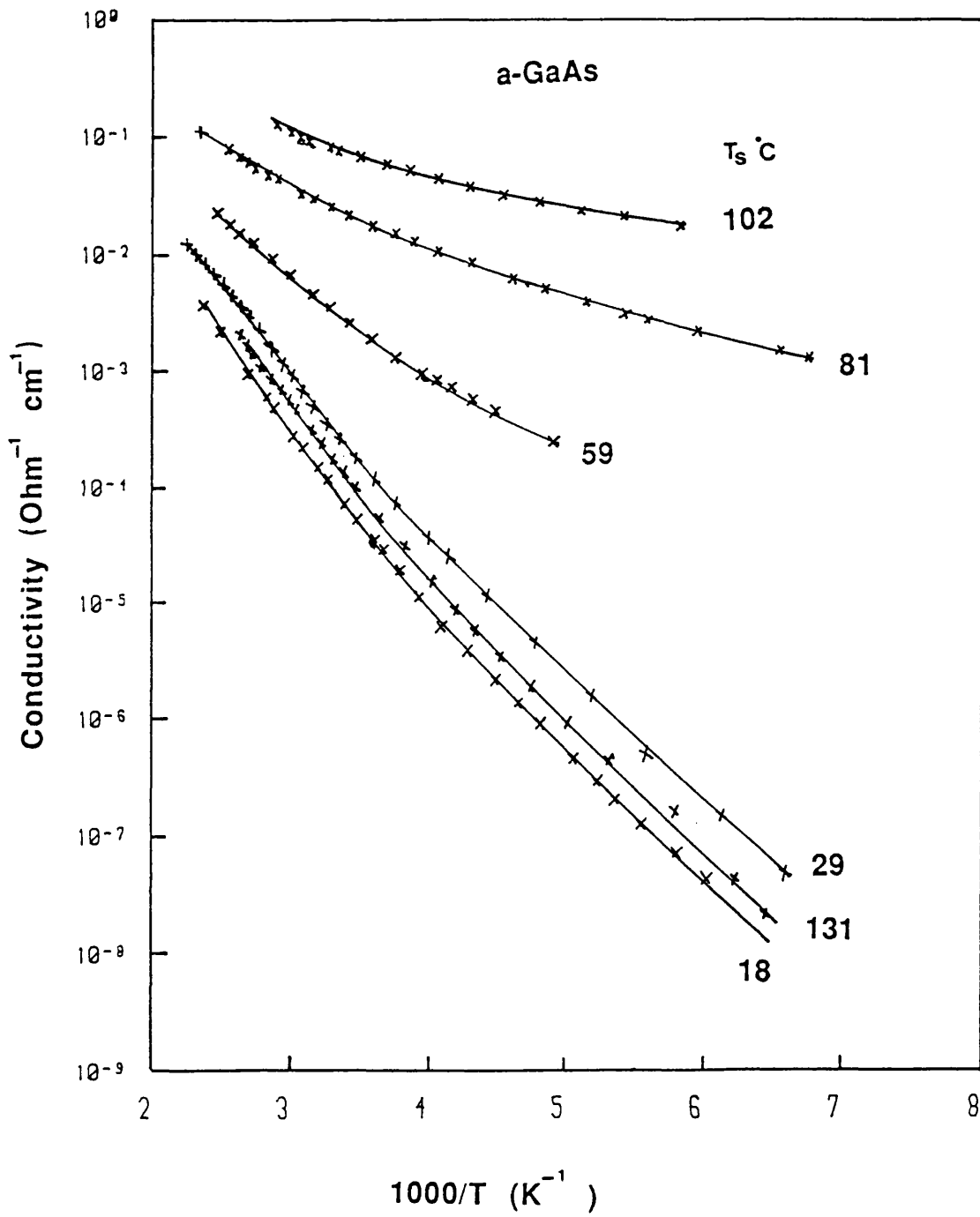


Fig. 4.11 Log σ versus $1/T$ for several a-GaAs films prepared at different substrate temperature (T_s).

cm⁻¹). The reported $\sigma_{r.t.}$ for stoichiometric a-GaAs films prepared by flash evaporation is of the order of $3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ [28]. However, Despax et al [29] found (for stoichiometric films) $\sigma_{r.t.}$ of the order of $0.1 \Omega^{-1} \text{cm}^{-1}$ for films reactively sputtered in AsH₃ and Monnom et al [30] obtained $\sigma_{r.t.}$ of about $0.5 \Omega^{-1} \text{cm}^{-1}$ for nearly stoichiometric films deposited at 200 °C by molecular beam epitaxy (MBE). These differences in the value of the conductivity of a-GaAs indicate that deviation from stoichiometry of the sample and preparation technique have an important influence on electrical characteristic of the material.

The reason for the increase in conductivity over the entire temperature range for the a-GaAs films deposited at 59 °C, 81 °C and 102 °C and the decrease of the activation energy with increasing T_s is not very clear. However, the curvature of the conductivity curves suggests that conductivity is occurring by hopping through localized states in the gap. We have calculated the T_0 factor from Mott's $T^{\frac{1}{4}}$ law for these samples. T_0 is found to be equal to 1.4×10^9 , 1×10^8 , 1.7×10^7 and 2.7×10^6 K for samples prepared at $T_s = 29$, 59, 81 and 102 °C respectively. This suggests that the density of states at the Fermi level $N(E_F)$ has increased by 10^3 with increasing temperature up to ~ 102 °C and is consistent with the increased optical absorption seen in Fig. 4.10a. The increase in conductivity and decrease in activation energy has been attributed by others to crystallization of the films [28,32]. This is not likely to be the case in our samples because, first, TEM diffraction patterns did not show this, and secondly, the absorption edge for a crystallized sample should shift towards higher energies and should be sharper than that for an amorphous film. This behaviour was not seen in our films; instead, the absorption edges for these three particular films tailed towards lower energies. However, the reason for the apparent decrease in the conductivity and

corresponding increase in the activation energy for the film at $T_s = 131^\circ\text{C}$ (Fig. 4.11) is not clear. The only comment that can be made is that the TO peak in the i.r. spectrum for this film is slightly broadened and shifts towards the amorphous phase position (see Fig. 4.16). No definite conclusion can be drawn and further studies are needed to clarify these suggestions.

The activation energies obtained from the straight portions (above 300 K) of the $\ln\sigma$ versus $1/T$ plots for the a-GaAs films is shown in Fig. 4.13. The activation energy decreases systematically with increasing T_s , except for the film prepared at $T_s = 131^\circ\text{C}$ which has an activation energy similar to those prepared near room temperature. The low activation energy has been attributed to crystallization of the films [27,28,32] but we do not think that our films are crystallized for the reasons mentioned above.

The temperature dependence of the conductivity of a-GaAs:H films prepared at different T_s , shown in Fig. 4.12, reveals different behaviour from those of a-GaAs films. The room temperature conductivity of the hydrogenated films is of the order of 10^{-8} - $10^{-7} \Omega^{-1} \text{cm}^{-1}$ which is lower than that of the unhydrogenated a-GaAs films by 4-5 orders of magnitude. Hydrogenation is in general found to reduce the conductivity and widen the optical gap of a-GaAs [21].

It can be seen in Fig. 4.12 that the conductivity does not change with substrate temperature up to 93°C , then increases abruptly above this temperature. The activation energies calculated from the most straight portion of the curves above room temperature are shown in Fig. 4.14. For the samples prepared at T_s up to 93°C , the activation energy is roughly constant and also correlates well with the corresponding optical gap (see Fig. 4.10), indicating that the Fermi level is approximately located in the mid gap. However, for the a-GaAs:H film prepared at $T_s = 118^\circ\text{C}$, the activation

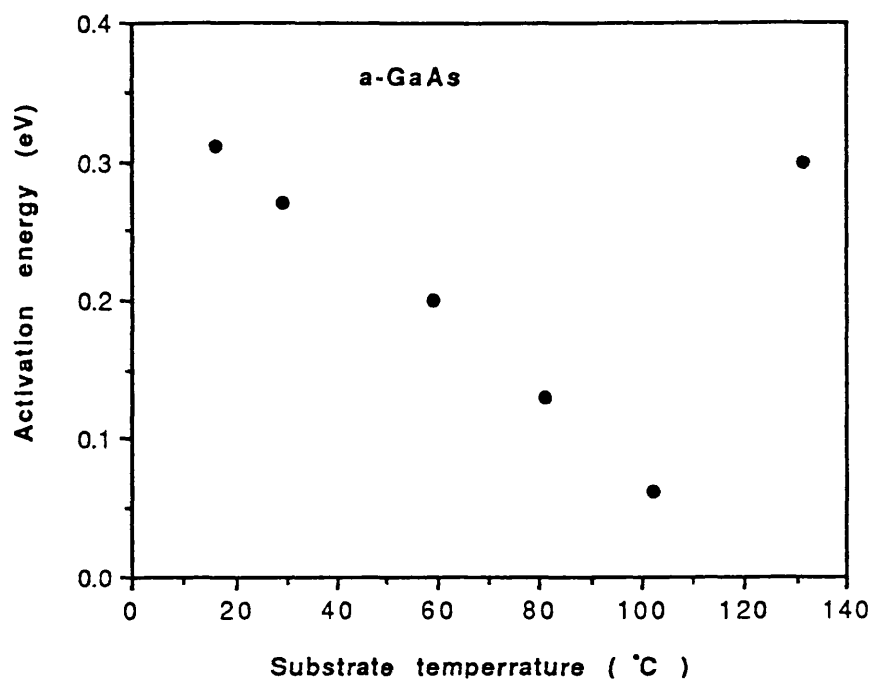


Fig. 4.13 Variations in activation energy as a function of substrate temperature for several a-GaAs films.

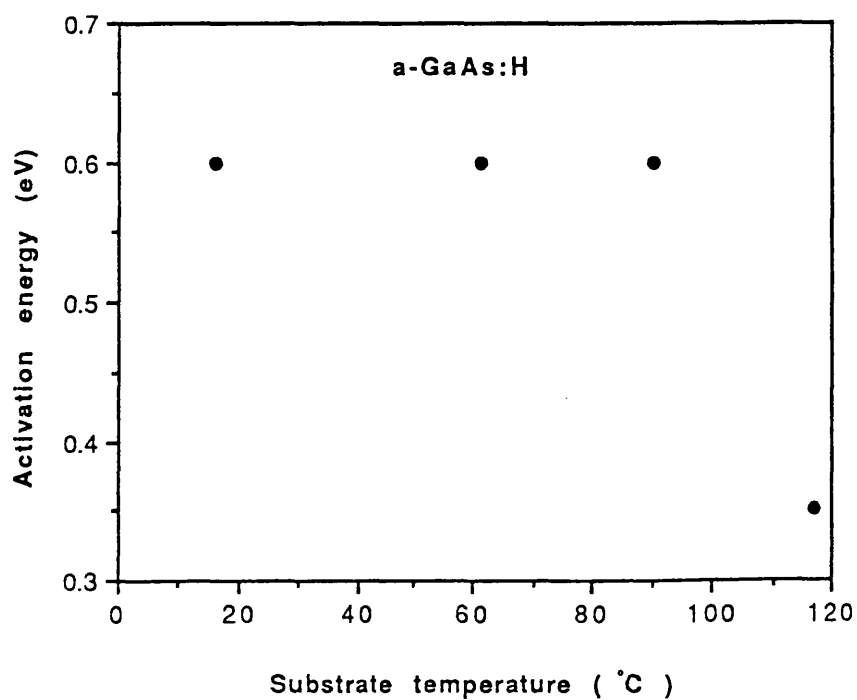


Fig. 4.14 Variations in activation energy as a function of substrate temperature for several a-GaAs:H films.

energy drops, while the corresponding optical gap increases. Since almost all the hydrogen in this film has evolved (see section 4.2.4), one would expect a reduction in the optical gap for an amorphous film. An increase in optical gap in this case is not very clear and may be attributed to the fact that this film is more ordered.

Since the conductivity curves of a-GaAs:H films (Fig. 4.12) show a continuous curvature upwards, there is the possibility of more than one conduction mechanism being involved (although the curvature of the conductivity curves is likely to be associated with the evolution of hydrogen from the samples at high temperatures). The expected conduction mechanism at low temperatures is hopping of charge carriers in localized states at the Fermi level. The data for one of the a-GaAs:H samples showing a continuous curvature in the $\log \sigma$ versus $1/T$ plot are replotted as $\log \sigma$ against $T^{-1/4}$ in Fig. 4.15. The figure shows that the data are fitted quite well by the relation 2.12 at low temperatures, such behaviour corresponding to variable-range hopping.

4.2.4 INFRARED SPECTROSCOPY

Fig. 4.16 shows the infrared transmission spectra near the TO normal mode for a-GaAs films deposited at different substrate temperatures. It is clear that the absorption peak for $T_s = 59, 81$ and 102°C shifts from $\sim 250\text{ cm}^{-1}$ (which is the reported amorphous peak frequency) towards $\sim 270\text{ cm}^{-1}$ (which is the crystalline peak position) and is increasingly sharpened. For the sample prepared at $T_s = 131^\circ\text{C}$, the peak shifts again towards the dotted line and broadens.

Fig. 4.17 shows the infrared transmission spectra from 2300 cm^{-1} to 200 cm^{-1} for the a-GaAs:H samples. For the first three samples, in addition to the known peaks at 1450 cm^{-1} and 550 cm^{-1} , a new small peak was detected at 1760 cm^{-1} . this

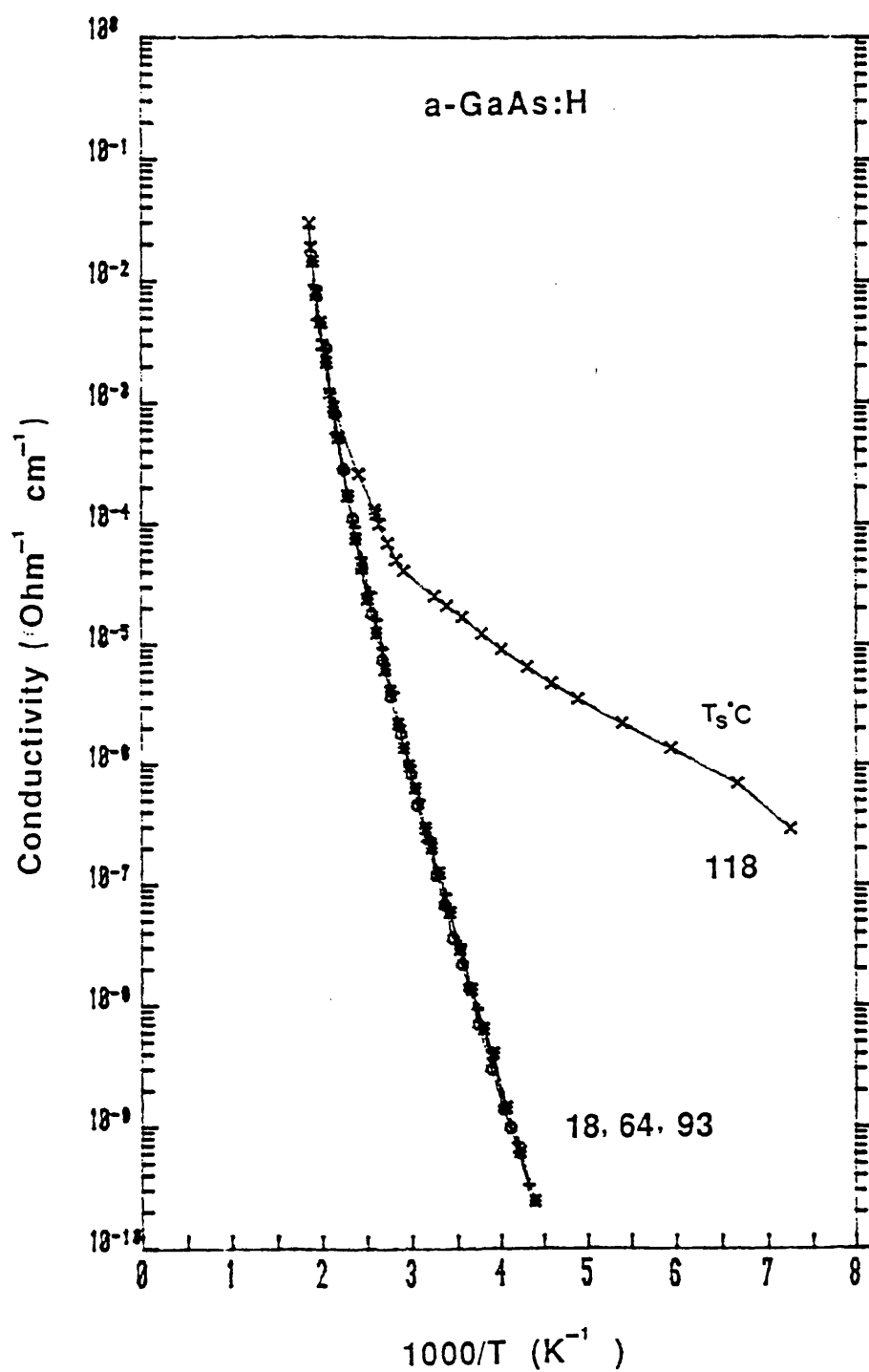


Fig. 4.12 $\text{Log } \sigma$ versus $1/T$ for several a-GaAs:H films prepared at different substrate temperatures (T_s).

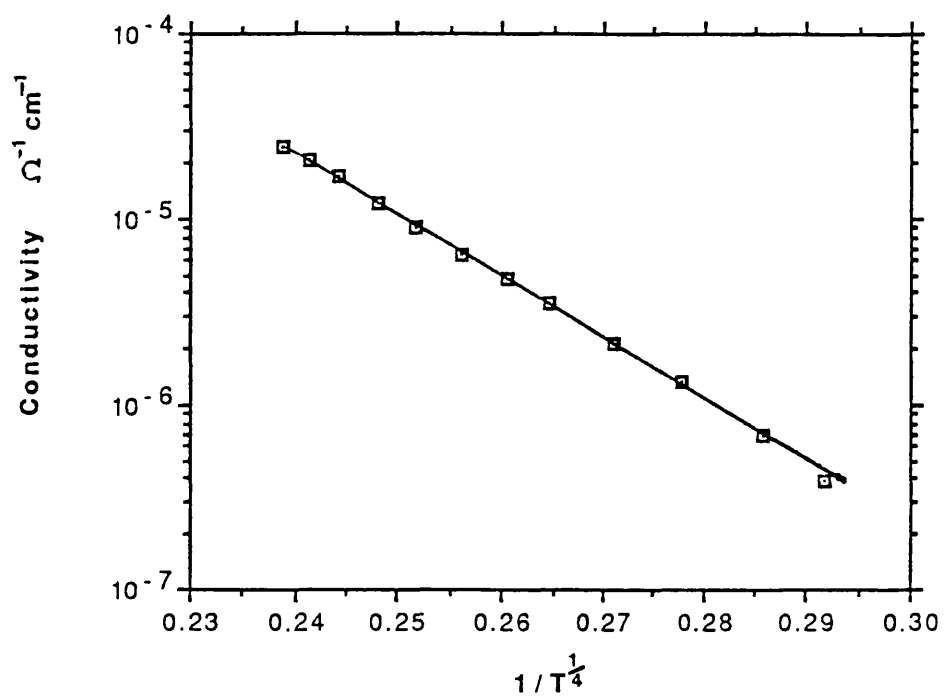


Fig. 4.15 Log σ versus $T^{\frac{1}{4}}$ plot for a-GaAs:H film.

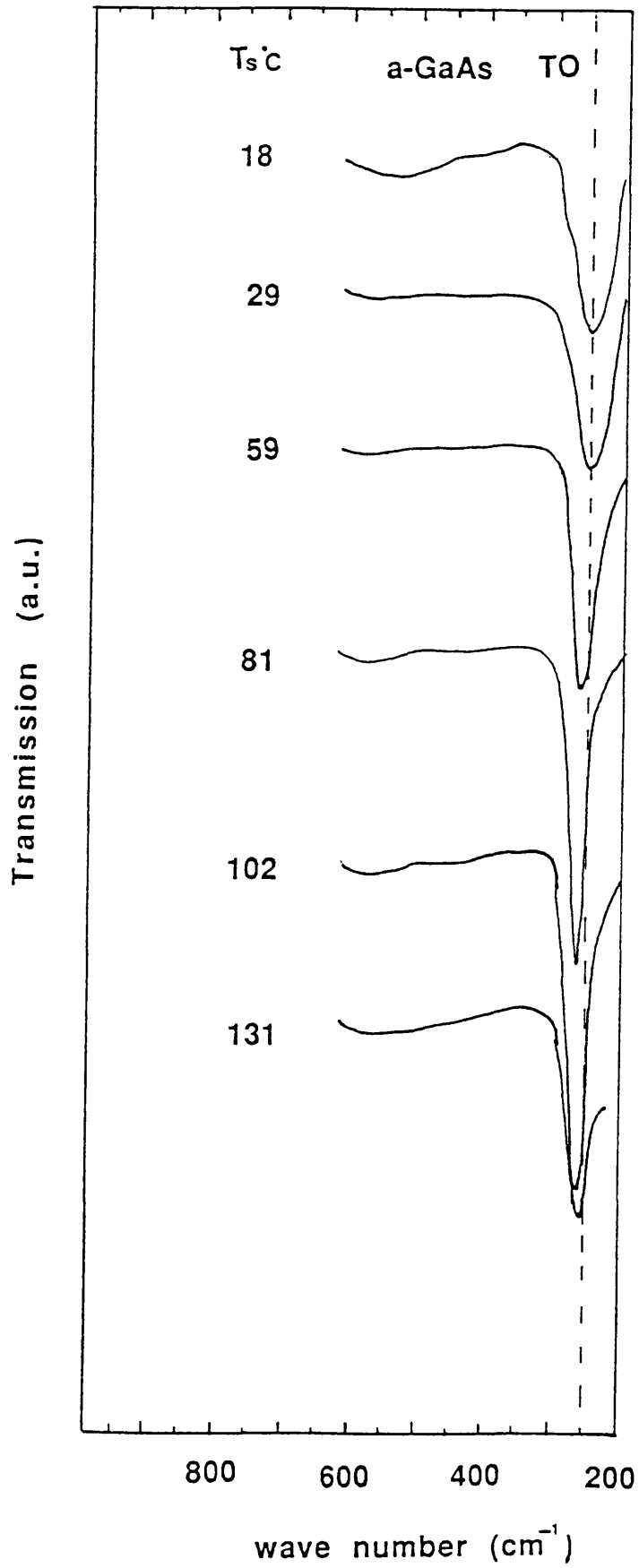


Fig. 4.16 Infrared transmission spectra of a-GaAs films prepared at different substrate temperatures (T_s).

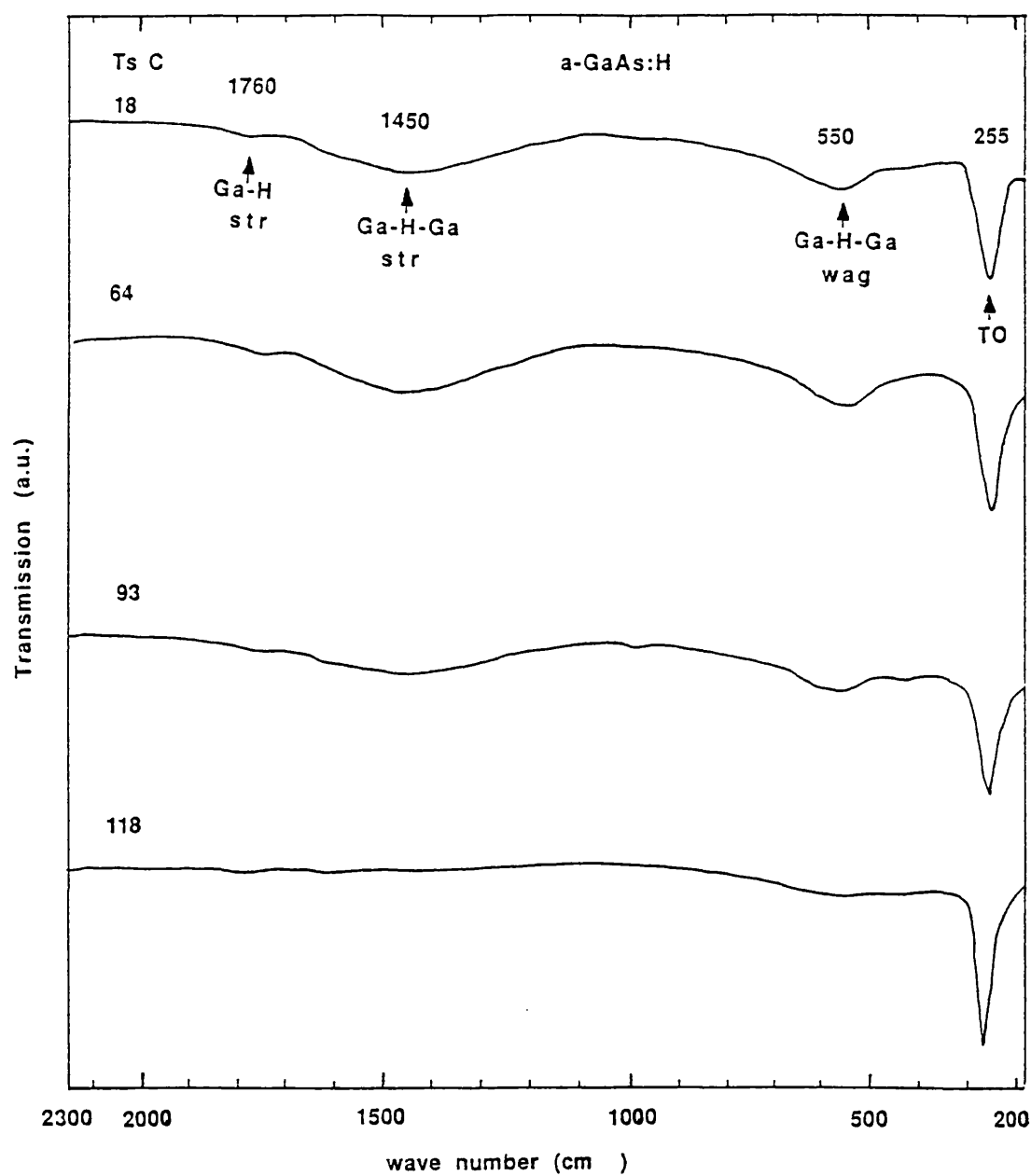


Fig. 4.17 Infrared transmission spectra of a-GaAs:H films prepared at different substrate temperatures (T_s).

peak has not seen in our previous work of a-GaAs:H films prepared at room temperature (see section 4.1.4) and has been assigned to a Ga-H stretching mode [18,19]. For the film deposited at $T_s=118^\circ\text{C}$, it can be seen that all the hydrogenic bands (1760, 1450 and 550 cm^{-1}) are nearly flattened out which means that most of the hydrogen in the film has evolved. Also, the TO mode shifts towards $\sim 270\text{ cm}^{-1}$ which is the known crystalline TO mode frequency.

4.3 a-Ga_{1-x}As_x FILMS

4.3.1 OPTICAL PROPERTIES

The dependence of the absorption coefficient on photon energy for a-GaAs films with varying composition is shown in Fig. 4.18. For the film with an excess As ($x = 0.56$), the absorption edge shifts to higher energy but there is practically no change in the absorption edge for films with $x = 0.56-0.67$. When more As is added to the film, ($x = 0.85$) the absorption edge shifts towards lower energies.

The optical gap E_0 was obtained from relation 2.17 using the experimental data in Fig. 4.18 for $\alpha > 10^4 \text{ cm}^{-1}$. The results are shown in fig. 4.19. For near-stoichiometric a-GaAs, E_0 is about 1.0 eV and remains roughly constant up to $x = 0.67$. At high As content, E_0 decreases slightly to about 0.9 eV. Similar results were obtained by Matsumoto and Kumabe [27] for a-GaAs films prepared by molecular beam deposition. However, Bandet et al [13] obtained different results. They found an increase in E_0 from about 1.0 eV at stoichiometry to about 1.35 eV at $x = 0.60$, after which E_0 remained roughly constant at higher As concentrations (the reported optical gap for a-As is about 1.1 eV, see Mott and Davis [34] p.427). These results are in contrast with those of Theye et al [41] for flash-evaporated a-GaAs films; they reported that for a-GaAs films with $x \approx 0.60$, there is no significant change in the optical gap. Our results are in a good agreement with the results reported in references [27] and [29].

4.3.2 ELECTRICAL PROPERTIES

The temperature dependence of dark d.c. conductivity for a-GaAs samples with different As content is shown in Fig. 4.20. It can be seen that the conductivity decreases when the

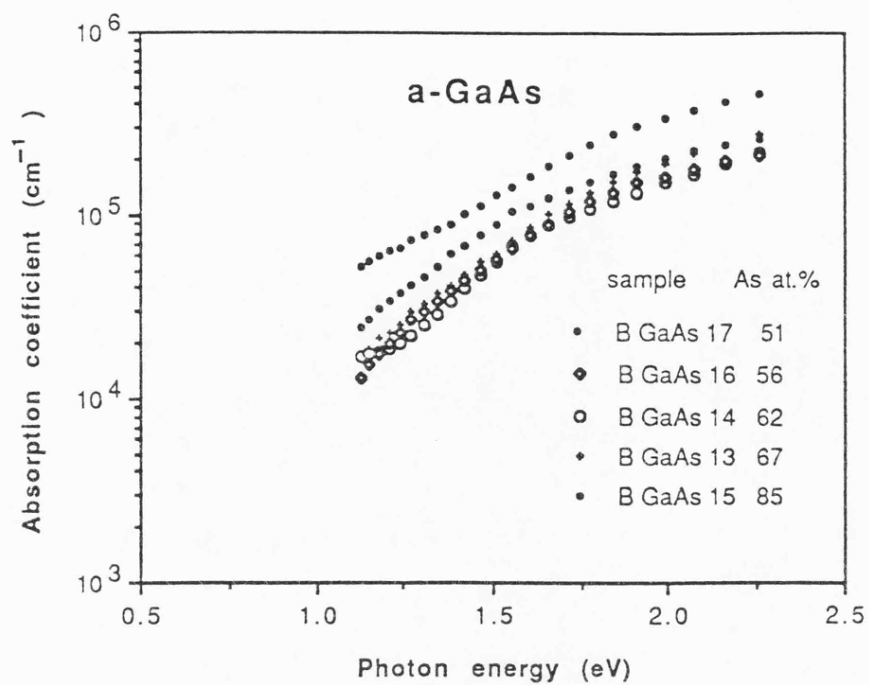


Fig. 4.18 Absorption coefficient α versus photon energy of a-GaAs films with various As concentrations.

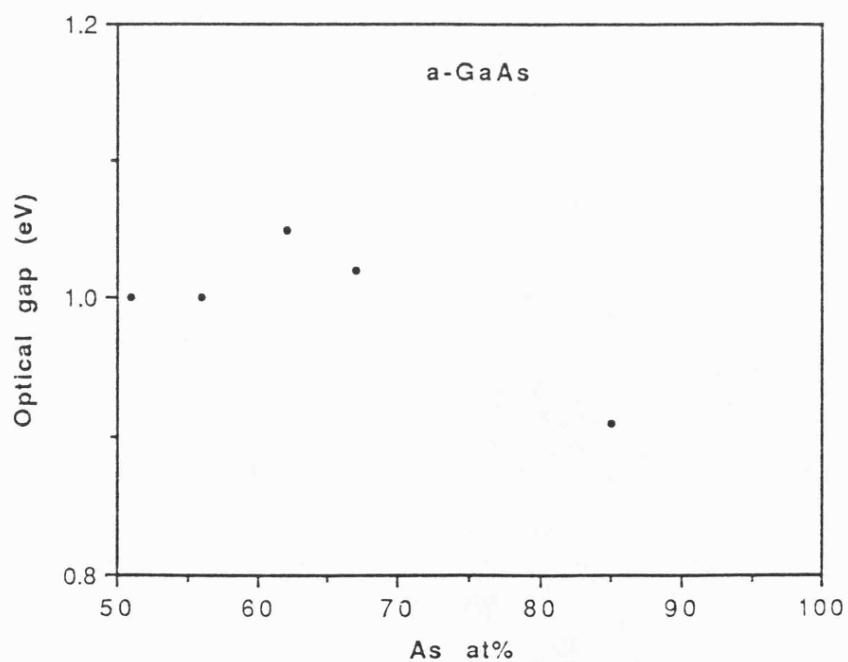


Fig. 4.19 Variation in optical gap as a function of As content in a-GaAs films.

composition of the films deviates from near stoichiometry to $x=0.56$, then remains nearly unchanged in the compositions range $0.56 < x < 0.67$. For the film with highest As content ($x=0.85$), the conductivity is higher than in the aforementioned range. Comparing our conductivity results with others, Gheorghiu et al [28] reported that for flash-evaporated a-GaAs, the conductivity increases with increasing As content, while Monnom et al [30] found that σ decreases with increasing As concentration up to about 70% above which it changes little. Despax et al [29] also showed a drastic decrease in the conductivity with increasing As content in a-GaAs film. Our results therefore, are in a fair agreement with the results of the last two authors.

The conductivity of our films exhibits an activated behaviour for a large range of temperatures and for all compositions. The activation energy was calculated from the $\sigma(T)$ curves above room temperature. Fig. 4.21 shows that the variation of activation energy E_a with As concentration is rather small ($0.45 < E_a < 0.5$ eV for $0.56 < x < 0.85$) which is in good agreement with the results of Matsumoto and Kumabe [27]. The optical band gap energy of the same films is between ~ 0.9 to 1.05 eV; the activation energy of the films is therefore approximately half the optical gap. This means that the Fermi level for the films is located near mid-gap.

The above optical and electrical data for a-Ga_{1-x}As_x do not change much over quite an appreciable composition range. However, the way in which excess As atoms are distributed throughout the film, i.e. whether they are randomly incorporated or segregated could play a major role [25]. Our infrared measurements (see next section) have shown a trend towards segregation of excess As in the film with $x = 0.85$.

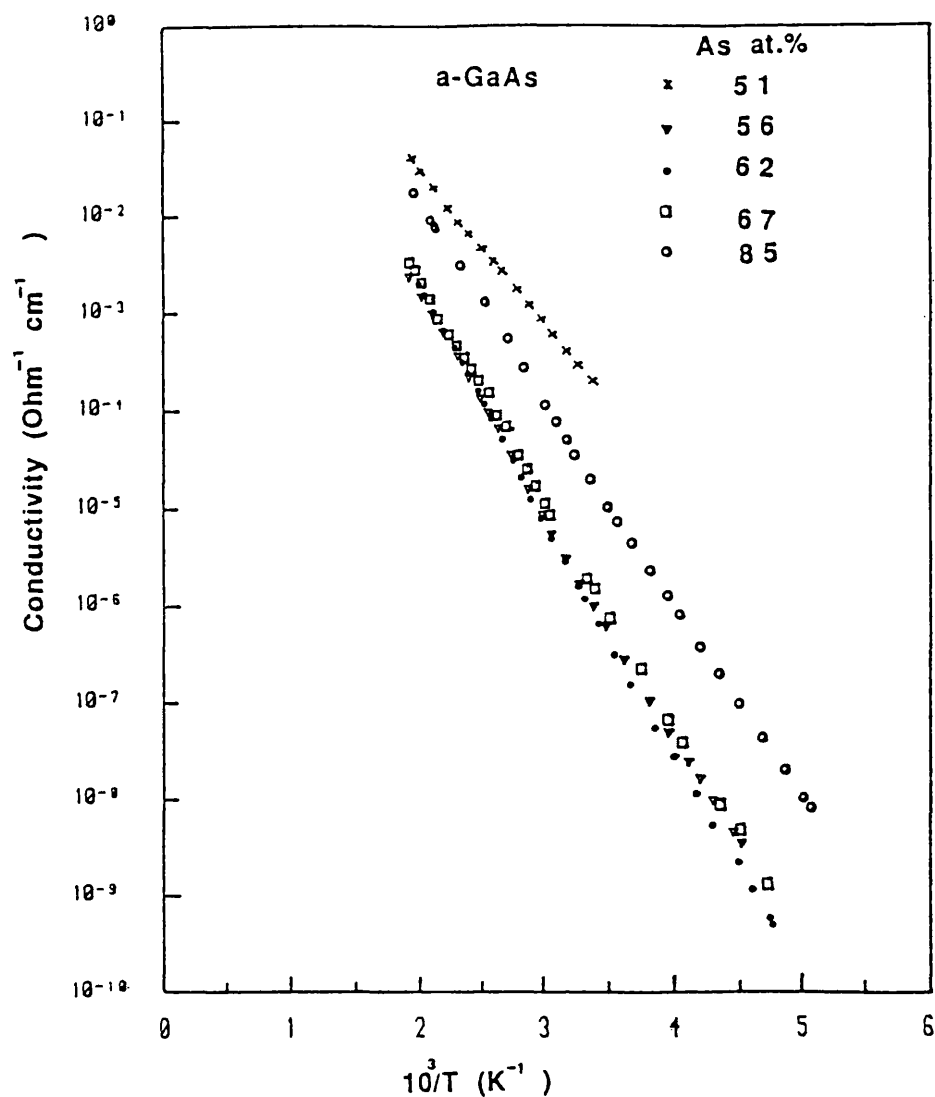


Fig. 4.20 Log σ versus $1/T$ for a series of a-GaAs films with different As content.

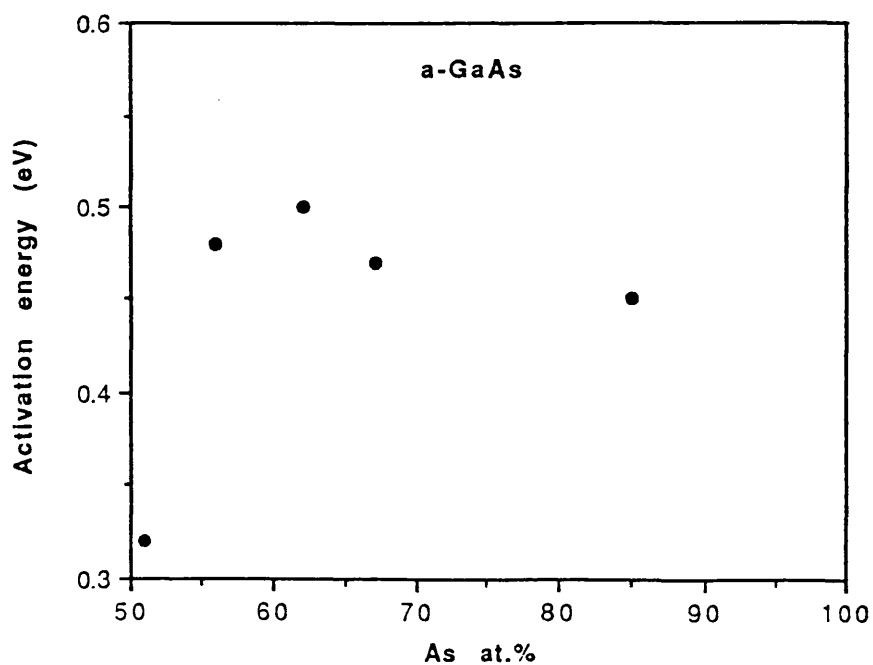


Fig. 4.21 Variation in activation energy as a function of As content in a-GaAs.

4.3.3 INFRARED SPECTROSCOPY

Fig. 4.22 shows infrared transmission spectra near the lattice fundamental absorption (TO) for $\text{a-Ga}_{1-x}\text{As}_x$ films with different compositions. It can be seen that with increasing As content the intensity of the band at about 250 cm^{-1} decreases and at $x=0.85$ the band becomes broad with a low intensity. Owing to the presence of some noise in this region of the spectra, it was not easy to differentiate between the a-As peak which is at about 230 cm^{-1} [34] and that of the a-GaAs peak at about 250 cm^{-1} . However, it is clear from the figure that the a-GaAs peak is reduced with increasing As concentration in the films. The question arises here as to what happens to excess As; is it incorporated in the a-GaAs network randomly or is it segregated? The answer to this question might be available from EXAFS measurements, which can yield coordination numbers and hence how the As coordination changes with increasing As (a-As is three-fold coordinated, while a-GaAs is four-fold coordinated). Such studies are underway.

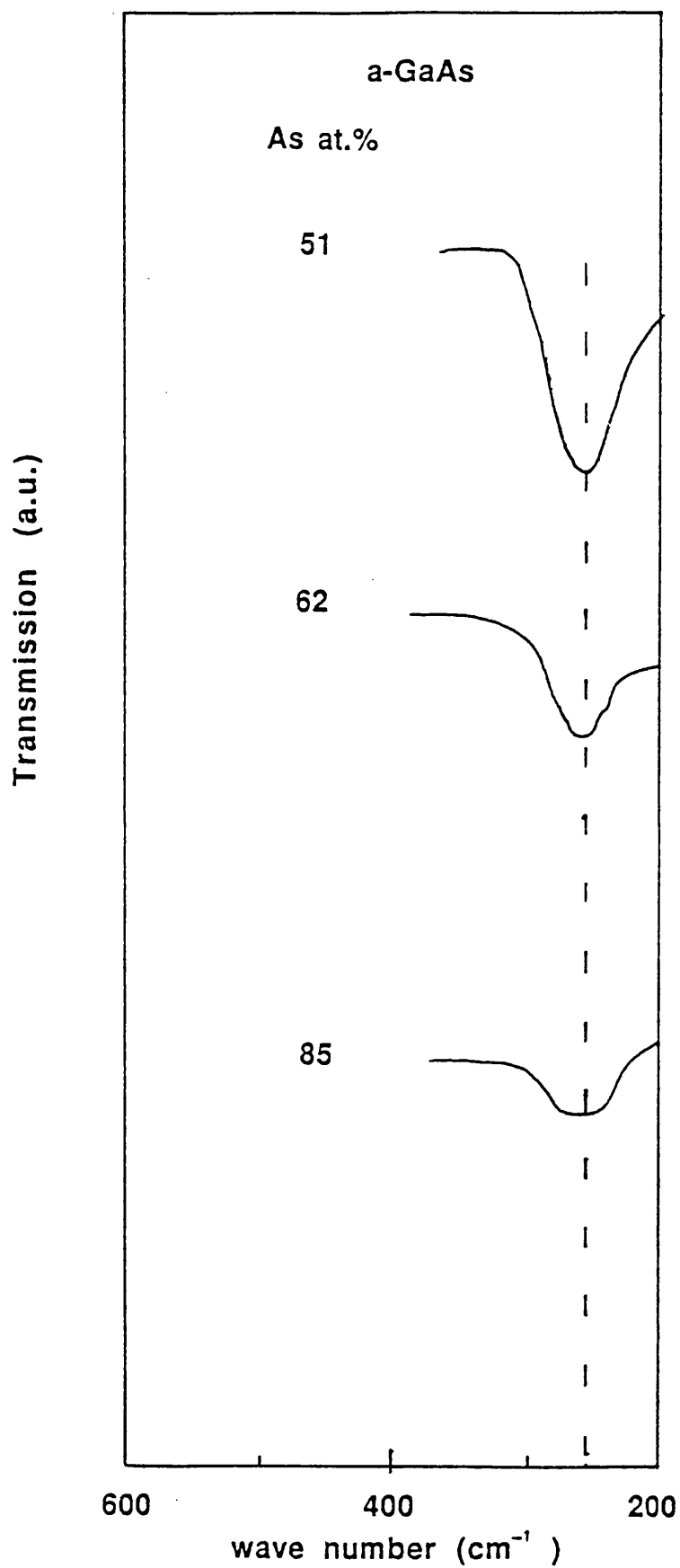


Fig. 4.22 IR transmission for a-GaAs films with different As content.

4.4 a-GaAlAs(:H)

Crystalline $\text{Ga}_{1-x}\text{Al}_x\text{As}$ material has been extensively studied because of its many applications in optoelectronics and other solid state devices such as semiconductor lasers and light emitting diodes.

Selected energy gaps can be obtained in the mixed crystal system GaAs:AlAs, within the limits imposed by the energy gaps of GaAs and AlAs. Junctions formed between $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and GaAs are of great importance for many optoelectronic devices, because of the small difference in lattice parameter between c-GaAs and c- $\text{Ga}_{1-x}\text{Al}_x\text{As}$, (for $0 \leq x \leq 1.0$ it is less than 0.15% at 300 K); leading to an insignificant concentration of undesirable interface states. The band gap energy in c- $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and its dependence on the alloy composition is known to be one of the most important device parameters; it varies according to the relations $E_g/\text{eV} = 1.424 + 1.247x$ ($0 < x < 0.45$) and $1.900 + 0.125x + 0.143x^2$ ($0.45 < x < 1.0$) [35].

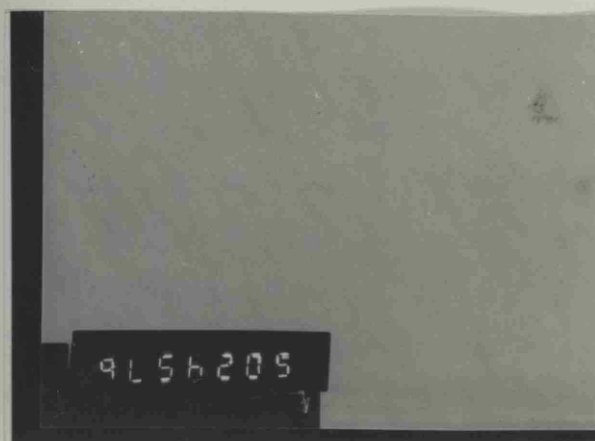
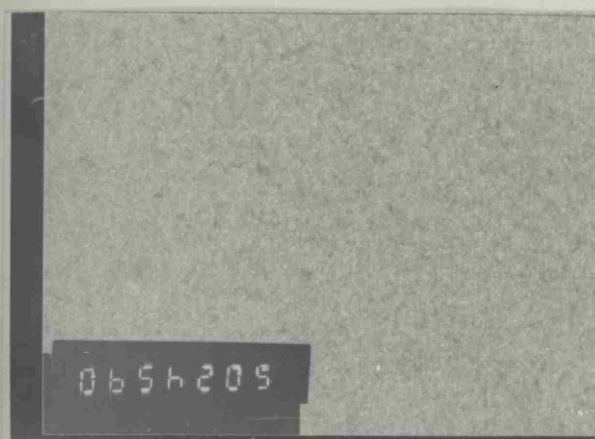
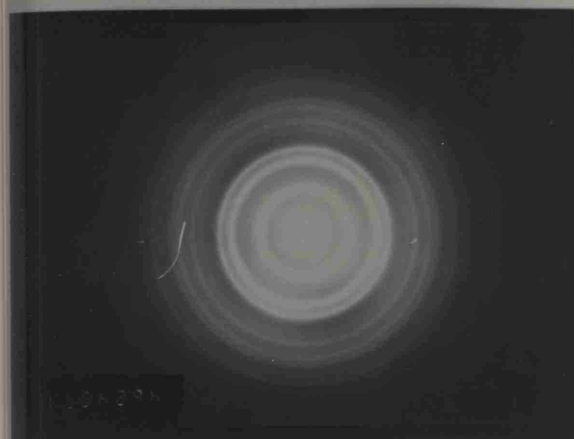
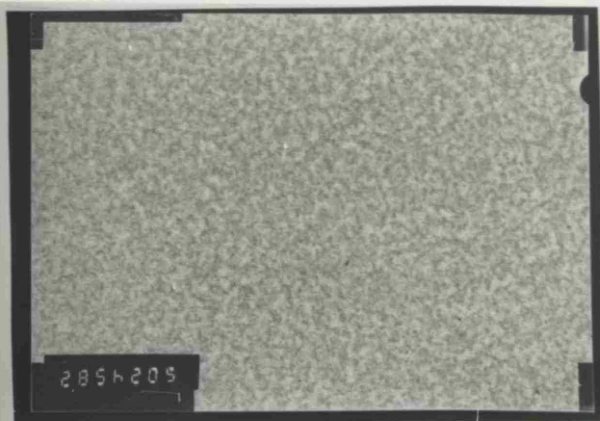
Amorphous GaAlAs(:H) has been prepared and characterized in the present work in order to compare amorphous and crystalline phases.

4.4.1 SAMPLE PREPARATION AND CHARACTERIZATION

Amorphous GaAlAs(:H) films were prepared in a similar way to a-GaAs using the same conditions of deposition (see section 3.1.3). The aluminium content of the film was altered by varying the number and the area of aluminium chips on the GaAs target. Aluminium with purity of 20 ppm was used in this work. For thickness, composition and structure measurements, see chapter 3 and Fig. 3.4.

Evidence for the amorphous structure was obtained using a TEM. The examined samples were amorphous up to about 30 at.% Al but exhibited a polycrystalline structure above this

Plate 4.3 Transmission electron micrographs of GaAlAs for various Al concentration ranging from (a) 0 at.%, (b) 15 at.%, (c) 32 at.% and (d) 45 at.%. Electron diffraction patterns for the same samples are shown in (e-h) respectively. The figure illustrates how the structure of the film changes from amorphous ($\text{Al} < 32 \text{ at.}\%$) to crystalline ($\text{Al} > 32 \text{ at.}\%$).



concentration. plate 4.3 shows the transmission electron micrographs and the electron diffraction pattern of GaAlAs for Al composition ranging from 0 to 45 at.%. It can be seen that the films containing up to 30 at.% Al are amorphous with almost no structure in the micrographs and with broad halos in the diffraction pattern, while above about 30 at.% Al, the rings become sharp which is indicative of crystalline material. In addition the corresponding micrographs show structure when the films are polycrystalline.

4.4.2 OPTICAL PROPERTIES

The absorption coefficients for hydrogenated and unhydrogenated a-GaAlAs as a function of photon energy for various Al concentrations are shown in Fig. 4.23. It can be seen that the absorption edge shifts towards lower energy and broadens with Al addition. At low photon energies and high Al content the edge becomes nearly flat. The reason for this behaviour is not clear but is probably associated with a high concentration of Al-related defect states in the gap.

The optical energy gap E_0 was determined from the Tauc law [36] (equation 2.17). Tauc plots obtained from experimental data in figure 4.23 are displayed in Fig. 4.24 for both hydrogenated and unhydrogenated a-GaAlAs films. The variation of the optical energy gap with Al concentration for both hydrogenated and unhydrogenated a-GaAlAs is shown in Fig. 4.25. This curve can be divided into two regions. In region 1 (Al content < 31 at.%), E_0 remains roughly constant for Al content less than 8 at.% but decreases for Al content above this value, while in region 2 (Al content > 31 at.%) E_0 increases with increasing Al content. As pointed out earlier (section 4.4.1), the films in the two regions have different structures; amorphous and polycrystalline respectively. Figure 4.25 also shows the variation of the optical gap in

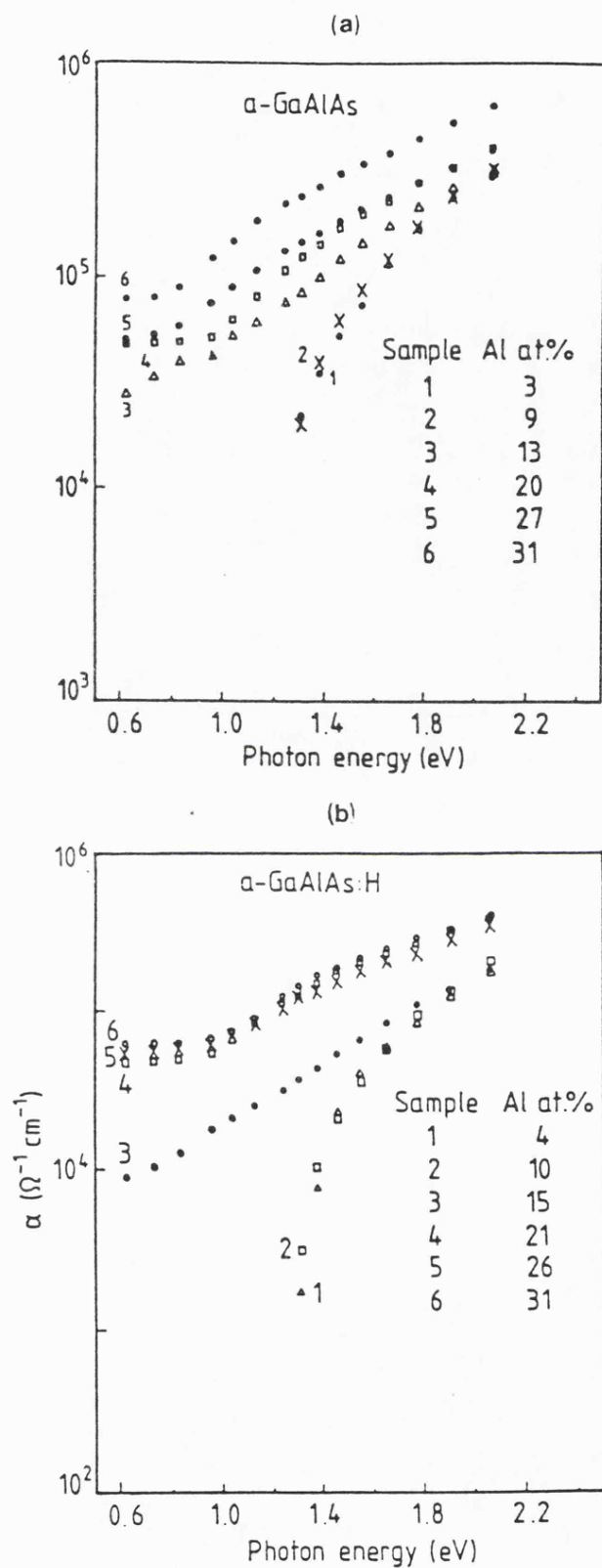


Fig. 4.23 Absorption coefficient α versus photon energy of films for various Al concentration (a) a-GaAlAs (b) a-GaAlAs:H.

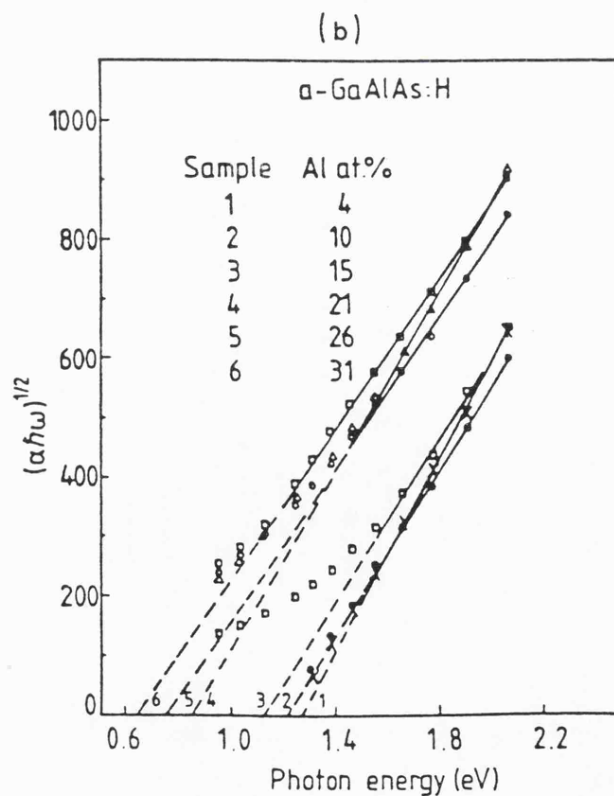
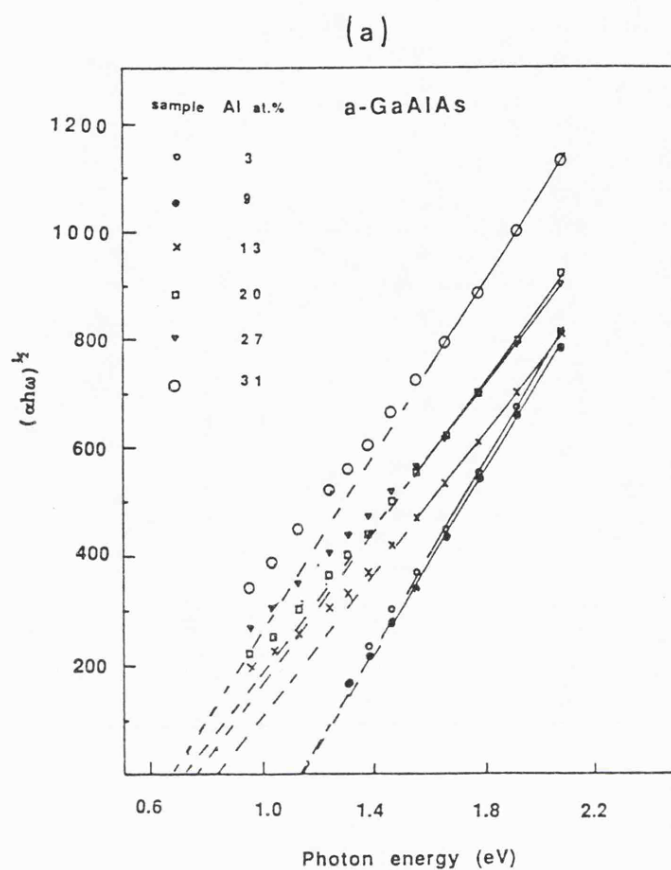


Fig. 4.24 Tauc plot of films for various Al concentrations
(a) a-GaAlAs (b) a-GaAlAs:H.

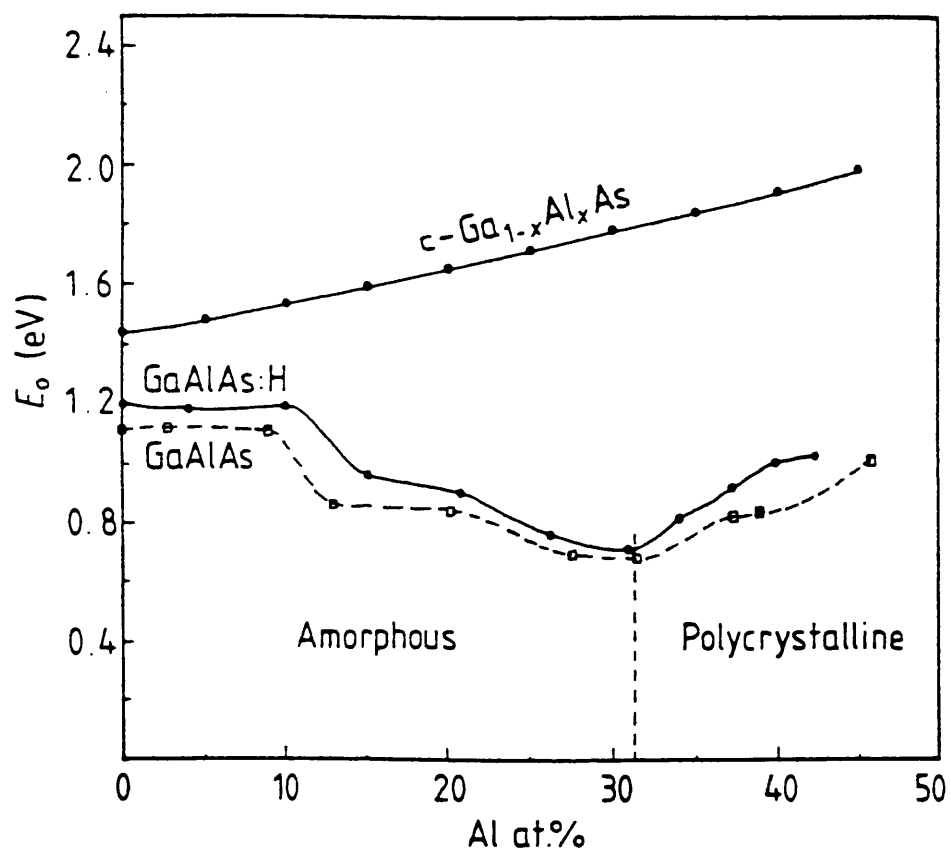


Fig. 4.25 Dependence of the optical gap E_0 on Al content of GaAlAs.

crystalline $\text{Ga}_{1-x}\text{Al}_x\text{As}$ [35].

The reason for the decrease in optical energy gap with increasing Al concentration in a-GaAlAs(:H) films, in contrast to an increase in c- $\text{Ga}_{1-x}\text{Al}_x\text{As}$, is not very clear¹. However, one can argue that in crystalline $\text{Ga}_{1-x}\text{Al}_x\text{As}$, Al is substitutionally incorporated in place of Ga atoms and only bonds between Ga-As or Al-As are expected. Wrong bonds have a very low probability of occurrence in the crystalline system. The energy gap in c-AlAs is higher than that for c-GaAs and increases monotonically with Al content. However, the situation is quite different in the a-GaAlAs(:H) system. Wrong bonds are expected in non-stoichiometric GaAs [16] and we expect them also in the ternary compound. Each Al atom will not necessarily substitute for a Ga atom in such a random network and therefore like-atom or wrong bonds are expected (e.g. Ga-Ga, Al-Al, As-As and Ga-Al). This is a possible explanation for the decrease of the energy gap with Al alloying.

For concentrations of Al higher than 30 at.%, the films are polycrystalline and the trends in the optical gap are then in the same direction as for crystalline GaAlAs.

4.4.3 ELECTRICAL PROPERTIES

The temperature dependence of the dark d.c. conductivity σ for samples with various Al concentration is shown in Fig. 4.26. It can be seen that with increasing Al content the conductivity rises, particularly when the Al content is increased from about 8.1 to 11.8 at.% Al. The high-temperature activation energies for a-GaAs:H and for a-GaAlAs:H with 6.1

¹It should be emphasized that the comparison of the variations of E_g with Al content for amorphous and crystalline forms shown in figure 4.24 is not strictly valid. Data for the crystalline form [35] refer to compositions along the $(\text{Ga}_{1-x}\text{Al}_x)\text{As}$ tie line (see figure 3.4) where our amorphous samples intersect this line but lie parallel to the $(\text{GaAs})_{1-x}\text{Al}_x$ tie line.

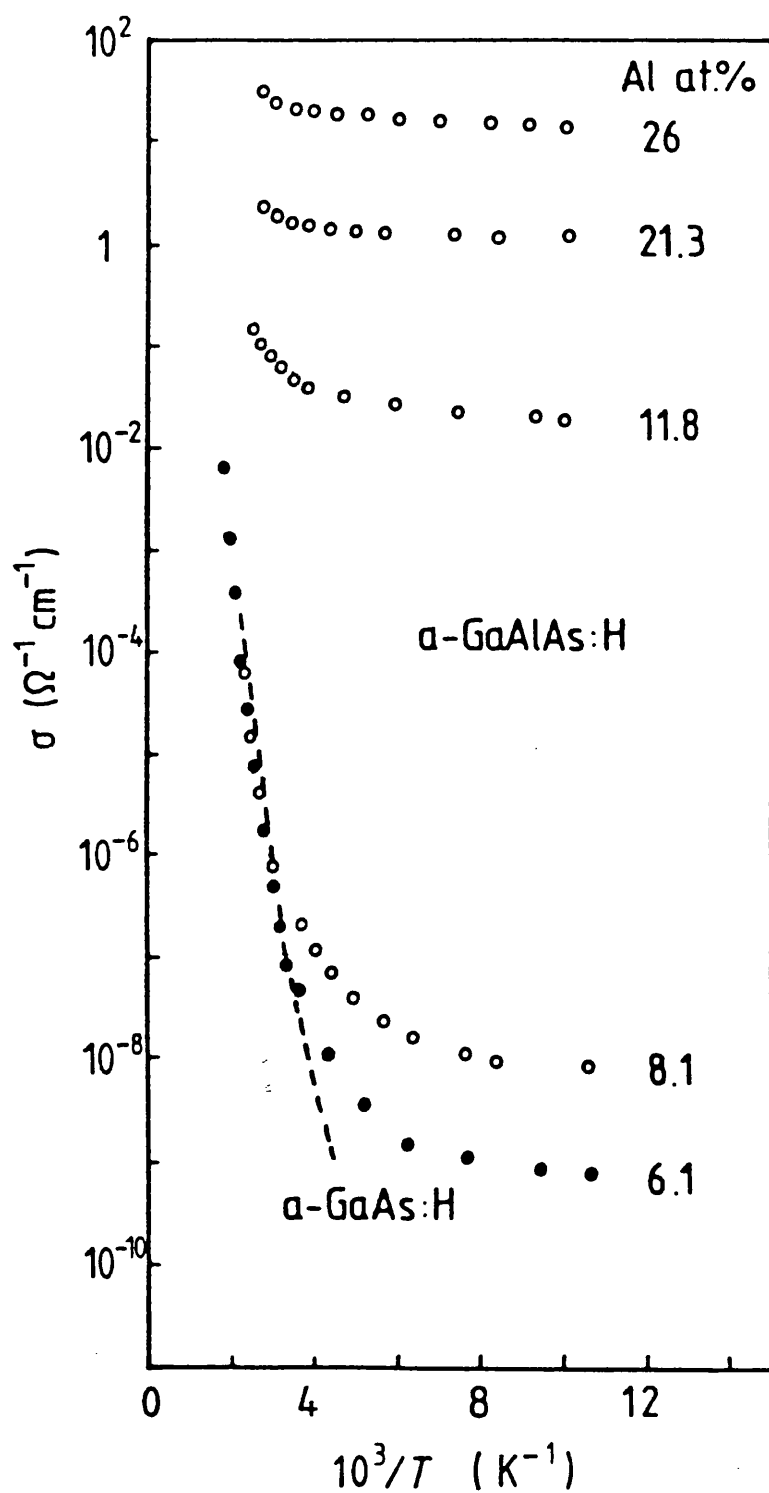


Fig. 4.26 Log σ versus $1/T$ for a series of $a\text{-GaAlAs:H}$.

and 8.1 at.% Al are all about 0.6 eV. Comparison with figure 4.25 shows that the optical gap is approximately equal to $2E_a$ for these samples and one can conclude that the Fermi energy is pinned close to mid-gap. At lower temperatures and for higher Al content, the conductivity is only weakly dependent on temperature, suggesting a mechanism of conduction by hopping in localized states near the Fermi energy.

4.4.4 INFRARED SPECTROSCOPY

Figure 4.27 shows infrared transmission spectra (a) for five unhydrogenated GaAlAs samples and (b) for hydrogenated GaAlAs samples with similar Al concentration. It can be seen that by adding Al to a-GaAs, in addition to the a-GaAs TO mode at about 250 cm^{-1} , a mode appears at about 350 cm^{-1} . Similar behaviour has been observed in c-Ga_{1-x}Al_xAs [43]. Also, two broad absorption bands, at $600\text{--}700\text{ cm}^{-1}$ and near 1600 cm^{-1} appear. In the hydrogenated samples (figure 4.27b), these two bands are stronger and one can determine their centre frequencies to be about 670 cm^{-1} and 1650 cm^{-1} . We have mentioned (section 4.1.4) that Ga-H-Ga bridge wagging and stretching modes occur at 530 and 1460 cm^{-1} respectively [19]. Bridging hydrogen has been found in a number of aluminium compounds (Al-H-Al bridges) such as $\text{Al}(\text{BH}_4)_2\text{H}$ and $\text{Al}(\text{BH}_4)\text{H}_2$ [20]. In these compounds, the Al-H-Al stretching vibrations have been reported to occur in a broad band between 1200 and 2200 cm^{-1} , centred near 1650 cm^{-1} . The Al-H-Al wagging modes lie between 470 and 1050 cm^{-1} with maximum at 730 cm^{-1} . So the broad band centred near 1650 cm^{-1} in our films can be assigned as an Al-H-Al stretching mode and that at 670 cm^{-1} to a wagging band. The shifts to higher wavenumbers in going from Ga-H bond to Al-H bonds are reasonable in view of the difference in the covalent radii r_c (r_c for Ga is $1.26\text{ \AA}$ and that for Al is $1.18\text{ \AA}$) since the vibration frequency is approximately proportional to $r_c^{-1.5}$ [19].

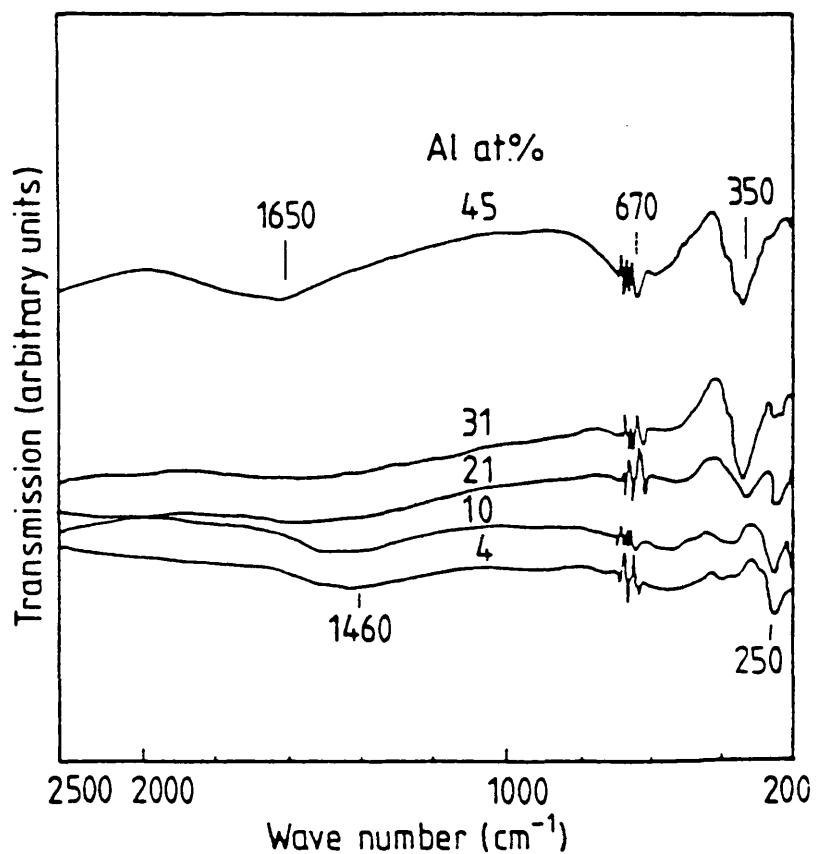
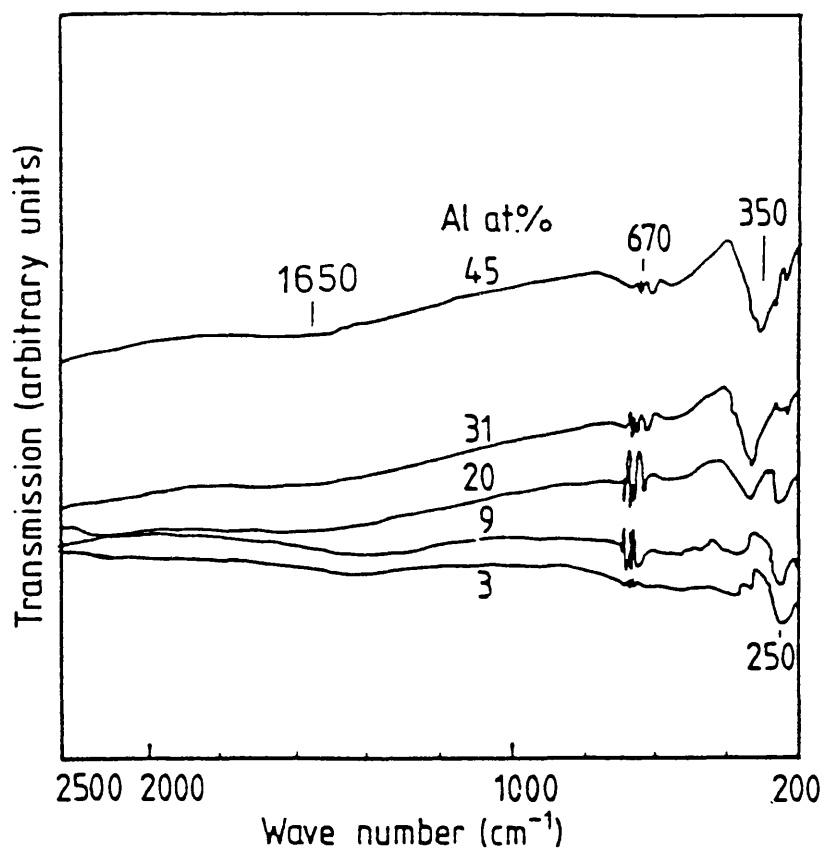


Fig. 4.27 Infrared transmission for a series of films of (a) GaAlAs (b) GaAlAs:H.

4.5 AMORPHOUS GaAsP Films

The III-V compounds can form mixed crystal systems and have been intensively investigated for both scientific and technological reasons. An exceedingly useful feature of III-V semiconductor materials is that their band gaps and other parameters can be adjusted for a particular application by controlling the alloy composition. For example, if a mixture of phosphorus and arsenic (both from group V in the Periodic Table) is combined with gallium (from group III), semiconductor in the system $\text{GaAs}_{1-x}\text{P}_x$ are formed. The resulting energy gaps of these material lie somewhere between the values for GaAs and GaP. By choosing the appropriate mixture of phosphorus, the band gap can be tuned to a particular value, making it is possible to fabricate light-emitting diodes (LEDs) of particular colour. Crystalline $\text{GaAs}_{1-x}\text{P}_x$ was one of the earliest ternary alloys used to make LED devices.

Since there is considerable experimental and theoretical information available on a-GaAs and a-GaP, and in addition, since the bond lengths of Ga-As and Ga-P are distinguishable (EXAFS measurements can be well analysed), we therefore chose a-GaAsP as a ternary mixture to study its structural, optical and electrical properties and to compare these with those of the crystalline form.

Amorphous GaAsP films with P contents varying from ~ 15-73 at.% were prepared in a similar way to a-GaAs. The P content of the film was altered by varying the number of P pieces on the c-GaAs target. The Ga/As ratio remained nearly constant in this set of films. Red phosphorus of 0.5 ppm was used in the present work.

4.5.1 OPTICAL PROPERTIES

There are some significant differences between a-GaAs and a-GaP. For example, in a-GaP, the absorption edge is broader and tails towards lower energies which suggests a higher density of defect states in the pseudogap and at the band edges. This high density of defect states was attributed not only to structural defects of dangling-bond type but also to the presence of an important proportion of chemical defects (wrong bonds) [1,41]. However, for a-GaP samples containing a large excess of P (≈ 0.66), the density of defect states was found to be lower. This was attributed to a self-compensating or alloying mode of incorporation [1]. Robertson [37] pointed out that the alloying effects which accompany a deviation from stoichiometry indicate that most of the group-V (P, As, etc.) atoms in excess should enter in a self-compensated mode, i.e. with their preferred three-fold coordination. By adding P to a-GaAs therefore, we expect properties which are a mixture between a-GaAs, a-GaP and possibly a-P.

The absorption coefficient α of a-GaAsP films was obtained from transmission data using relations 2.19 and 2.21. Fig. 4.28 shows the dependence of the absorption coefficient on photon energy for a-GaAsP films. As shown in the figure, there is no significant change in the absorption edge in the high-absorption region for films containing ~ 15 -57 at.% P, but for the specimen with 73 at.% P, the absorption edge has shifted to a higher energy. However, in the low-absorption region, it can be observed that for samples containing 31-73 at.% P, the absorption edges tail towards low energies. It can also be seen that the absorption coefficient in this region increases with increasing P content in the film for samples of P between 15 to 57 at.%, while for the sample with 73 at.% P, the absorption coefficient is lower. This behaviour may be associated with the fact mentioned earlier that the density of defect states is lower for samples containing large excess of P.

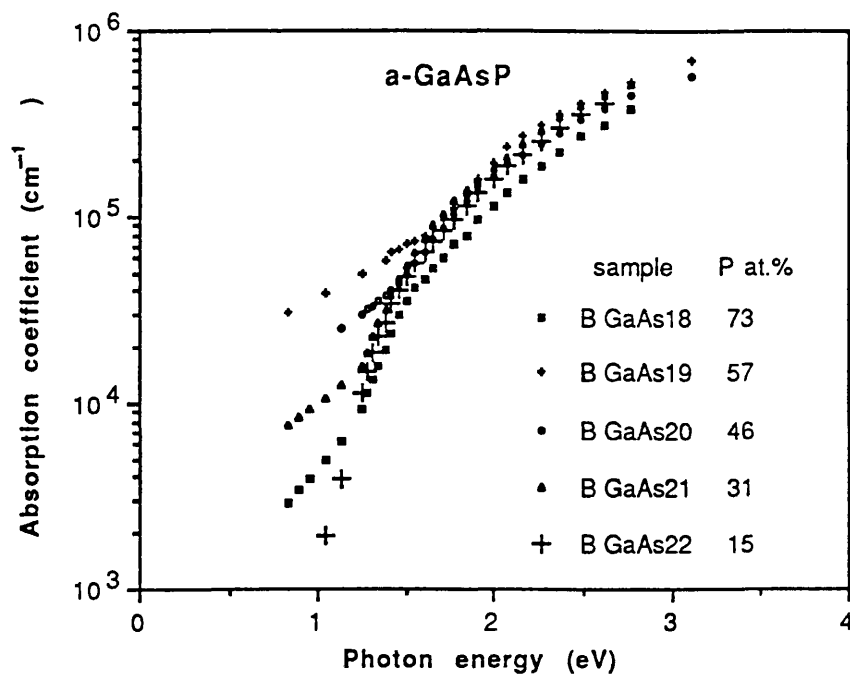


Fig. 4.28 Absorption coefficient α versus photon energy of a-GaAsP films for various P concentrations.

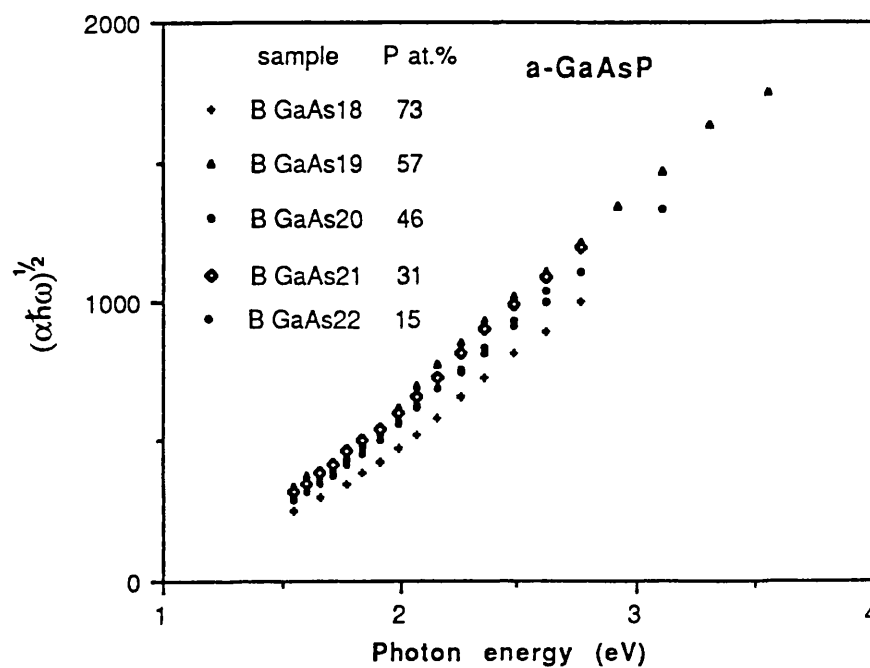


Fig. 4.29 Tauc plot for a-GaAsP films with various P concentrations.

The optical gap (Tauc gap) was determined using relation 2.17. The Tauc plots obtained from the experimental data in Fig. 4.28 are shown in Fig. 4.29. It can be seen that E_0 increases from 1.0 eV for a-GaAs to ~ 1.2 eV for a-GaAsP film containing 15 at.% P and to ~ 1.3 eV for the specimen with 73 at.% P as shown in Fig. 4.30 (for comparison, we have plotted the variation of optical gap in c-GaAs_{1-x}P_x alloys in Fig. 4.31 [42]). This behaviour may be explained as follows: As phosphorus is added to a-GaAs, most of it is incorporated in the film as Ga-P bonds. Therefore, the optical gap increases towards that of a-GaP as the P content in the film increases. The number of Ga-As bonds is rapidly reduced and much of the film becomes like a-GaP (see infrared spectra Fig. 4.34 and EXAFS results chapter 5). At high P content, EXAFS results suggests the presence of P-P bonding. This may explain the increase of E_0 to ~ 1.3 eV for the specimen with 73 at.% P (the optical gap of a-P is 1.75 eV [46]).

It should be mentioned here that optical data reported in the literature for a-GaP exhibit large variations. Early measurements on evaporated films, obtained by a three-temperature-zone technique at low substrate temperatures [38], gave an optical gap of ~ 1.0 eV. Matsumoto and Kumabe [39] reported an optical gap of 1.17 eV for non-annealed sputtered a-GaP films. Gheorghiu and Theye [1] reported an optical gap of 1.2 eV for non-annealed flash-evaporated a-GaP films. A large optical gap of ~ 1.8 eV was also given for plasma-deposited a-GaP films which contained an excess of P (Ga/P ≈ 0.91) [40]. These discrepancies can be related, to a certain extent, to deviation from stoichiometry of the samples [1]. Gheorghiu and Theye found that films with atomic Ga/P ratios between 0.6 and 0.85 had a larger optical gap ($E_0 = 1.3 - 1.4$ eV).

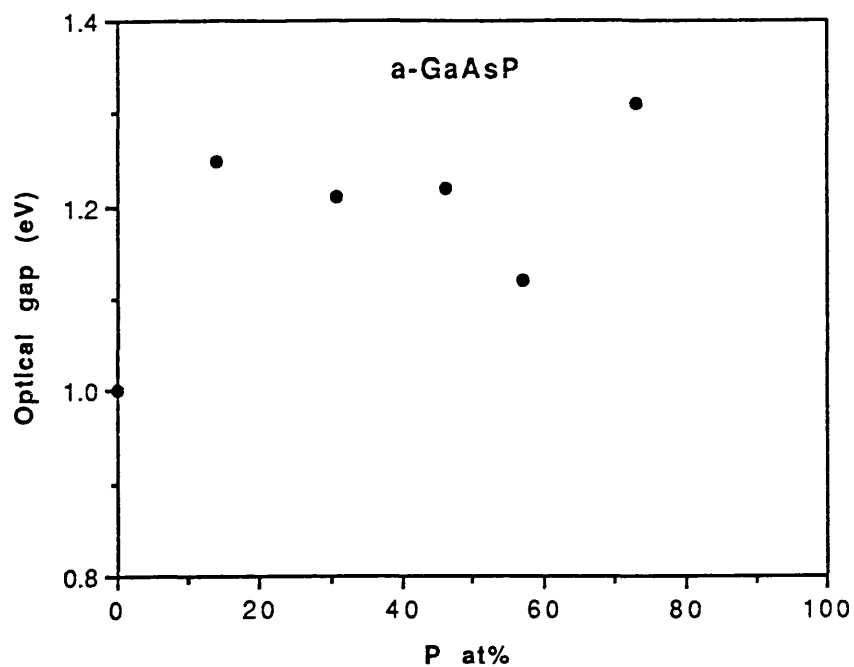


Fig. 4.30 Dependence of the optical gap E_o on P content of a-GaAsP.

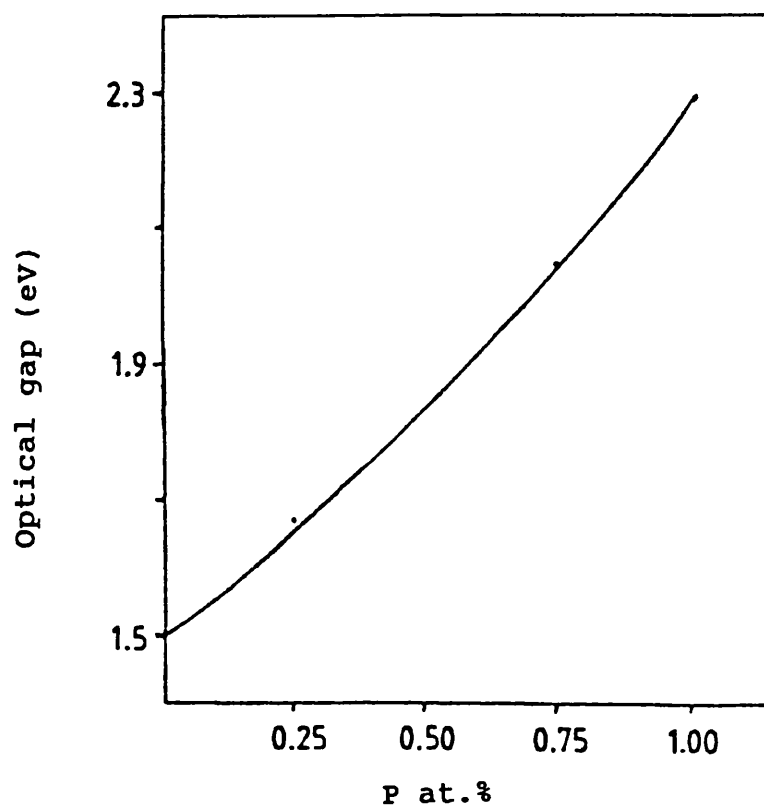


Fig. 4.31 The calculated variation of the band gap of the alloy $\text{GaAs}_{1-x}\text{P}_x$ with respect to x for x ranges from 0.0 to 1.0 (after 42).

4.5.2 ELECTRICAL PROPERTIES

The electrical dark d.c. conductivity measurements on a-GaAsP were carried out between ~ 200 and 500 K. The temperature dependence of the conductivity σ of a-GaAsP films for various P contents is shown in Fig. 4.32. It is known from the previous results that $\sigma_{r.t.}$ for our a-GaAs films is of the order of 10^{-4} - $10^{-3} \Omega^{-1} \text{cm}^{-1}$ (it is not shown in Fig. 4.32 but see, for example, Fig. 4.6). By adding P to the a-GaAs films, $\sigma_{r.t.}$ decreases to 10^{-7} - $10^{-6} \Omega^{-1} \text{cm}^{-1}$ and then decreases systematically with increasing P content.

The conductivity of these films exhibits an activated behaviour over a large range of temperature. The activation energy E_a was calculated from the σ curves above room temperature. Fig. 4.33 shows the variation of the activation energy versus P at.%. It can be observed that E_a varies from $\sim 0.5 - 0.53$ eV for a-GaAsP films (with P content varying from $\sim 15 - 73$ at.%) while the optical gap for the same films is between ~ 1.2 and 1.3 eV. Therefore the activation energy is appreciably smaller than $E_o/2$; this suggests that the Fermi level is shifted towards one of the bands. Similar behaviour (i.e. $E_a < E_o/2$) has been observed for a-GaP films [33]. It was reported that the a-GaP films contained an appreciable amount of wrong bonds [41]. These bonds are expected to introduce a variety of localized tail or gap states which may influence the electronic properties. Soft X-ray emission and absorption measurements performed on amorphous and crystalline GaP show the presence of a high density of additional states at the top of the valence band in a-GaP, while the bottom of the conduction band is practically unmodified [25]. This may explain the shift of the Fermi level towards one of the bands.

4.5.3 INFRARED SPECTROSCOPY

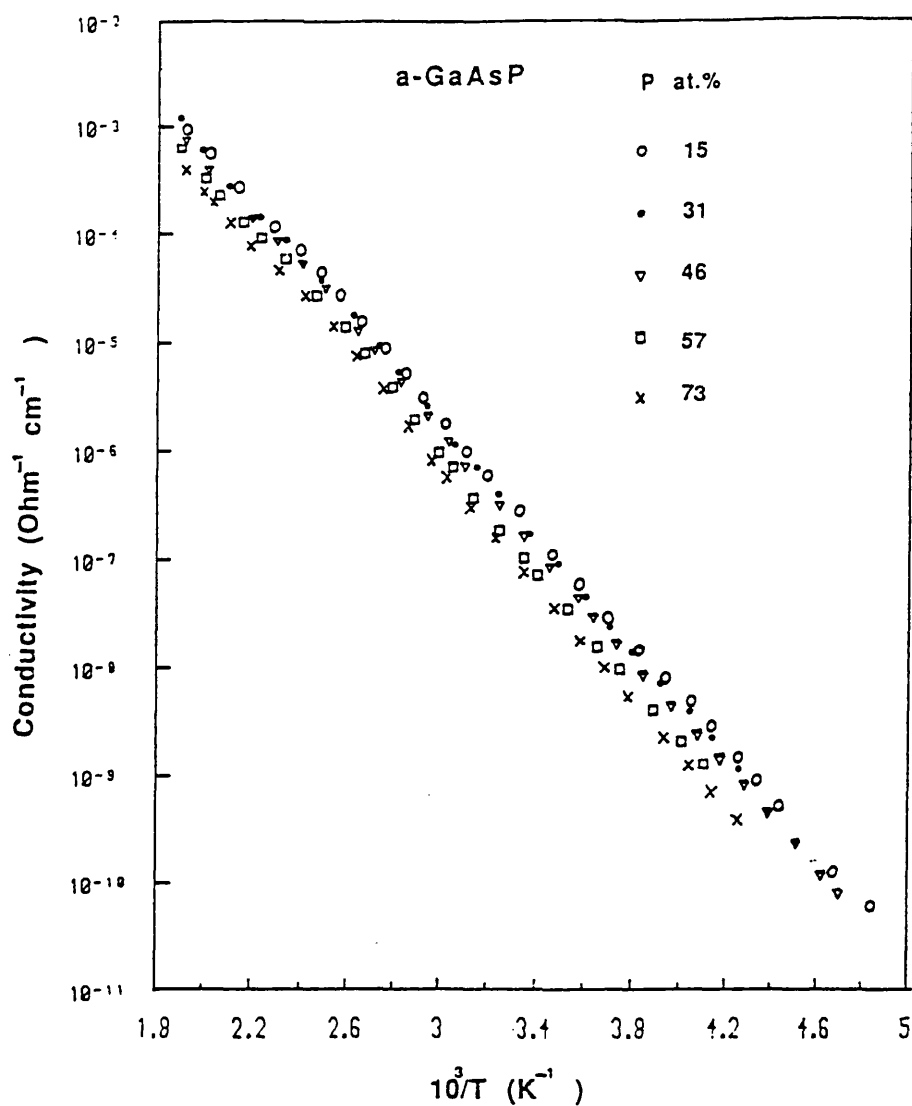


Fig. 4.32 Log σ versus $1/T$ for a-GaAsP with different P content.

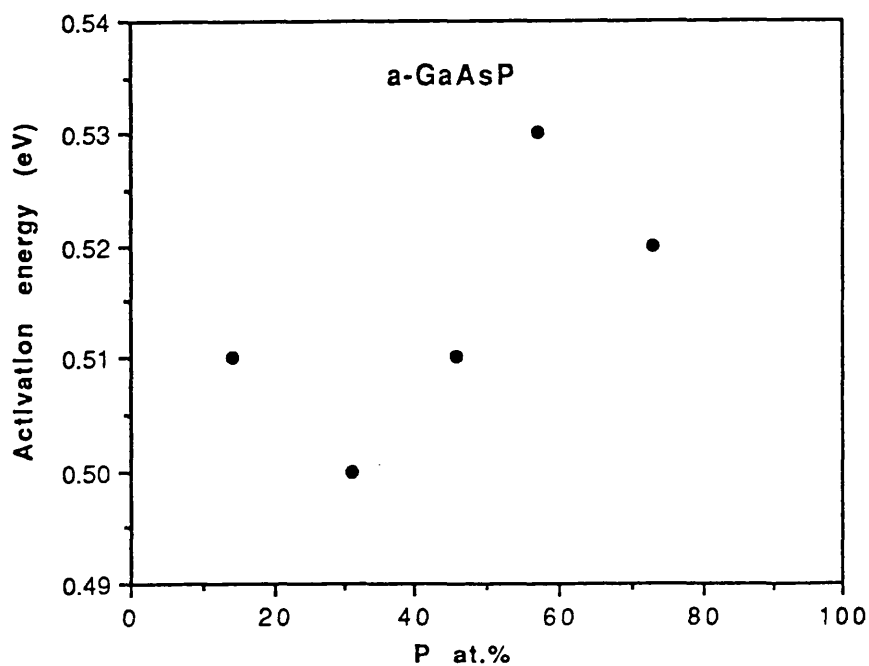


Fig. 4.33 Variation in activation energy as a function of P content in a-GaAsP.

The infrared transmission spectra of the a-GaAsP samples were measured from 4000 cm^{-1} to 200 cm^{-1} . The spectra did not show any structure at high wavenumbers. In Fig. 4.34 we have plotted the transmission of a-GaAsP films in the low-wavenumber region. It can be clearly seen that by adding P to a-GaAs, in addition to the a-GaAs TO mode at $\sim 250\text{ cm}^{-1}$, a mode appears at $\sim 340\text{ cm}^{-1}$, which is the reported TO mode for a-GaP [24]. However, the a-GaAs TO mode gradually loses its strength with increasing P content, while the a-GaP TO mode become more prominent. Similar behaviour has been observed in GaAlAs alloys (see section 4.4.4). Two-mode behaviour was also observed in crystalline $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and $\text{GaAs}_{1-x}\text{P}_x$ [43,44]. Our infrared results suggest that most of the P atoms bond with Ga forming a-GaP and that the amount of a-GaAs left in the network reduces quickly with very little a-GaAs left at high P content. However, it is not easy to decide from infrared results whether all the P in the films is bonded to the Ga atoms only or whether there is any P-P bonding. EXAFS results (to be reported in chapter 5) shows that at high P content in the film, there is an appreciable amount of P-P bonding. Infrared and EXAFS results are consistent with the optical and electrical results for these samples.

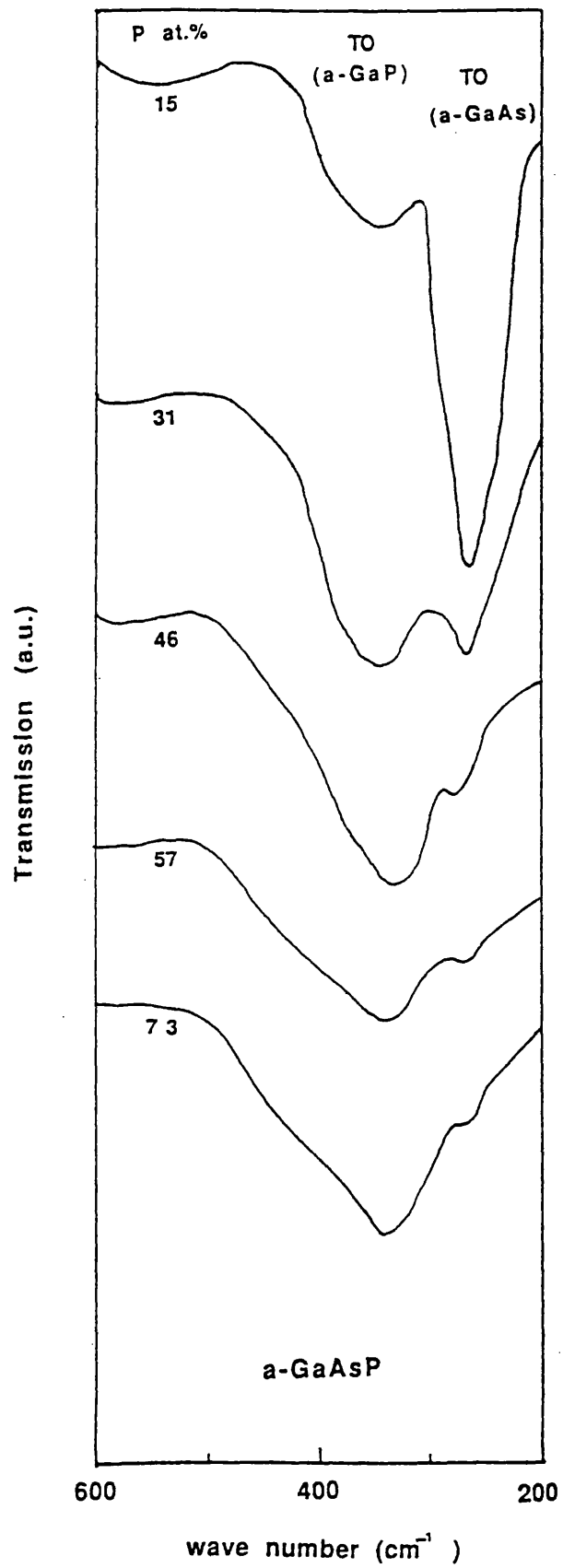


Fig.4.34 IR transmission for a series of films of a-GaAsP.

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CHAPTER 5

EXAFS STUDY OF α -GaAsP

5.1 INTRODUCTION

There are three processes that lead to attenuation of a high energy X-ray beam in a solid. These are photoelectric absorption, scattering and pair production. Each of these processes dominates in a given region of photon energies. The energy range for EXAFS is from 1-40 keV, at which energies photoelectric absorption makes the dominant contribution.

When an X-ray beam of intensity I_0 is incident on a thin film of thickness x , the transmitted beam of intensity I follows an exponential attenuation relation

$$I = I_0 \exp(-\mu x) \quad 5.1$$

where μ is the absorption coefficient.

In photoelectric absorption, the energy of the incident X-ray photon $\hbar\omega$ is transferred to core electron of an atom and is thereby elevated to a higher energy level. The energy of the outgoing photoelectron is given by

$$E_f = \hbar\omega - E_b \quad 5.2$$

where E_b is the binding energy of the electron.

An X-ray absorption edge occurs when an electron is excited from its bound core state, such as the K shell to the first unoccupied level in the conduction band if allowed according to selection rules. On the high-energy side of the absorption edge, the emitted electron is assumed to be unbound i.e. it has a continuous distribution of allowed energies. For

an isolated atom such as a monoatomic gas atom (e.g. argon), the emitted photoelectron can be represented as a spherical wave of a wavelength $\lambda=2\pi/k$, where k is the wavevector given by

$$k^2 \hbar^2 / 2m = \hbar\omega - E_0 \quad 5.3$$

where E_0 is the threshold energy of the absorption edge. In the case of an isolated atom, the absorption coefficient shows no fine structure and varies smoothly with incident photon energy above the absorption edge in the (see dashed line in Fig 5.1a). When other atoms surround the absorbing atom (as in a molecular gas or any condensed phase), the absorption coefficient shows fair structure in the form of oscillations extending to energies of some hundreds of electron volts above the edge. The EXAFS (Extended X-ray Absorption Fine Structure) region refers to oscillations from about 50 eV above the edge onwards. The first 50 eV or so above the absorption edge is known as the XANES (Absorption Near-Edge Structure).

The presence of these oscillations may be explained as follows: the outgoing emitted photoelectron wave scatters from the nearby atoms (surrounding the one being excited) producing ingoing waves (see Fig 5.1b). Interference effects occur between the outgoing photoelectron wave and the back-scattered waves producing constructive or destructive interference which gives rise to the observed oscillations. Constructive interference increases the absorption above, while destructive interference reduces it below, the isolated atom value, as shown in the solid line of Fig 5.1a. The absorption coefficient for a condensed sample can therefore be written as

$$\mu(k) = \mu_0(k) + \chi(k)\mu_0(k) \quad 5.4$$

where μ_0 is the smoothly varying background which corresponds

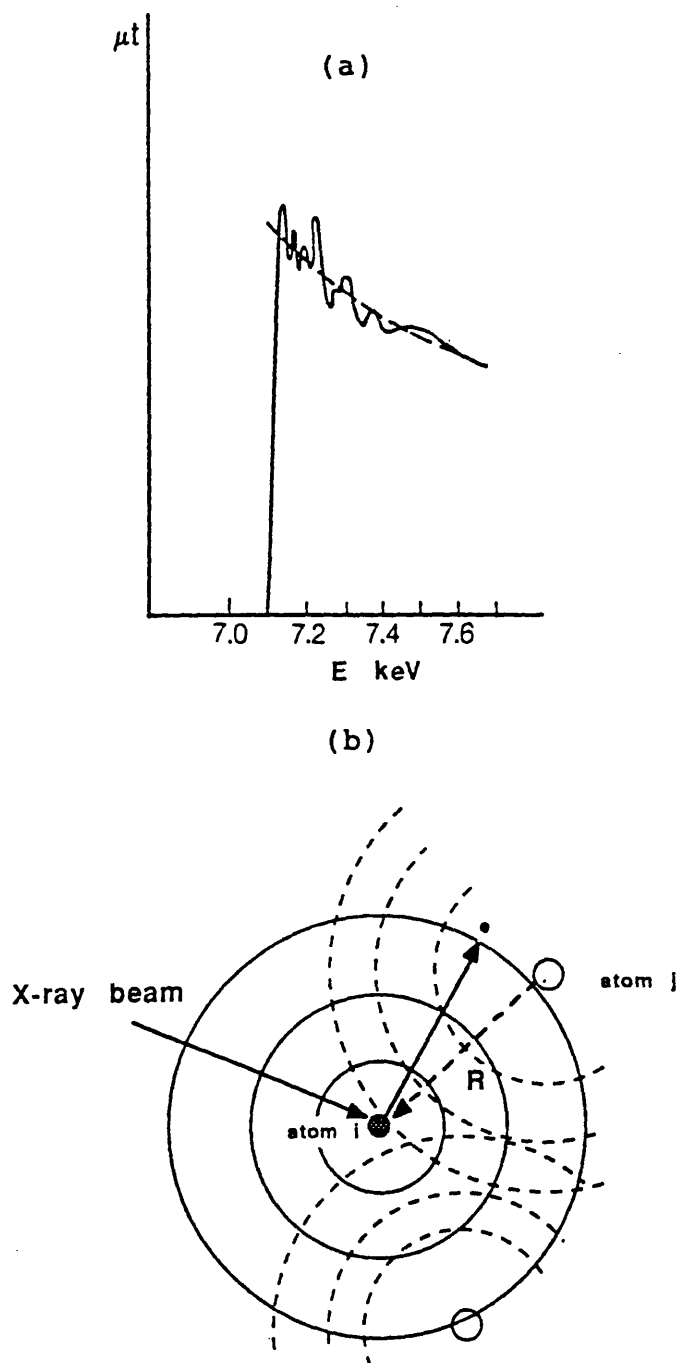


Fig. 5.1 (a) Shows a typical EXAFS spectrum. The dashed line is the smooth atomic absorption factor μ_0 . [after ref.3]. (b) Schematic diagram showing the outgoing photoelectron (solid lines) and the backscattered waves (dashed) interfere to give EXAFS

to the absorption coefficient of an isolated atom, k is the photoelectron wavevector (defined in equation 5.1) and $\chi(k)$ is the fine structure or EXAFS function, arising only from the interference between outgoing and ingoing electron waves. It is therefore given by

$$\chi(k) = [\mu(k) - \mu_0(k)] / \mu_0(k) \quad 5.5$$

It is this function which contains all the valuable structural information about the atomic environment immediately surrounding the absorbing atom, such as the number and identity of the nearby atoms, as well as their distances together with the spread in these values from the central atom. The EXAFS function can be expressed [1] in terms of these parameters by

$$\chi(k) = \sum_j N_j / k R_j^2 |f_j(k, \pi)| \sin(2kR_j + 2\delta + \psi_j) \exp(-2R_j/\lambda) \exp(-2\sigma_j^2 k^2) \quad 5.6$$

The summation is over the number of shells contributing to the EXAFS function and k is the photoelectron wavevector. R_j is the average distance of atom j from the excited atom and N_j is the number of atoms in the shell at average distance R_j . δ is the phase shift due to the passage of photoelectrons through the potential of the emitting atom and ψ_j is the phase of the back-scattered wave. $|f(\pi)|$ is the amplitude of the back-scattered wave which is energy dependent. λ is the elastic mean free path of the photoelectron and the second exponential containing σ_j^2 is a Debye-Waller factor term, where σ_j^2 is the mean square variation of the atom about R_j . In a crystal, σ_j^2 is due to thermal motion only, while in an amorphous system (which is the subject of this work) there will also be contributions to σ_j^2 from the static or structural disorder.

The above formula shows that from analysis of the

absorption spectrum for a given atom in a material, one can determine N_j , R_j and σ_j and also, through the characteristic energy dependence of $|f_j(\pi)|$, the type of atoms surrounding the central atom.

In the above formula, it is assumed that the outgoing waves are plane whereas in fact they are spherical. The Plane Wave Approximation (PWA) theory is accepted and valid for the high-energy region of the EXAFS spectrum. However, for lower energies the plane wave approximation may break down because it leads to errors in the calculated phase of $\chi(k)$ which in turn gives error in calculating R_j [2]. Since the low-energy part of the EXAFS spectrum contains most of the structural information, by using the PWA means either disregarding the low-energy data or obtaining suspect results if the whole spectrum is used. This is a problem especially when atoms are involved since they strongly scatter only low-energy electrons [3]

In order to obtain more accurate results from the lower energy part of the spectrum, exact EXAFS theory should be used. This theory was established by Lee and Pendry in 1975 [4] but is mathematically complicated and computationally slow. A simpler and quicker form of this theory was developed by S. Gurman et al in 1984 [2] and is called the Fast Curved Wave (FCW) theory. For single scattering both PWA and FCW theories agree down to low energies, with double scattering this is not the case and for triple scattering there is no agreement at all, which makes PWA inadequate to describe EXAFS data for multiscattering processes [3].

In equation 5.6, λ is the elastic mean free path of the photoelectron which implies that there is no contribution from inelastic scattering processes. The effect of these processes should be taken into account when exact EXAFS theory is used. Inelastic scattering processes are responsible for damping the EXAFS signal since they contribute the absorption

coefficient, and are usually divided [3] into (i) extrinsic inelastic scattering which include the interaction between photoelectron and other electrons and (ii) intrinsic inelastic scattering which involves the excitation and relaxation of other electrons in the central or absorbing atom. These processes may be explained as follows. When an electron from a low-lying core level is excited to a propagating state, a sudden change in the potential of the central atom occurs; a core hole is created and of course the atom is unstable. An electron from a higher state will fill the hole. This process may lead to the excitation of another electron to a higher energy state (shake-up), or the central atom may lose some of the weakly bound electrons (shake-off). The created core hole has a finite lifetime and this is found to be longer than the time taken by the photoelectron to travel from the central atom and scatter back. Therefore there is a possibility that the photoelectron faces a different potential on returning to the central or absorbing atom, which would tend to prevent interference effects and weaken the EXAFS signal [3]. In practice the shake-up and shake-off processes are included in the theories by multiplying $\chi(k)$ by an amplitude factor $A(k)$ treated as an empirical fitting parameter.

5.2 EXAFS MEASUREMENTS AND DATA ANALYSIS

EXAFS measurements have been used to determine the local atomic structure of $a\text{-Ga}_x\text{As}_y\text{P}_z$ films with P-contents varying between 0 and 73 at.%. The X-ray absorption measurements were carried out at the Synchrotron Radiation Source (SRS) at the SERC Daresbury Laboratory, U.K. Two stations, 3.4 and 7.1, were used for the present work 3.4 for the P K-edge and 7.1 for Ga and As K-edges. The experiments were performed at room temperature.

Films of about 0.2 μm thick and 1 cm x 2 cm in area and

deposited on copper substrates were used at station 3.4. The synchrotron radiation was monochromatized by a InSb double crystal. The samples in this station were placed in an evacuated chamber. The absorption was measured using the electron drain current method, in which the current due to the electron ejection caused by X-ray photoabsorption was measured.

Films for station 7.1 (Ga and As edges) were deposited on mylar substrates and stacked to obtain total thicknesses of about 10-20 μm . The X-ray beam was monochromated using a Si (111) double-crystal. Measurements on this station were performed in transmission mode, in which the absorption was obtained directly by monitoring the incident I_0 and transmitted I_t X-ray intensities simultaneously using two ionization chambers. The absorption could then be calculated using equation 5.1. further details for both 3.4 and 7.1 may be found elsewhere [5,6].

EXAFS data from P K-edge, Ga K-edge and As K-edge were energy calibrated using the computer programs PLOTEK (for data recorded on station 3.4) or EXCALIB (for data recorded on station 7.1). Both these and other programs referred to in this section are readily available at Daresbury Laboratory. The measured absorption contained background absorption μ_0 . The first step in the data analysis was to remove the contribution of μ_0 from the measured data using the techniques of pre- and post-edge background subtraction using the EXBACK programme to obtain a pure EXAFS function $\chi(k)$. The data were converted into k-space by means of equation 5.2. In order to compensate for amplitude reduction at high k-values, $\chi(k)$ were multiplied by some power of k to give $k^n\chi(k)$ (n is normally 1-3). The weighted spectra were then analysed using the EXCURV 88 programme, based on the fast curved wave theory [2,3], using least-square curve fitting analysis.

The EXCURV 88 analysis allows one to determine the

structural parameters N_j , R_j and σ_j^2 . The programme evaluates these using the above weighted experimental spectra, comparing them to similarly k -weighted theoretical spectra, and refining the difference between them iteratively until the least-squares fit index is minimised. It was recognised that it was important to choose sensible initial values of N_j , R_j , $A_j=2\sigma_j^2$, etc.. at the start of the iteration. The required phase shifts were taken from the EXAFS data bank. At each stage, the data can be Fourier transformed into real space. In order to eliminate the low k -range ($k < 3 \text{ \AA}^{-1}$) and minimise the effect of noise at large k , a region of interest can be selected using a suitable window. It can then be back transformed into k -space where the parameters readjusted, the process repeated until satisfactory results are achieved.

5.3 RESULTS AND DISCUSSION

EXAFS measurements were performed using the 2 GeV Synchrotron Radiation Source with a beam current of $\sim 200 \text{ mA}$. As mentioned previously the K edges of P, Ga and As in a-GaAsP were investigated. Fig. 5.2a shows the P K edges for $0.15 \leq z \leq 0.73$. The figure reveals two features; first the development in the EXAFS function and secondly the increase in the height of the absorption edge with increasing P-content. Typical K edges of Ga and As are shown in Figs. 5.2b,c. The ability to determine from EXAFS the environment around each type of atom separately makes it particularly attractive for compound studies. This occurs because the X-ray absorption edges of many atoms are far enough separated in energy that their EXAFS spectra do not overlap. This can be seen quite clearly in Fig. 5.2.

Pre-edge and post-edge absorption was removed from the spectra for each absorption edge, which allowed the oscillatory EXAFS contribution $\chi(E)$ to be isolated. Fig.

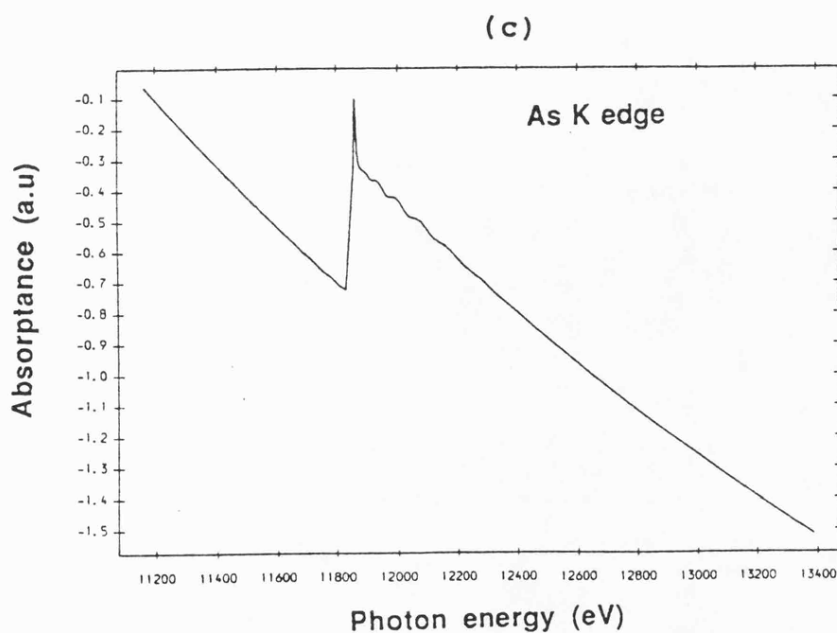
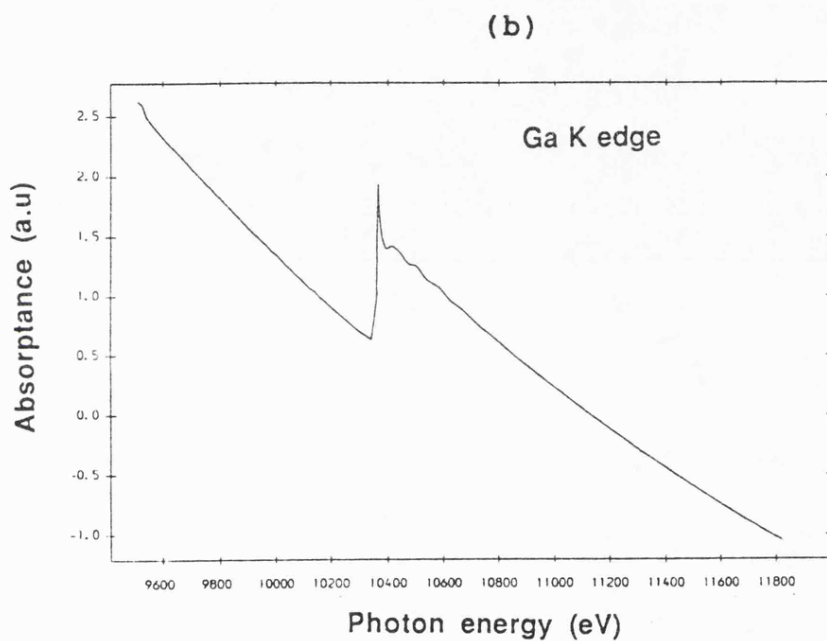
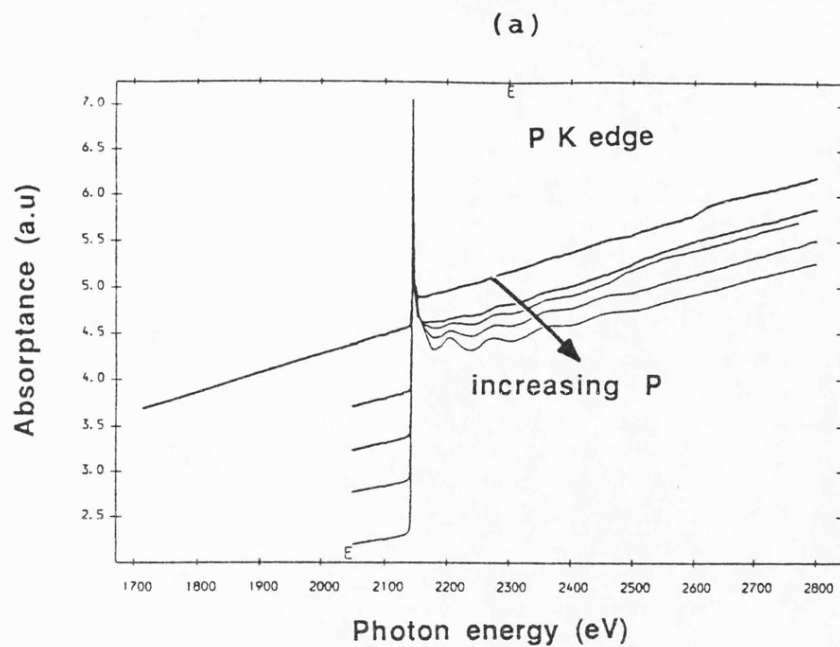


Fig. 5.2 (a) Typical P K edges for a series of a-GaAsP films, (b) Ga K edge, (c) As K edge.

5.3a,b show examples of the $k^3 \chi(k)$ data for Ga and As K edges respectively and Fig. 5.3c shows $k^2 \chi(k)$ as a function of k for a P K edge. Fig. 5.3e,d,f show the corresponding Fourier transforms (FT). Only one peak can be detected in the FT curves, which corresponds to the first-nearest-neighbour shell.

Least squares curve fitting was used to analyse the EXAFS spectra, as mentioned earlier. For a-GaAsP, it is assumed that there are two types of atom around each central atom (absorbing atom). Since Ga and As atoms are very close in atomic number, they therefore have very similar phase shifts and will be practically indistinguishable. Due to this similarity, Ga and As are considered as identical scatterers. For example, if Ga is the central atom the surrounding atoms are expected to be X and P, where X denotes a Ga or As atom. Similarly, for As central atoms there are surrounding X and P atoms. The same is true for P central atoms.

The values for the interatomic distances, obtained using the data analysis procedure described in section 5.2 from Ga K edge data ($R_{\text{Ga-X}}$ and $R_{\text{Ga-P}}$), As K edge data ($R_{\text{As-X}}$ and $R_{\text{As-P}}$) and P K edge data ($R_{\text{P-P}}$ and $R_{\text{P-X}}$), are shown in Figs. 5.4a,b,c respectively as a function of P at.%. The accuracy for R values is $\pm 0.02 \text{ \AA}$. It can be seen that both $R_{\text{Ga-X}}$ and $R_{\text{As-X}}$, obtained from Ga K edge data and As K edge data respectively, are equal to $\sim 2.42\text{--}2.43 \text{ \AA}$. These are therefore consistent with one another, if it is assumed that Ga-As bonds outnumber As-As and Ga-Ga wrong bonds. It should be noted that the above deduced values for the Ga-As bond length are close to the value found in c-GaAs

of $2.45 \text{ \AA}$. $R_{\text{As-X}}$ is practically independent of the P concentration, while $R_{\text{Ga-X}}$ exhibits a tendency to increase at high P concentration. This could be interpreted as indicative of the presence of Ga-Ga wrong bonds (the covalent radius of Ga is $1.26 \text{ \AA}$ according to the definition of Pauling [9], and $R_{\text{Ga-Ga}} = 2.48 \text{ \AA}$ in Ga_2 molecules [10]) if one were to look only

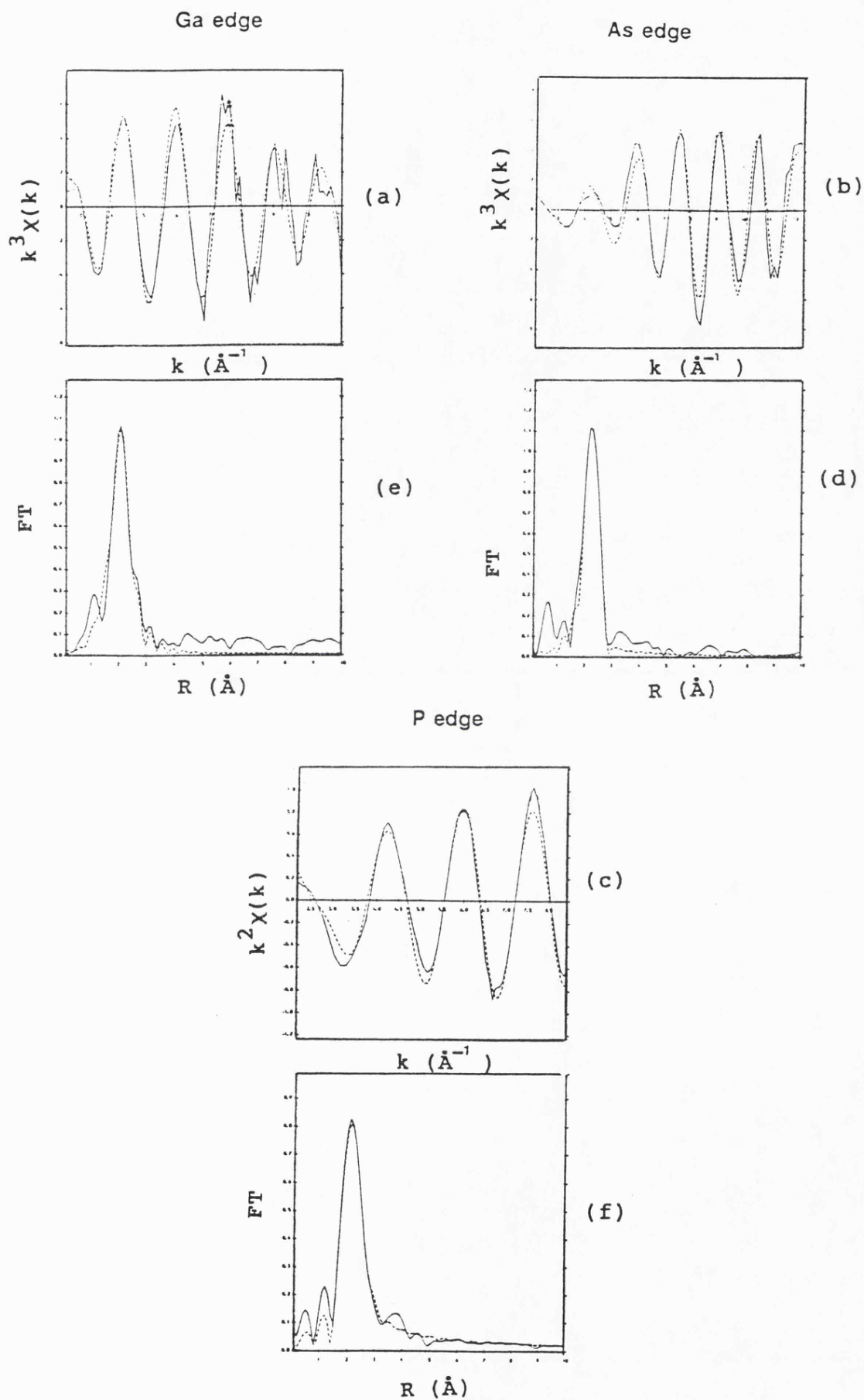


Fig. 5.3 Typical EXAFS spectrum for a-GaAsP obtained from (a) Ga K edge, (b) As K edge and (c) from P K edge. (e), (d), (f) Corresponding Fourier transform. Solid lines - experiment, dotted lines - theory.

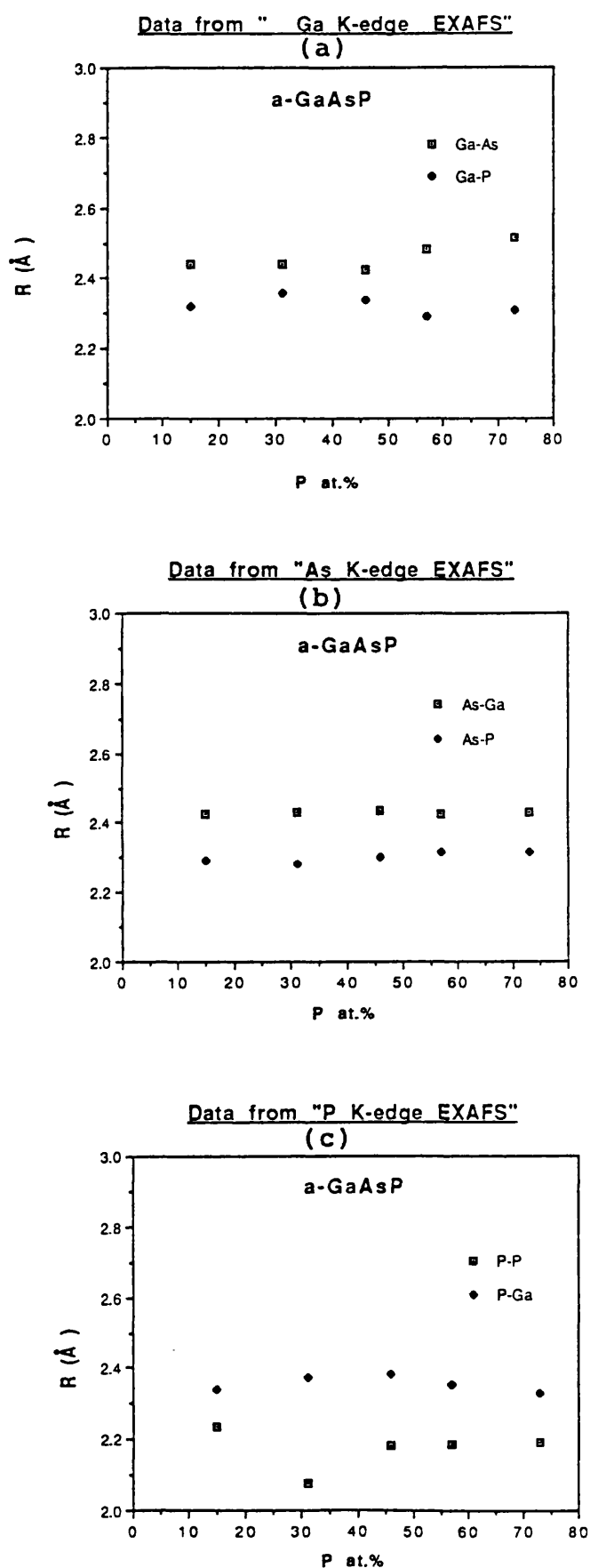


Fig. 5.4 The average interatomic distances for the first shell as a function of P concentration for a-GaAsP obtained from (a) Ga K edge (b) As K edge and (c) P K edge.

at this parameter and ignore others such as coordination number and Debye-Waller factor A. If we first assume that this increase is due to Ga-Ga wrong bonds, then we should expect the coordination number $N_{\text{Ga-X}}$ (deduced from Ga K edge data) to have some value at high P content. Fig. 5.5a shows that $N_{\text{Ga-X}}$ nearly vanishes; in addition, if there were any appreciable amount of Ga-Ga wrong bonds in these samples, there should be an associated static disorder and the Debye-Waller factor A would therefore not go to zero, as in Fig. 5.7 ($A_{\text{Ga-X}}$). From these results therefore, we suggest that if Ga-Ga wrong bonds nevertheless exist in our a-GaAsP samples at high P content, they should do so in very small quantities.

The average interatomic distances $R_{\text{Ga-P}} = 2.33 \text{ \AA}$ and $R_{\text{P-X}} = 2.35 \text{ \AA}$, obtained from Ga K edge data and P K edge data respectively and shown in Figs. 5.4a,c as a function of P at.%, are also consistent with one another, assuming that P-Ga bonds outnumber P-As bonds. These values are reasonably close to the Ga-P bond length in c-GaP ($2.36 \text{ \AA}$). Figs. 5.4b,c show that $R_{\text{As-P}} = 2.30 \text{ \AA}$ and $R_{\text{P-P}} = 2.20 \text{ \AA}$ respectively.

Figs. 5.5a,b show the average coordination numbers as a function of the P at.%; $N_{\text{Ga-X}}$, $N_{\text{Ga-P}}$ were obtained from EXAFS analysis of Ga K edge data, and $N_{\text{As-X}}$, $N_{\text{As-P}}$ from As K edge data. As the Phosphorus content increases in the a-GaAsP samples, $N_{\text{Ga-X}}$ reduces rapidly (figure 5.5a) while $N_{\text{Ga-P}}$ (figure 5.5b) increases quickly. These results confirm that most of the Ga atoms bond with P atoms, leaving the a-GaAsP network with very little Ga-As bonding at high P content. In other words the Ga bonding environment appears to be partially ordered, with Ga-P bonding maximized. From Fig. 5.5c we see that at high P-content $N_{\text{As-X}}$ is greater than $N_{\text{Ga-X}}$. Since X denotes either Ga or As (indistinguishable from one another as mentioned earlier), it is possible that, at high P-content we are detecting As-As bonds rather than As-Ga bonds. This suggestion seems reasonable since we know (from Fig. 5.5b)

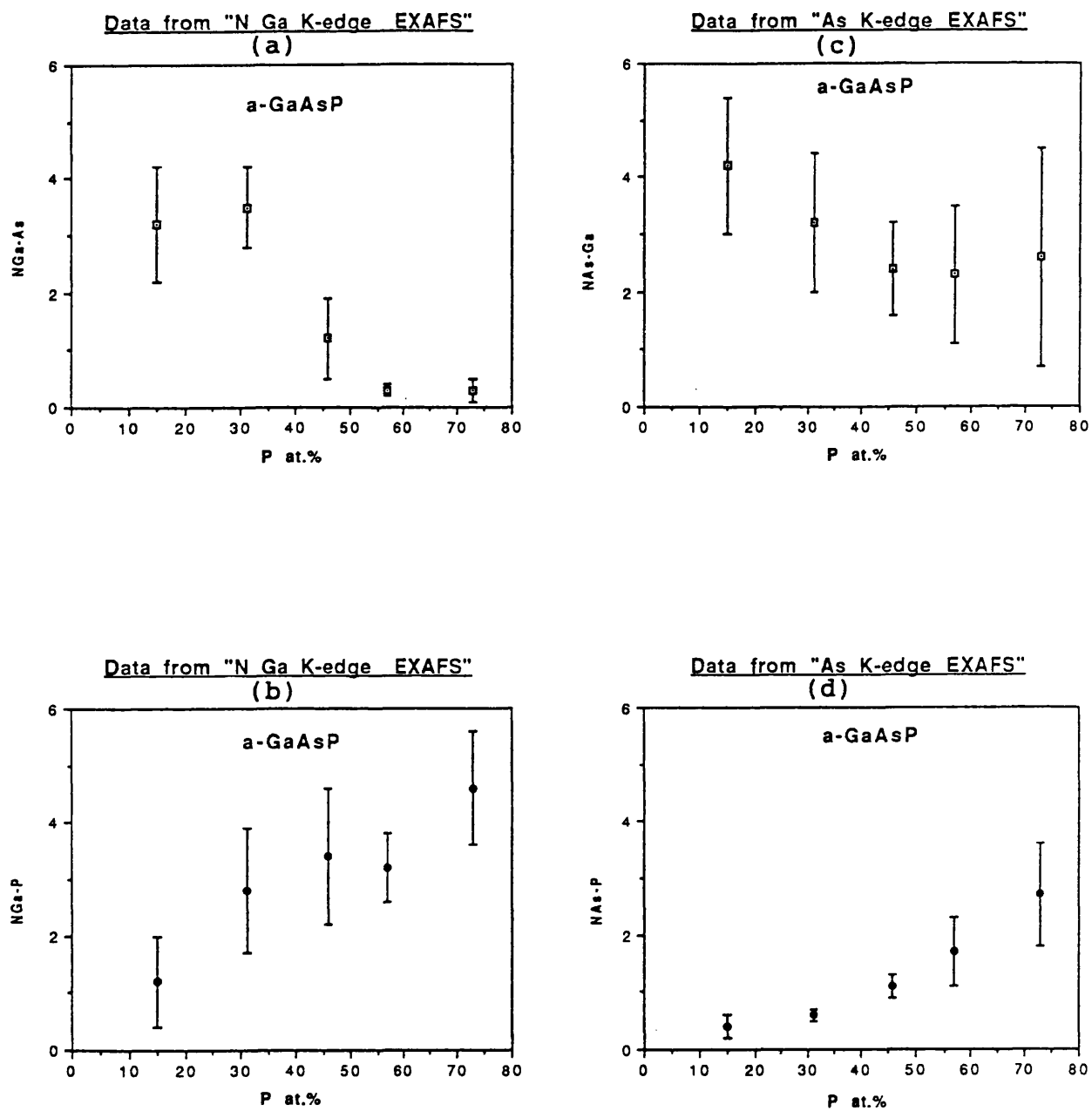
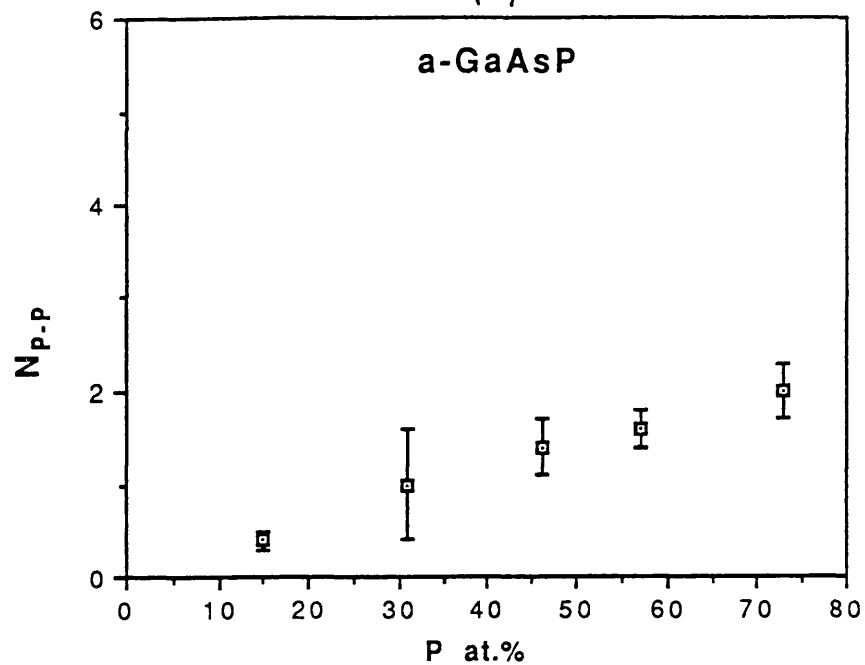


Fig. 5.5 Average first shell coordination as a function of P concentration for a-GaAsP (a) and (b) from Ga K edge, (c) and (d) from As edge.

Data from "P K-edge EXAFS"

(a)



(b)

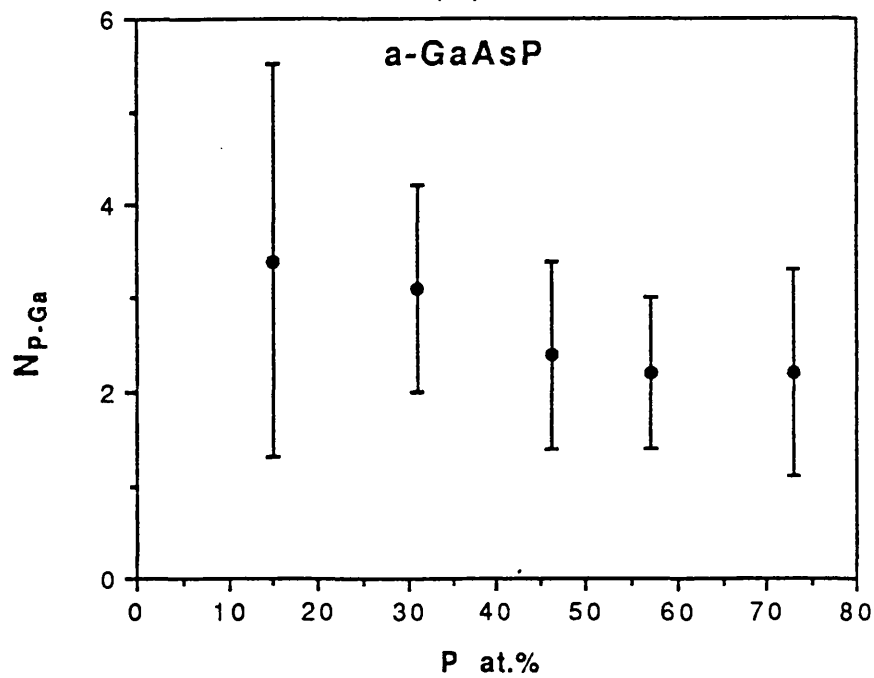


Fig. 5.6 Average first shell coordination as a function of P concentration for a-GaAsP obtained from P K edge.

that at high P-content virtually all the Ga atoms are bonded to P atoms, leaving the As atoms to bond to P atoms (which from Fig. 5.5d we know to be true) and possibly to themselves. These results are in a quite good agreement with those obtained from infrared spectroscopy given in chapter 4, Fig. 4.34. The EXAFS results also reveal that the total coordination number for both Ga and As is four. Figs. 5.6a,b show that the total coordination number for P is also four. It can be seen (Fig. 5.6a) that N_{P-P} increases slowly but doesn't reach $N=3$, at least over the composition range studied.

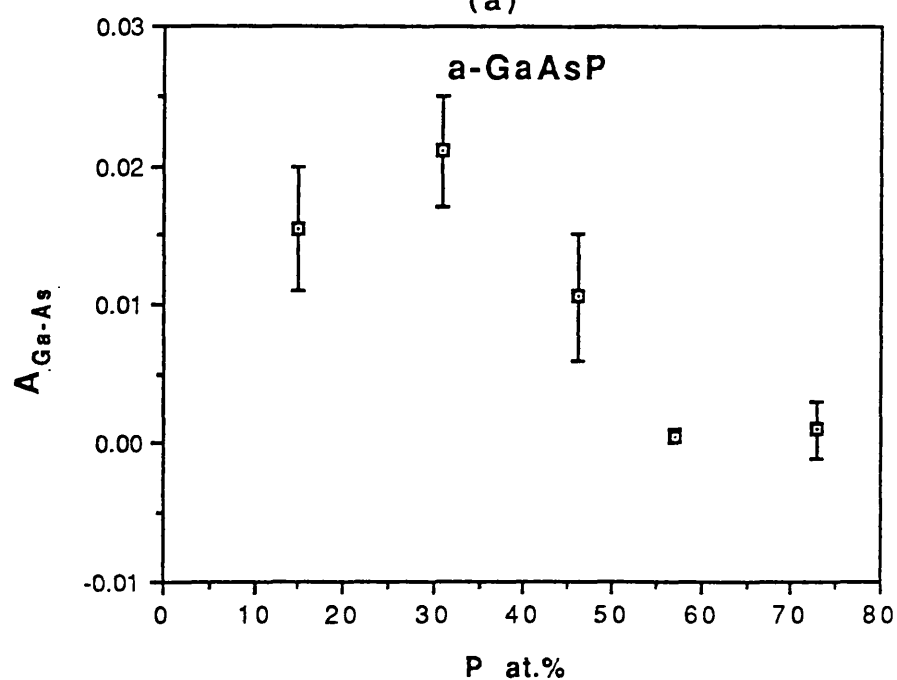
It was found that the measured mean square variation in bond lengths σ_j^2 , which contain contributions from both thermal and static disorder, were fairly small ($\sigma_j \leq 0.1 \text{ \AA}$). Fig. 5.7a,b shows A_{Ga-X} and A_{As-X} obtained from Ga and As K edge data respectively. A_{Ga-X} reduces rapidly with P content, while A_{As-X} is larger at high P-content. This observed difference at high P-content, as for the corresponding partial coordinations, may suggest the presence of As-As bonds.

The above structural information is well correlated with optical results obtained for the same samples (see chapter 4, Fig. 4.30). It can be seen that the optical gap increases rapidly from 1.0 eV at 0 at.% P to ~ 1.25 eV when the P content of the film increases, and to about 1.3 eV at 73 at.% P. The optical gap of a-GaP ranges from 1.2 to 1.4 eV. These results are consistent with the EXAFS suggestion that Ga-P bonding rapidly replaces Ga-As bonding in the amorphous network; even at 73 at.% P, both EXAFS and optical data suggest an appreciable amount of Ga-P bonding, in addition to some P-P bonds in the network (the optical gap of P = 1.75 eV [11]). It can be seen from Fig. 4.30 that there is an increasing trend in the optical gap at P=73 at%.

In conclusion, for the a-GaAsP films studied in the present work, Ga-P bonding increases rapidly at the expense of Ga-As bonding as the P-content is increased. No appreciable

Data from "N Ga K-edge EXAFS"

(a)



Data from "As K-edge EXAFS"

(b)

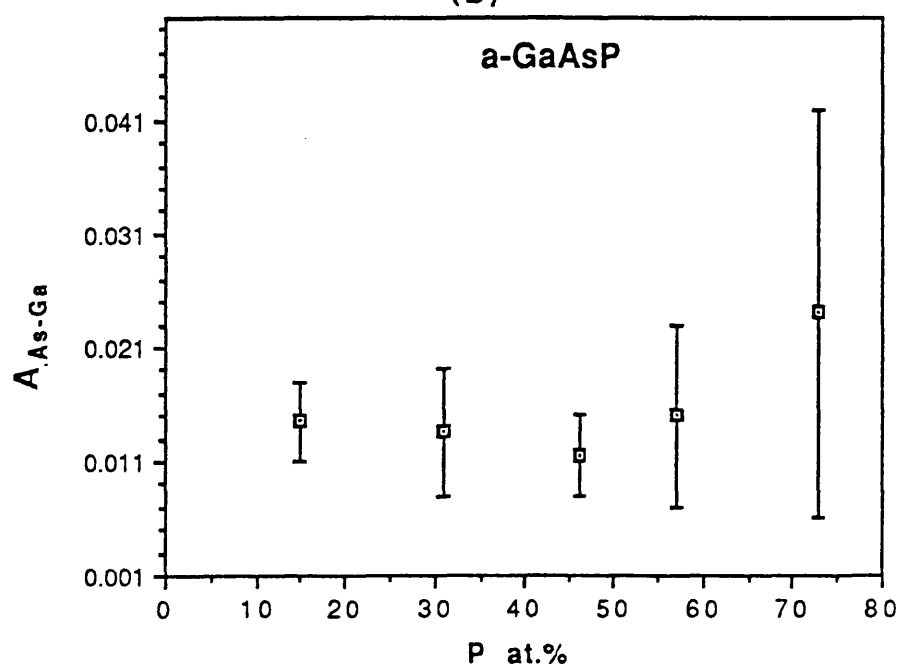


Fig. 5.7 Debye-Waller factor A as a function of P at.% for a-GaAsP (a) $A_{\text{Ga-As}}$ obtained from Ga K edge, (b) $A_{\text{As-Ga}}$ from As K edge.

amount of Ga-Ga bonding was detected, while P-P and P-As bonds were detected at high P content; there is a possibility of As-As bonds at high P-content.

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CHAPTER SIX

SUMMARY AND CONCLUSIONS

We have tried in this work to establish a correlation between the deposition conditions, film composition, electrical, optical and structural properties of a-GaAs and related compounds prepared by r.f. sputtering.

The films of a-GaAs(:H) prepared with different hydrogen contents, at different substrate temperatures and with different As concentrations, were deposited by sputtering from a crystalline GaAs target in argon or in a mixture of hydrogen and argon. Thin films of a-GaAlAs and a-GaAsP were similarly prepared but from a crystalline GaAs target on which pieces of Al or P had been laid.

For the a-GaAs films, the refractive index was found to decrease with increasing hydrogen content. This was attributed to a lowering of the density and to an increase of the average Penn gap E_g . The absorption coefficient at a given photon energy decreased with increasing hydrogen and the absorption edge shifted towards higher energy. This was attributed partly to elimination of defect states from the gap by hydrogen. Infrared measurements revealed the presence of Ga-H-Ga bonds in the hydrogenated samples and it was suggested that these bridges could also lead to an increase of the energy gap. Conductivity measurements on a-GaAs(:H) films above room temperature showed an activated behaviour characteristics of band-like conduction in extended states with an activation energy approximately equal to half the optical gap. Annealed a-GaAs:H films showed an increase of conductivity and decrease of activation energy which was attributed to hydrogen evolution. I.R. measurements supported this suggestion and showed that the hydrogen evolved from a-GaAs:H above about 150°C. The deposition rate of a-GaAs films was found to decrease rapidly when the ratio $H_2/(H_2+Ar)$ in the sputtering

gas mixture changed from 0% to 20%.

Hydrogenated and unhydrogenated a-GaAs were prepared at different substrate temperatures T_s between room temperature and 130 °C. TEM measurements showed that the films were amorphous throughout the temperature range of investigation. The optical gap E_o of unhydrogenated films increases slightly with increasing T_s , while for hydrogenated films it remained roughly constant up to about 90 °C then increased quite rapidly. This increase in E_o was attributed to a better ordered amorphous films. It was found that there was a marked increase in conductivity and decrease of activation energy for the a-GaAs films prepared at $T_s = 59, 81, \text{ and } 102$ °C. This was attributed to the fact that these films possess a large density of defects; however, no definite conclusion can be drawn and further investigations are needed to clarify these suggestions.

In the case of a-GaAs films prepared with different As concentrations, E_o was found to remain roughly constant for compositions that were nearly-stoichiometric up to 67 at.% As. For higher As content, E_o decreased slightly from ~ 1.0 eV to ~ 0.9 eV. On the other hand the electrical conductivity decreased by many orders of magnitude when the composition was changed over the same range. The activation energy obtained from $\log \sigma$ versus $1/T$ plots above room temperature were found to be equal to approximately $E_o/2$ for all films which suggests that the Fermi level is located near the mid gap. From i.r. measurements it is difficult to conclude whether excess As is incorporated randomly in the a-GaAs network or whether it is segregated. EXAFS measurements are underway to determine this.

Amorphous GaAlAs(:H) films were prepared for the first time using r.f. sputtering. TEM measurements showed that the films were amorphous up to ~ 30% Al. For concentrations of Al higher than 30 at.%, the films were polycrystalline. An

interesting results was that the optical gap decreases with increasing Al content in contrast to c-GaAlAs for which the gap increases. This behaviour was attributed to the presence of wrong bonds. Two broad absorption bands entered at $\sim 670 \text{ cm}^{-1}$ and 1650 cm^{-1} and were identified and assigned to Al-H-Al wagging and stretching modes respectively.

For a-GaAsP films studied in the present work, the optical gap increased from 1.0 eV to about 1.3 eV as the P content was increased up to 73 at.% P. Infrared and EXAFS measurements are consistent and show that the Ga-P bonding increases rapidly at the expense of Ga-As bonding. No appreciable numbers of Ga-Ga bonds were detected. P-P and P-As wrong bonds were detected at high P content and there is also the possibility of the existence of As-As wrong bonds.

In summary, a fairly comprehensive set of measurements on amorphous GaAs, GaAlAs and GaAsP have been made with a view to characterizing new III-V binary and ternary compounds semiconductors. The results show some similarity in behaviour of the materials to a-Si:H but in many other ways they are very different. The roles of hydrogen content and substrate temperature on the properties of the films show distinctive behaviours, relating in part to the different defects and hence gap state distributions. The alloy work has revealed (in particular by the increase in energy gap of GaAs on alloying with Al) the importance of chemical disorder (wrong bonds) in these alloys. Infrared and EXAFS studies have helped in determining the local atomic structure.

Similar studies to the above on other III-V material (e.g. GaP and InP) would clearly be of interest and it is hoped that this work has paved the way for further exploration at Leicester and elsewhere.