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Ellipsometry and optical measurements on amorphous thin films of As_2Se_3

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Thin films of amorphous $AsSe_{3/2}$ have been prepared by thermal evaporation of the material under a vacuum of 1.33×10^{-3} Pa. Reflectivity, transmission and ellipsometric measurements of the films have been carried out. The optical energy gap and the absorption coefficient as a function of wavelength were obtained. Two absorption bands were observed and interpreted in terms of defects in the $AsSe_{3/2}$ system (homopolar bonds). Analysis of reflection and transmission spectra shows that the electron density at band tails of both conduction and valency bands follows $N(E) \propto E^{1/2}$ (Tauc plots). No considerable variations were observed on changing the film thickness.

1. Introduction

Arsenic selenide (As_2Se_3) in the amorphous state has properties which are very sensitive to the conditions of preparation such as temperature, pressure and illumination as well as to chemical alloying. Theoretically, the only possible chemical bond in such a compound is the heteropolar bond As–Se, which should be considered ideal for the application of random network theory [1]. However, Boolchand *et al.* [2], using Mössbauer spectroscopy, have proved the presence of some kind of equilibrium between the expected heteropolar bond As–Se and some structural defects due to the presence of homopolar bonds of the type As–As and Se–Se. Such an equilibrium can be affected by the conditions of preparation. Using the Mössbauer technique, Wells and Boolchand [3] were able to study the effect of anion alloying in the system $AsSe_{3/2-x}Te_x$. However, using Raman scattering and extended X-ray absorption fine structure (EXAFS), Nemanich *et al.* [4] were able to prove the existence of homopolar bonds in prepared As_2S_3, $GeSe_3$ and As_2Se_3 films. Moreover, annealing reduces the concentration of such bonds and the properties approach those of the bulk. Optical parameters such as complex dielectric function, absorption coefficient and optical energy gap are sensitive to the presence of such structural defects in bonding.

The effect of homopolar bonds on the width of the optical gap is not clear. The presence of such bonds reduces the band gap in Ge–Se, whereas in As–S, the width of the gap shows a tendency to increase by homopolar bond formation. In contrast, such bonds have little effect on the band gap in the case of the As–Se system [5].

In the present work we have used different optical techniques, namely ellipsometry, reflection and transmission as a function of the incident wavelength, to study the possible electronic transition mechanisms in thin amorphous films of different thicknesses as well as in the bulk amorphous $AsSe_{3/2}$.

2. Experimental procedure

Amorphous $AsSe_{3/2}$ was synthesized by fusing spectroscopically pure elements in evacuated quartz tubes under a vacuum of 1.33×10^{-2} Pa at 950 °C. The details of preparation are given elsewhere [6–8]. Thin films of $AsSe_{3/2}$ were then prepared by thermal evaporation under a vacuum of 1.33×10^{-3} Pa, on glass substrates kept at room temperature during evaporation.

Reflection and transmission spectra were measured using a spectrophotometer Model PMQ11 (Carl Ziess). Transmission measurements covered the range 185–2600 nm, while reflection covered the range 325–2500 nm. Experimental details of ellipsometry are discussed in a previous publication [9].

3. Results

The prepared $AsSe_{3/2}$ thin films were checked by X-ray diffraction study. The pattern obtained showed no characteristic peaks, confirming the amorphous nature of the films.

The measured reflection and transmission spectra, $R(\lambda)$ and $T(\lambda)$, are given in Fig. 1a and b, respectively. The transmission spectrum shows a clear absorption edge at about 300 nm ($\sim$4.1 eV). The edge is not sharp

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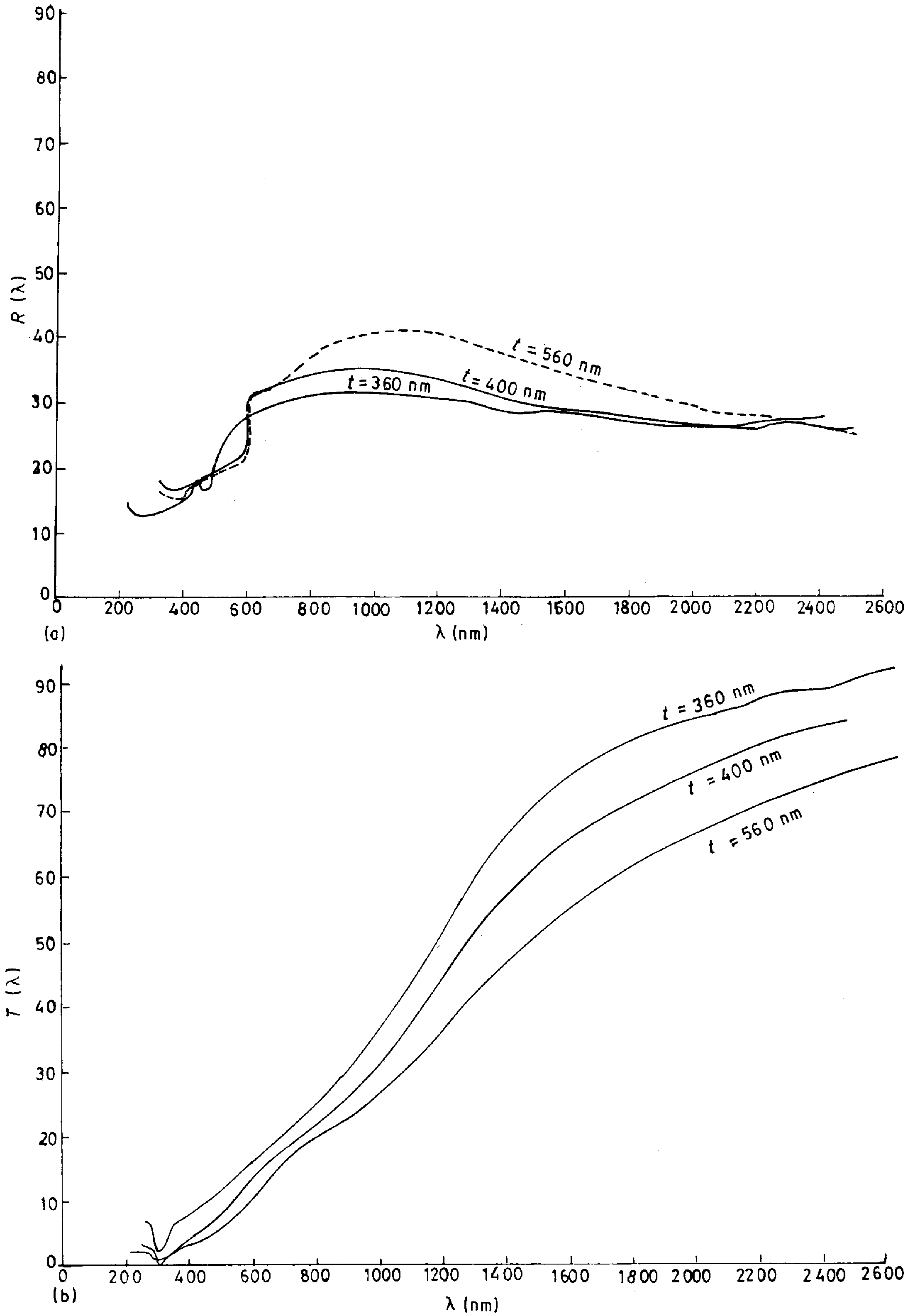

Figure 1 (a) Reflection spectra, $R(\lambda)$, and (b) transmission spectra, $T(\lambda)$.

but extends over a wide range of wavelengths, a behaviour which is familiar for amorphous structures according to the Urbach theory [10]. Reflection exhibits an edge at about 600 nm for all prepared films (about 1.9 eV). In the range from 800 to 2200 nm, both reflection and transmission exhibit very weak interference effects.

Near the absorption edge the reflection, R, and transmission, T, are connected as a first approximation by

$$T = (1 - R)e^{-\alpha t}$$

where α is the absorption coefficient and t the film thickness; then $\alpha = \omega(R, T)/t$ where $\omega(R, T) = \ln[(1 - R)/T]$. Demichelies *et al.* [11] suggested a simple method for estimation of the optical gap, E_g, using reflection and transmission measurements. They made use of the relation between α and E:

$$\alpha^{\tau} E^{\sigma} = A(E - E_g) \qquad (1)$$

where E is the photon energy. Equation 1 then takes the form

$$[\omega(R, T)]^{\tau} E^{\sigma} = A(E - E_g) \qquad (2)$$

where the values of τ and σ depend on the transition mechanism (direct or indirect), and the film structure (polycrystalline or amorphous) [12, 13]. When the transition probability matrix element is independent of the energy, it can be shown that τ for indirect transition is given by

$$\tau = \frac{1}{\chi + \nu + 1} \qquad (3)$$

where χ and ν are the exponents of the energy dependence of conduction and the valency electron density of states, respectively, near the gap.

Fig. 2 illustrates the linear dependence of $[\omega(R, T)]^{1/2} E$ on E, i.e. $\tau = 1/2$ and $\sigma = 1$. This means that the results obtained follow Tauc plots [14]. The values of the estimated optical gap for the investigated samples are listed in Table I.

Ellipsometric measurements were carried out for both bulk amorphous $AsSe_{3/2}$ and films. The values obtained for the optical constants n and K were used to determine the absorption coefficient $\alpha = 4\pi K/\lambda$. Fig. 3 represents the absorption coefficient as a function of the photon energy for bulk and films. The optical absorption curves of bulk and thin films follow the same pattern; two bands at energies around 1.7 and 2.7 eV are observed, the energies of which vary slightly with the film thickness. At the same time the

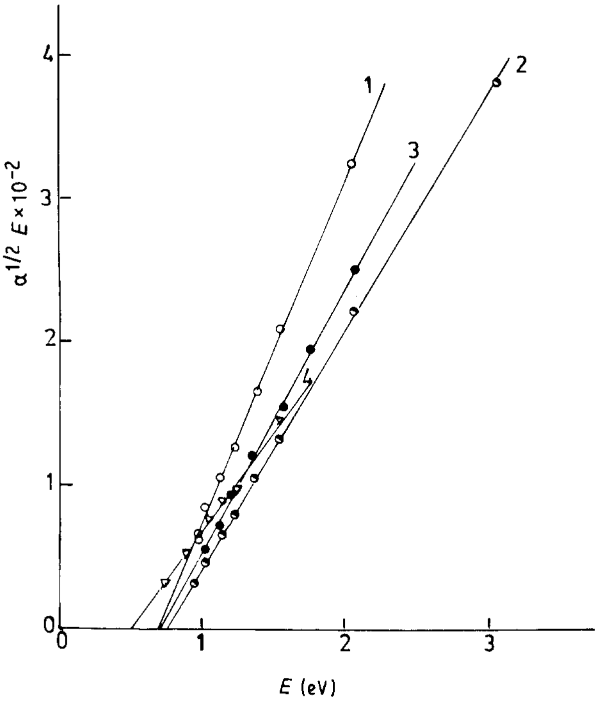

Figure 2 Relation between $\alpha E^{1/2}$ and the energy E; t (nm) = (1) 260, (2) 360, (3) 400, (4) 560.

TABLE I Estimated values of optical gap

Film thickness, t (nm)	Optical gap, E_g (eV)
260	0.80
360	0.75
400	0.70
560	0.45

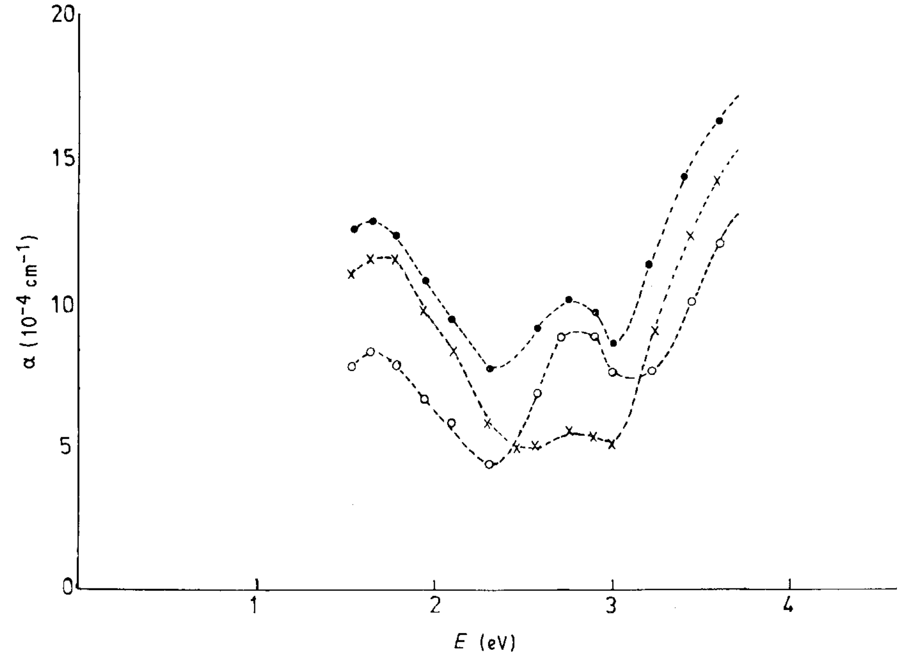

Figure 3 Relation between the absorption coefficient and the photon energy for (○) bulk material, and films of thickness (×) 360 and (●) 400 nm.

height of the high-energy band is less for films as compared to that of bulk, whereas the band at 1.7 eV exhibits the opposite trend.

The value of 1.7 eV is comparable with the transition value observed by Street *et al.* [5]. The differences are most likely to be due to different structural features of the films such as dangling bonds and voids, which define the number of extralocalized states between the mobility edges of the deposited films [5].

4. Discussion

The linear dependence in Fig. 2 suggests the indirect transition as the possible absorption mechanism, where both $N_v(E)$ and $N_c(E)$ in all thicknesses are proportional to $E^{1/2}$, where $N_v(E)$ and $N_c(E)$ are the electron densities in the valency and conduction bands, respectively. In other words the electron density curves are almost thickness-independent and obey the relation $N(E) \propto E^{1/2}$. On the other hand, the optical gap decreases with increasing film thickness. This is most likely to be due to the fact that at low thicknesses the films are not continuous and we are actually dealing with a two-dimensional network. On increasing the film thickness the physical properties approach those of the bulk, which could explain the decrease of the optical gap by a factor of ~ 2. The strength of the absorption band at ~ 1.7 eV increases on going from bulk to thin films. This allows us to conclude that such an increase is due to homopolar bonds, since the concentration of the latter is higher in thin films [4]. On the other hand, the band located at 2.7 eV, which exhibits a reverse trend, is most probably due to heteropolar bonds.

According to Tauc [14], the band picture retains its meaning in amorphous systems. The band structure of single crystals of $AsSe_{3/2}$ has been obtained [15]. The possible defects and their energy levels were given. In such a case one should consider that the electronic structure of the amorphous state is no more than a modified form of that of crystal.

In the crystal there are two types of defect C'_j and P'_j which characterize chalcogen (Se) and prictide (As) atoms, respectively [15]. The coordination number is j whereas the number of primes denotes the number of homopolar bonds. Considering the possible transitions and their energies given by Vanderbilt and Joannopoulos [15], one can easily assign the observed bands. The band observed at ~ 1.7 eV is more likely to be due to the P''_2 (−) defect $A''_s(-)$, whereas the band located around 2.7 eV is most probably due to the localized levels formed by heterobonds $C_sP''_s(+)$ or $C'_3C'_2(+)$.

5. Conclusions

In amorphous As_2Se_3 films heteropolar bonds As–Se are acceptable; however, homopolar bonds of the type As–As and Se–Se exist. Defects are related to such homopolar bonds, which contribute to changes in optical absorption.

Optical absorption occurs at ~0.9, ~1.7 and ~2.7 eV. The first band is explained in terms of indirect optical transition across the gap. The second absorption band at ~1.7 eV could be accounted for in terms of homopolar bonds. The third absorption band at ~2.7 eV is related to the localized levels formed by heterobonds $C_sP''_s(+)$ or $C'_3C'_2(+)$.

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