

Growth and optical properties of ZnIn_2Se_4 films

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Thin films of ZnIn_2Se_4 were deposited on quartz substrates at 297 K by the conventional thermal evaporation technique. The as-deposited films were amorphous. On annealing at 623 K under vacuum for 3 h, the films crystallized with a preferred (1 1 2) orientation corresponding to the chalcopyrite-type structure. Films deposited on a quartz substrate heated to 573 K were also crystalline. The optical constants were computed from the measured transmittance and reflectance at normal incidence of light in the wavelength range 400 to 2000 nm. The analysis of the data gave a direct gap of 2.2 and 2.06 eV for the amorphous and crystallized films, respectively. The dispersion curve exhibited a peak above the absorption edge. An indirect gap of 1.8 eV for the crystallized films and a direct forbidden gap of 1.75 eV for the amorphous films were also deduced. A direct allowed transition with a gap of 2.065 eV and an indirect transition with a gap of 1.69 eV were deduced for the crystalline films deposited on the heated substrate.

1. Introduction

II–III₂–VI₄ semiconductor compounds (II = zinc, cadmium or mercury; III = aluminium, gallium or indium; VI = sulphur, selenium or tellurium) were first grown by Hahn *et al.* [1] and Goryunova *et al.* [2]. They possess two kinds of crystalline structure: (i) lattices in which cation atoms have a tetrahedral surrounding; (ii) lattices in which cation atoms have both tetrahedral and octahedral surroundings.

ZnIn_2Se_4 is a tetrahedrally coordinated semiconductor which crystallizes in the uniaxial defect chalcopyrite structure of space group $S_4^2\text{-I}\bar{4}$ [1]. Up to now it has been the subject of relatively little interest; only some fundamental properties such as photoconductivity and optical absorption have been investigated. The photoconductivity of ZnIn_2Se_4 was first studied by Beun *et al.* [3] and later this work was extended by others [4–6]. There is a certain disagreement regarding the value of the energy gap. The reported values of a direct energy gap at room temperature are 1.82 eV [7], 2.0 eV [4] and 1.9 eV [5]. However, a value of 1.63 eV was mentioned for an indirect gap [8]. The residual conductivity inherent in ZnIn_2Se_4 [9] may be used to develop memory cells.

To our knowledge, no work concerning thin ZnIn_2Se_4 films has been reported. In this paper the growth and optical properties of ZnIn_2Se_4 films, deposited by a thermal evaporation technique on quartz substrates, are reported.

2. Experimental techniques

Ingots of ZnIn_2Se_4 were prepared by fusion of stoichiometric quantities of the pure elements in vacuum-sealed silica tubes which were left at 1050 °C for 10 h, and then cooled to room temperature over 48 h. X-ray

powder diffraction revealed a single phase of chalcopyrite-type structure, the lattice parameters agreeing with those reported by Hahn *et al.* [1].

Thin films of ZnIn_2Se_4 were deposited by a thermal evaporation technique on quartz substrates at different temperatures using a high-vacuum coating unit (Edwards 306 A). The working vacuum was kept at about 10^{-5} Pa during deposition. The film thickness was determined using a quartz crystal thickness monitor, and also interferometrically.

The transmittance, T , and reflectance, R , of ZnIn_2Se_4 films, deposited on quartz substrates, at normal incidence of light in the wavelength range 400 to 2000 nm were measured using a double beam spectrophotometer (Cary 2390, Varian) with a reflection stage. The X-ray diffraction patterns of the films were recorded using an X-ray diffractometer (Philips PW 1700).

From the measured R , T values and the film thickness, d , the refractive index, n , and the absorption index, k , were computed using a modified method [10] of the Abele and Theye technique [11] based on solving the following two non-linear equations,

$$f_t(n, k) = T_{(n,k)} - T_{\text{exp}} = 0 \quad (1)$$

$$f_r(n, k) = R_{(n,k)} - R_{\text{exp}} = 0 \quad (2)$$

where f_t and f_r are the difference between theoretical and experimental values of T and R and $T_{(n,k)}$ and $R_{(n,k)}$ refer to Murmann's exact equations [12]. Expanding the two equations in a Taylor series around the starting point (n_0, k_0) and ignoring higher order partial derivatives, one obtains

$$\left(\frac{\partial f_t}{\partial n}\right)_{n_0, k_0} \Delta n + \left(\frac{\partial f_t}{\partial k}\right)_{n_0, k_0} \Delta k = 0 \quad (3)$$

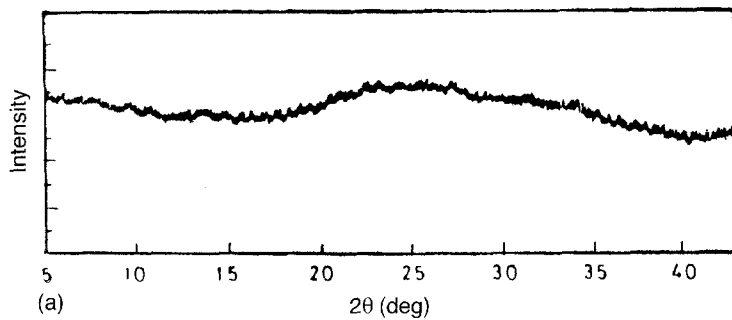
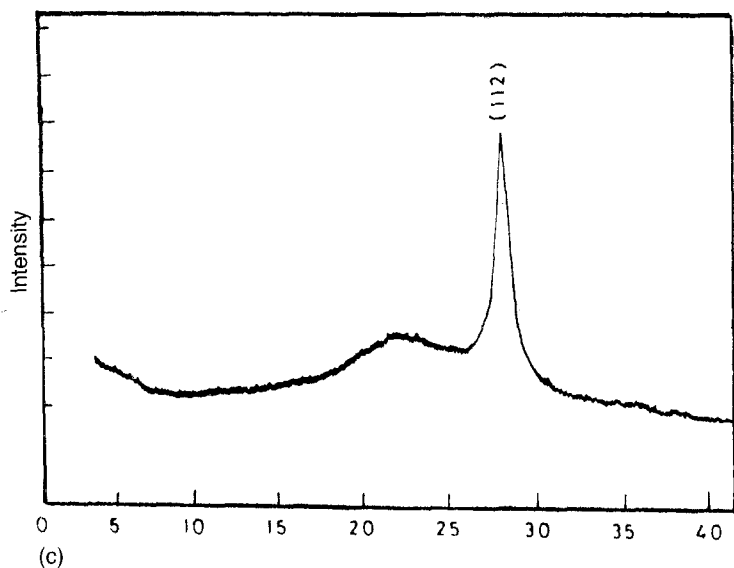
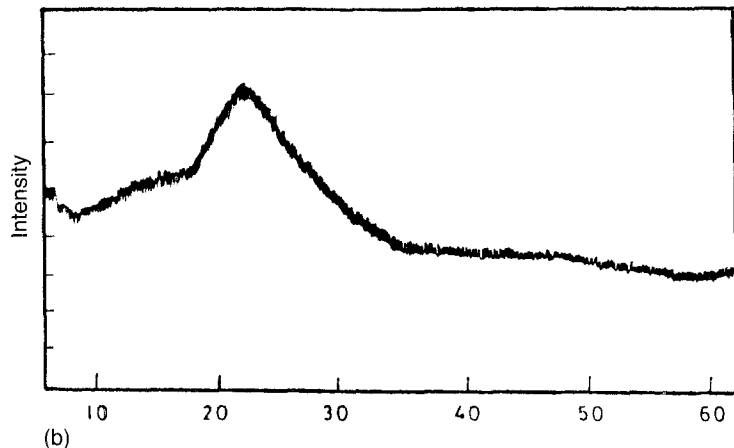


Figure 1 X-ray diffraction patterns of as-deposited ZnIn₂Se₄ films on (a) quartz substrate, (b) annealed in vacuum at 220 °C for 3 h, and (c) annealed in vacuum at 350 °C for 3 h.



$$\left(\frac{\partial f_r}{\partial n}\right)_{n_0, k_0} \Delta n + \left(\frac{\partial f_r}{\partial k}\right)_{n_0, k_0} \Delta k = 0 \quad (4)$$

Equation 3 or 4 is divided by the largest non-zero coefficient to obtain an expression for one variable in terms of the other. The resulting expression for the variable is used in Equation 3 or 4 wherever that variable has appeared. Thus, a solution of the two simultaneous equations could be obtained.

3. Results and discussion

3.1. As-grown films

X-ray diffraction patterns of films deposited on quartz substrates at room temperature, showed that these films were completely amorphous (Fig. 1a). All the films were n-type with a high resistivity (10 cm) as indicated by the hot probing technique.

The transmittance, T , and reflectance, R , at normal incidence of light in the wavelength range 400 to

2000 nm for five samples of ZnIn₂Se₄ films of thickness 90, 117, 130, 136.5 and 179 nm are shown in Figs 2 and 3, respectively.

The variation of the refractive index, n , and the absorption index, k , with the wavelength are shown in Fig. 4. The dispersion curve has a peak at 490 nm corresponding to $n = 2.91$, above the absorption edge.

The spectral behaviour of the absorption coefficient, $\alpha = 4\pi k/\lambda$, is shown in Fig. 5. At the absorption edge, the absorption coefficient rises suddenly, reaching a value of $2.2 \times 10^5 \text{ cm}^{-1}$ at 500 nm. Plotting α^2 against photon energy, $h\nu$, yields a straight line (Fig. 6) in the region above 2.37 eV, indicating a direct allowed optical transition following the relation [13]

$$\alpha = (A_d/h\nu)(h\nu - E_g)^{1/2} \quad (5)$$

A_d is a constant, called the quality factor with an energy gap, $E_g = 2.2 \text{ eV}$, obtained by extrapolating the straight line to zero absorption. Below 2.50 eV, a straight line resulted from the $\alpha^{2/3} - h\nu$ plot, indicating

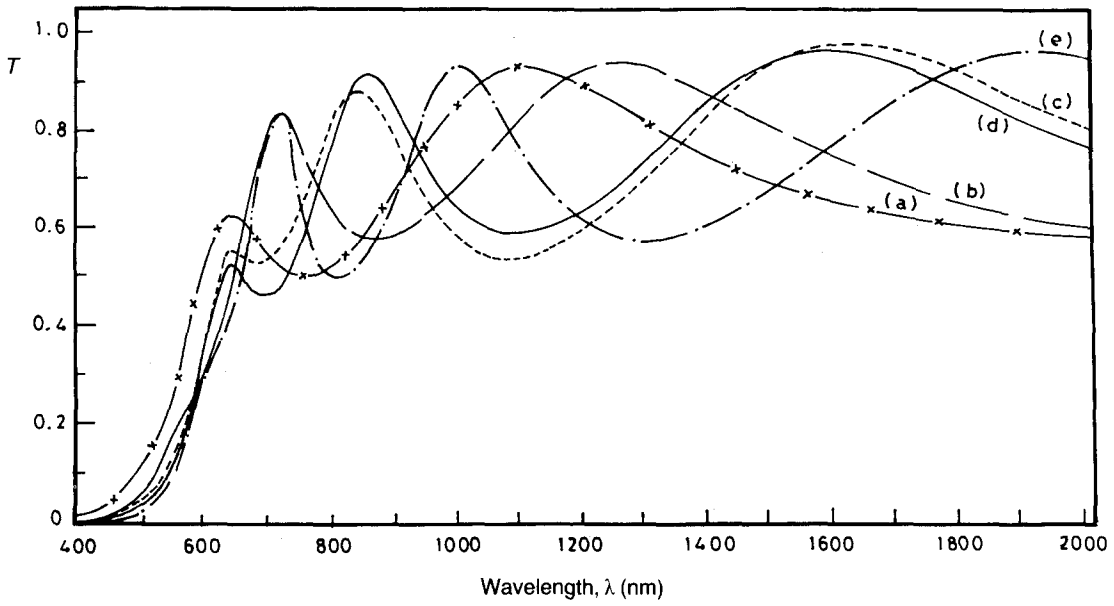


Figure 2 Transmittance of as-deposited ZnIn_2Se_4 films in the wavelength range 400 to 2000 nm; film thickness (a) 90 nm, (b) 117 nm, (c) 136.5 nm, (d) 130 nm, (e) 179 nm.

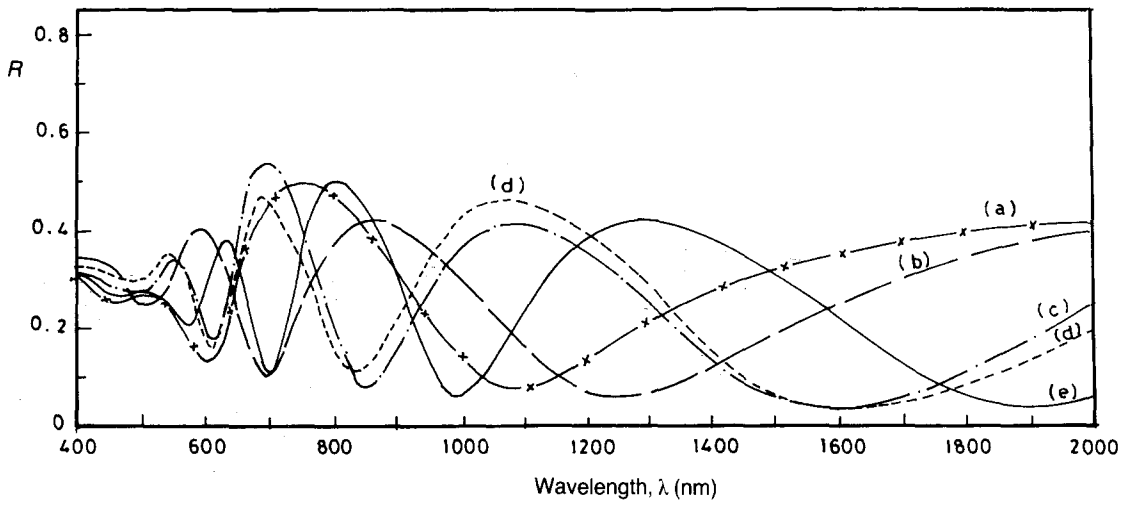


Figure 3 Reflectance of as-deposited ZnIn_2Se_4 films in the wavelength range 400 to 2000 nm for the same films in Fig. 2.

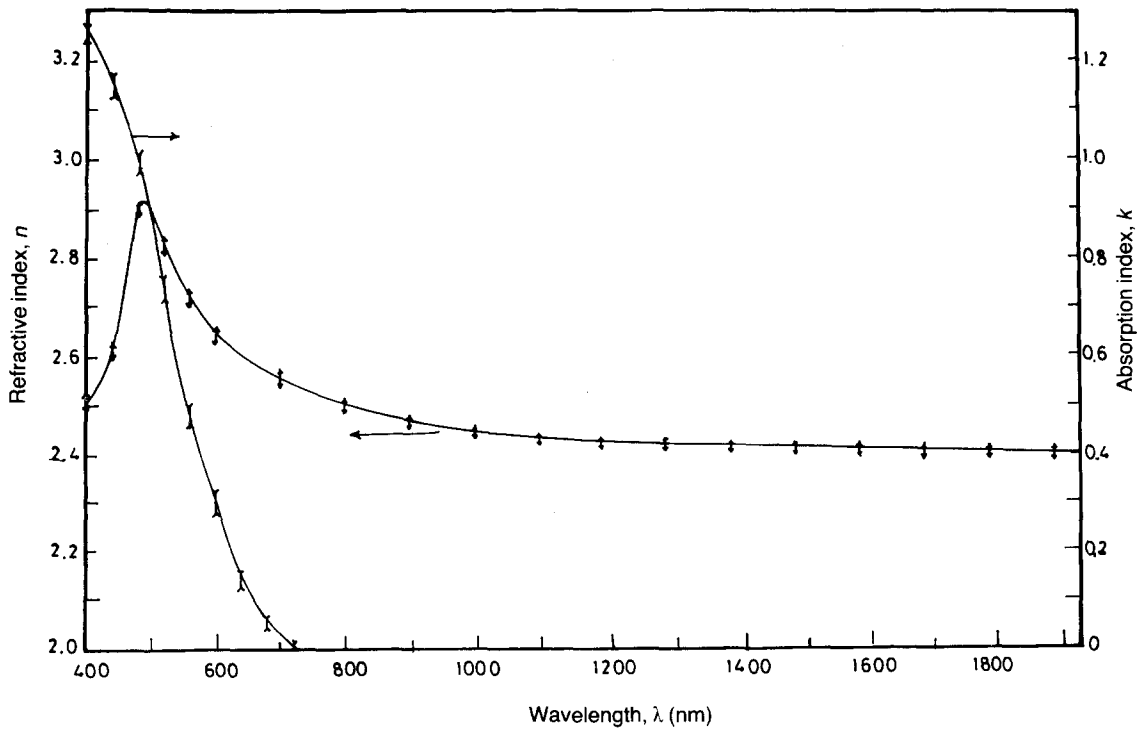


Figure 4 Spectral behaviour of n and k for as-deposited ZnIn_2Se_4 films.

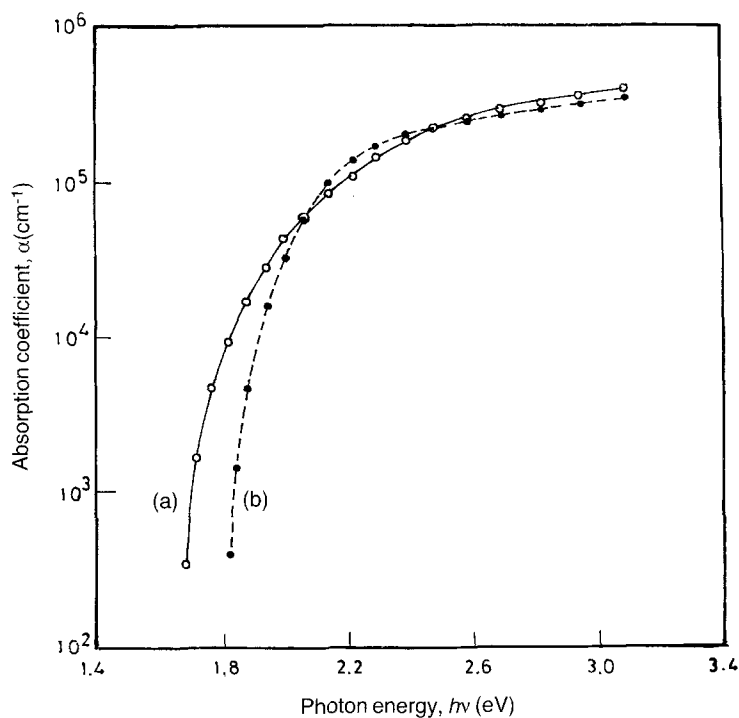


Figure 5 Spectral behaviour of the absorption coefficient, α , plotted against photon energy, $h\nu$: (a) as-deposited film and (b) film annealed in vacuum at 350 °C for 3 h.

a direct forbidden transition with an energy gap $E_g^f = 1.75$ eV (Fig. 6).

3.2. Annealed films

On annealing the as-deposited ZnIn_2Se_4 films in vacuum ($\approx 10^{-4}$ Pa), the films crystallized. Crystallization begins at 220 °C (Fig. 1b) and at 350 °C the amorphous film transforms to the crystalline state with a preferred (112) orientation (Fig. 1c) corresponding to the chalcopyrite-type structure.

The transmittance, T , and reflectance, R , at normal incidence of light for the vacuum-annealed films at

350 °C for 3 h are shown in Figs 7 and 8, respectively. The spectral behaviour of the refractive index, n , and the absorption index, k are given in Fig. 9. The refractive index attains a peaked value at 530 nm corresponding to $n = 2.785$, associated with the absorption edge. Hence, the peaked value of the refractive index shifts to the long wavelength side on crystallization.

The spectral behaviour of the absorption coefficient for the annealed film is shown in Fig. 5, where it appears that the absorption edge shifts to the low-energy side. Plotting α^2 against $h\nu$ yields a straight line above 2.12 eV (Fig. 10) indicating a direct optical

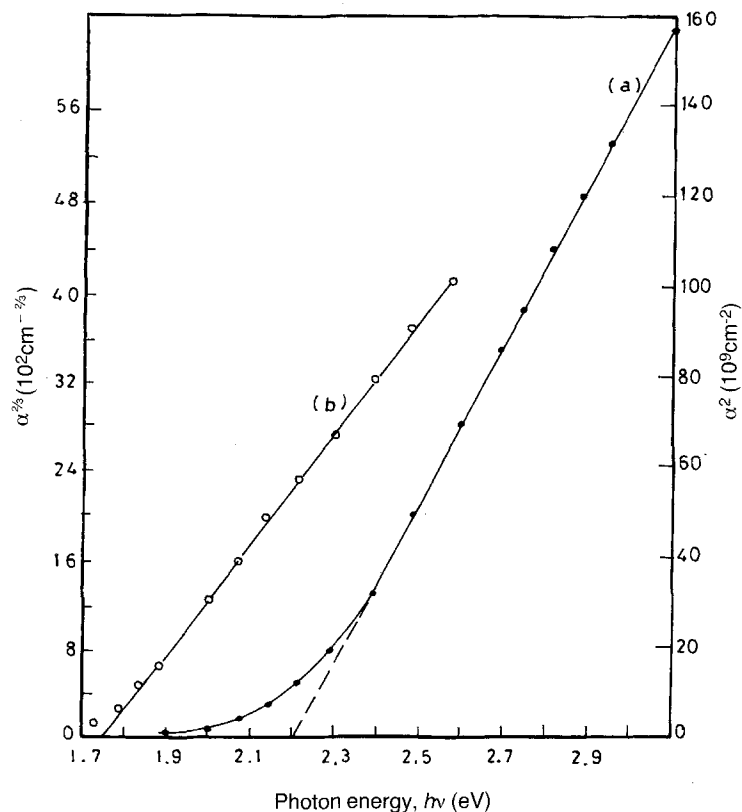


Figure 6 Plots of (a) α^2 against $h\nu$ and (b) $\alpha^{2/3}$ against $h\nu$ for as-deposited ZnIn_2Se_4 films.

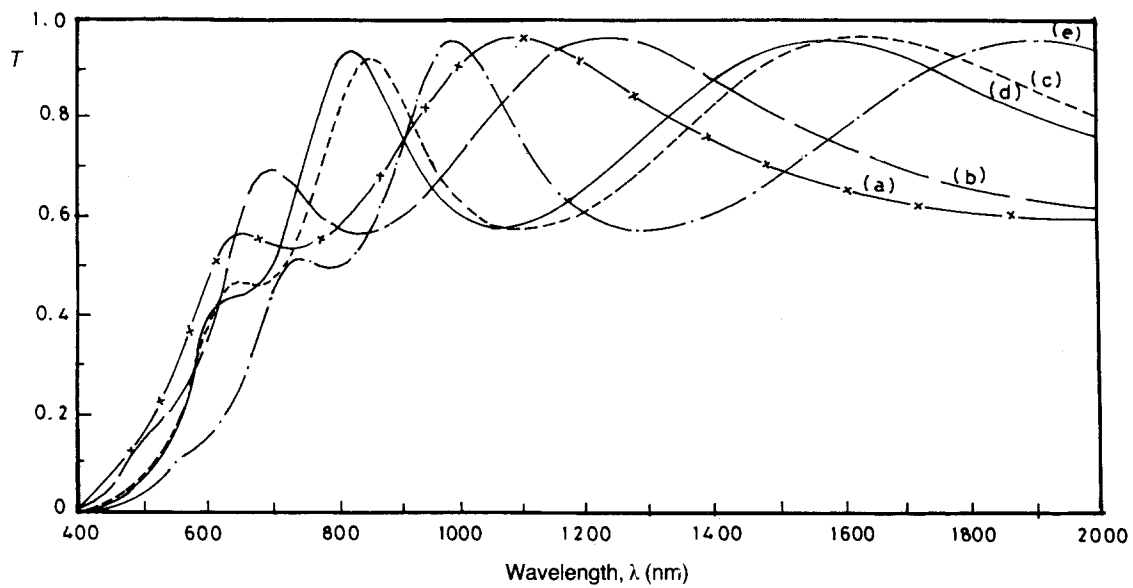


Figure 7 Transmittance of as-deposited ZnIn_2Se_4 films after being annealed at 350°C for 3 h in vacuum; film thickness (a) 90 nm, (b) 117 nm, (c) 136.5 nm, (d) 130 nm and (e) 179 nm.

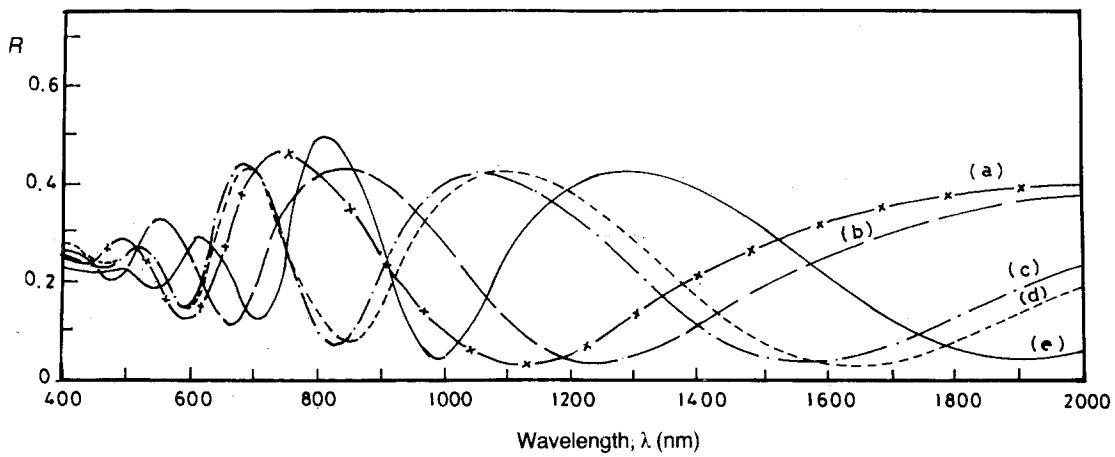


Figure 8 Reflectance of the same films as in Fig. 7.

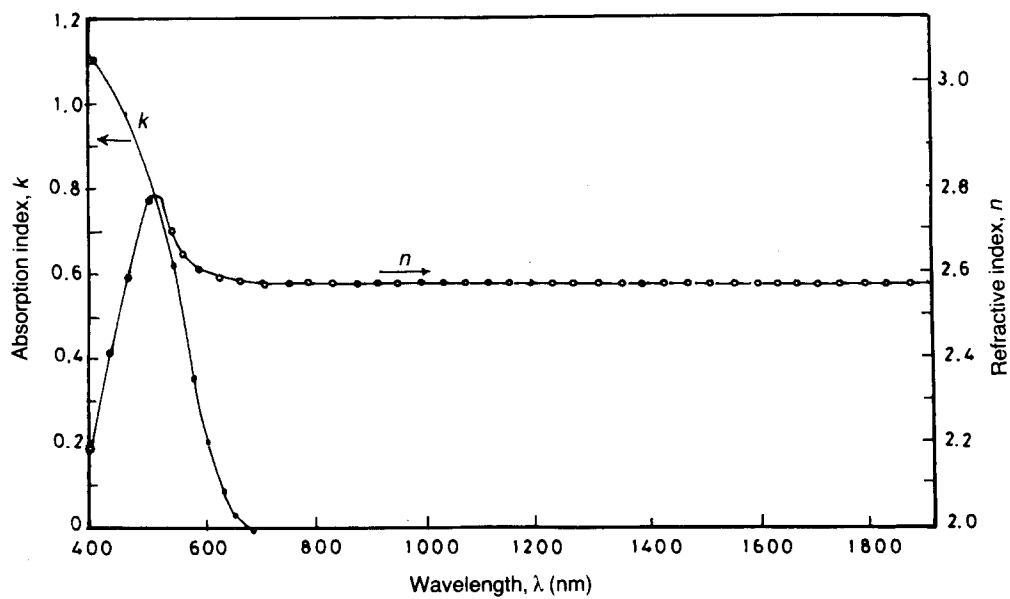


Figure 9 Spectral behaviour of n and k of annealed ZnIn_2Se_4 films.

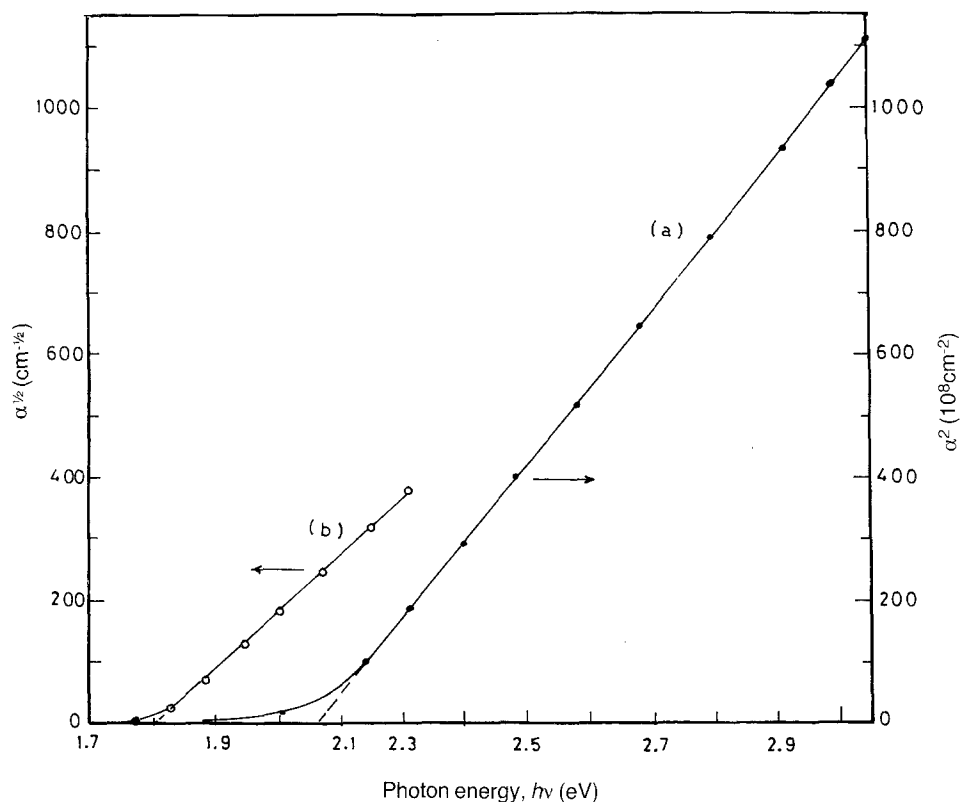


Figure 10 Plots of (a) α^2 against $h\nu$ and (b) $\alpha^{1/2}$ against $h\nu$ for annealed ZnIn_2Se_4 films.

transition with energy gap 2.06 eV. Below 2.15 eV, a straight line is attained from the $\alpha^{1/2}-h\nu$ plot, indicating an indirect optical transition following the relation [13]

$$\alpha = (A_i/h\nu)(h\nu - E_g^i)^2 \quad (6)$$

with an energy gap $E_g^i = 1.8$ eV (Fig. 11).

3.3. Films deposited on a heated substrate

When deposition occurred on heated quartz substrates, it was found that ZnIn_2Se_4 films also have an amorphous structure as long as the substrate temperature, $T_s < 423$ K. When $T_s > 423$ K, crystalline films

were obtained, corresponding to the chalcopyrite-type structure with lattice parameters $a = 0.47$ nm and $c = 1.17$ nm. The films had a predominant (1 1 2) reflecting plane; the intensity of the corresponding diffraction line increased on raising the substrate temperature to 573 K (Fig. 11). Above $T_s = 573$ K, the film orientation distorted and another predominant reflecting plane (the (004) plane) occurred in addition to the (1 1 2) plane.

The transmittance, T , and reflectance, R , of the crystalline ZnIn_2Se_4 films, deposited on quartz substrates heated to 573 K, at normal incidence of light in the wavelength range 400 to 2000 nm are represented in Figs 12 and 13 for six films of thickness 50, 52.4,

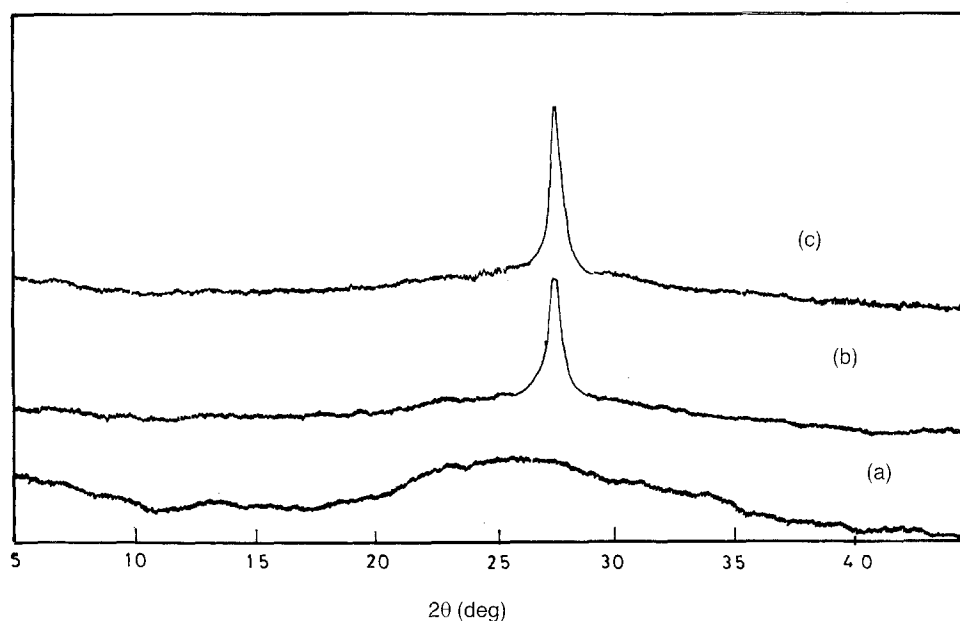


Figure 11 X-ray diffraction patterns of ZnIn_2Se_4 films deposited on quartz substrates at $T_s =$ (a) 297 K, (b) 473 K, and (c) 573 K.

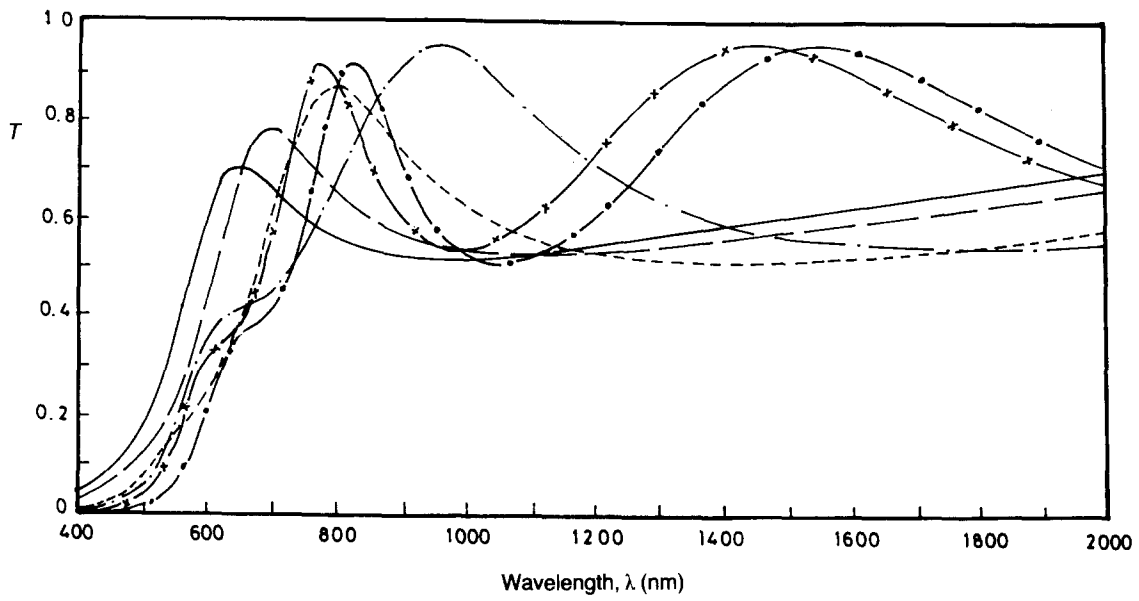


Figure 12 The transmittance, of crystalline ZnIn_2Se_4 films deposited on quartz substrates at 573 K. Film thickness: (a) 50 nm, (b) 52.4 nm, (c) 66.9 nm, (d) 70 nm, (e) 110 nm and (f) 142 nm.

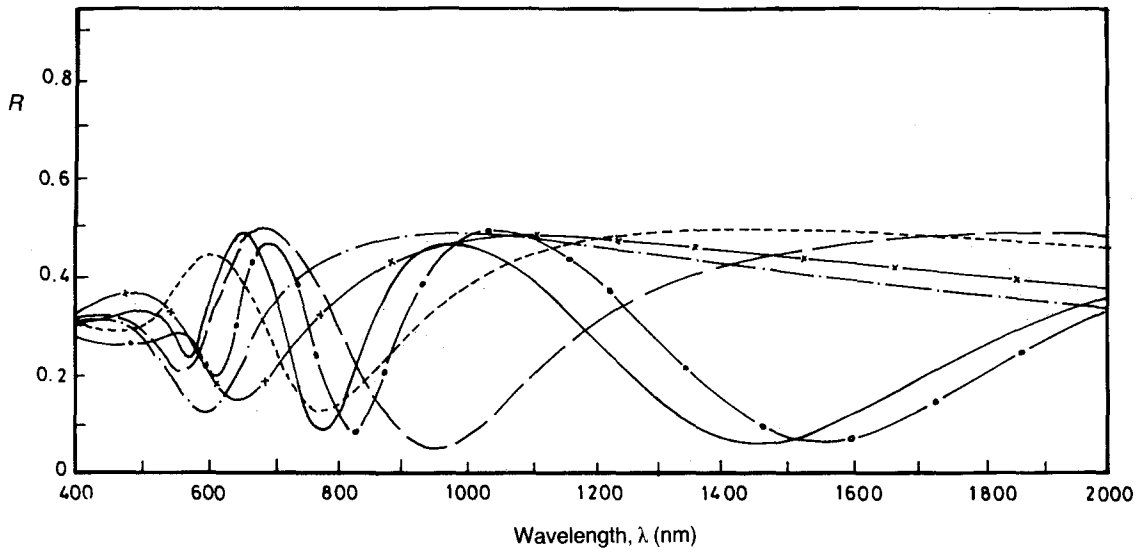


Figure 13 The reflectance of crystalline ZnIn_2Se_4 films deposited on quartz substrates at 573 K, for the thicknesses as in Fig. 2.

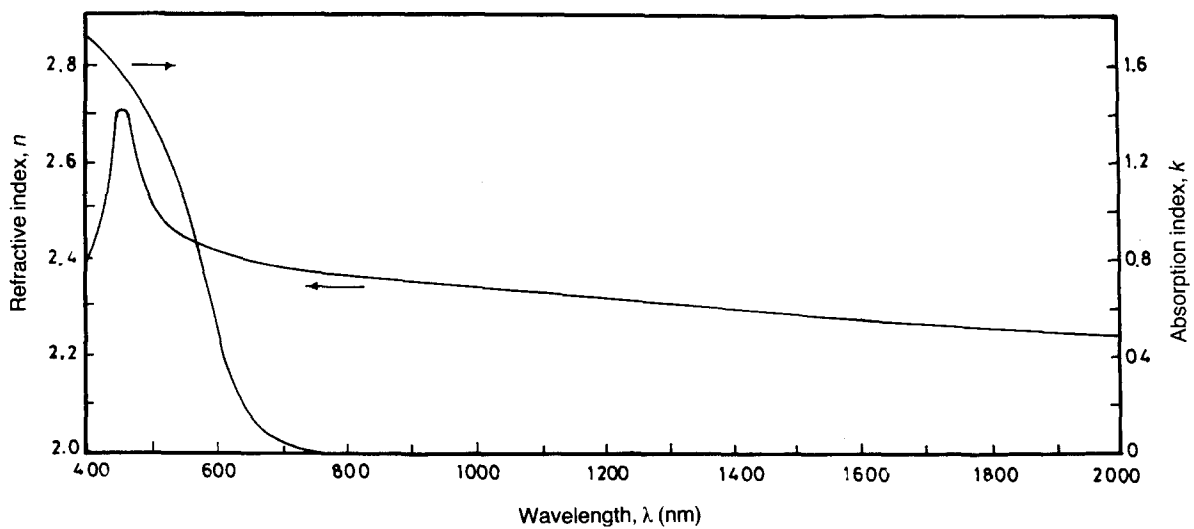


Figure 14 Spectral behaviour of the refractive index, n , and the absorption index, k , of crystalline ZnIn_2Se_4 films.

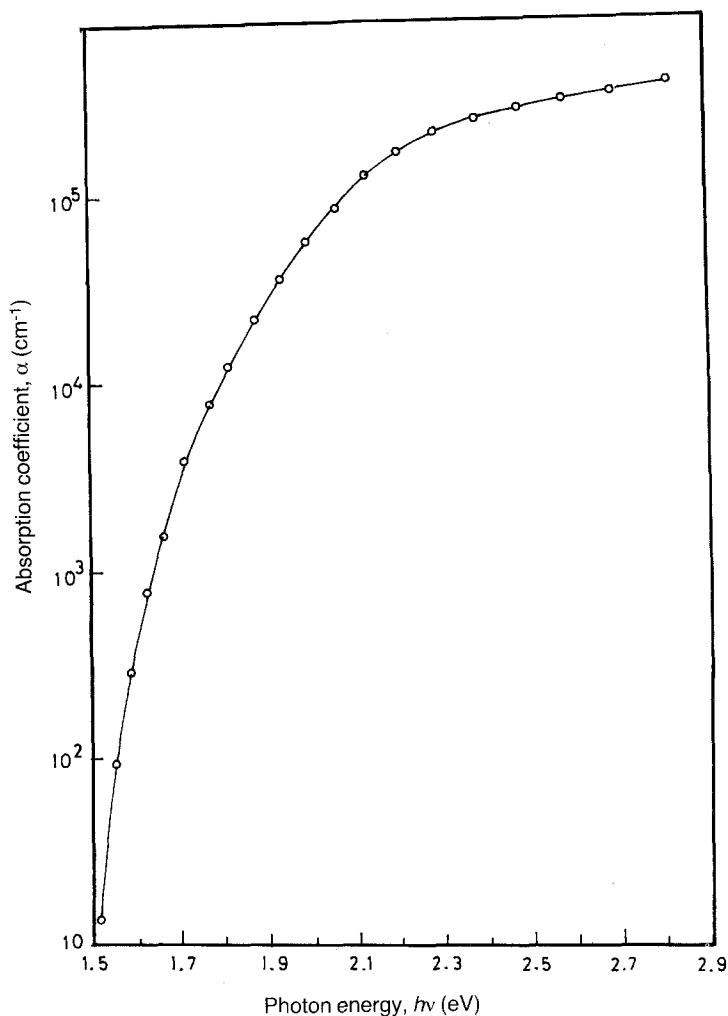


Figure 15 Spectral behaviour of the absorption coefficient, α , of crystalline ZnIn_2Se_4 films.

66.9, 70, 110 and 142.1 nm. At long wavelengths below the absorption edge $T + R = 1$ indicating no scattering.

The spectral behaviour of the refractive index, n , and the absorption index, k , is shown in Fig. 14. The

refractive index exhibits a peak at 450 nm, above the absorption edge, corresponding to $n = 2.705$.

At the absorption edge, the absorption coefficient, $\alpha = 4\pi k/\lambda$, rises reaching a value of $6.7 \times 10^4 \text{ cm}^{-1}$ at 620 nm (Fig. 15). Plotting α^2 against photon energy,

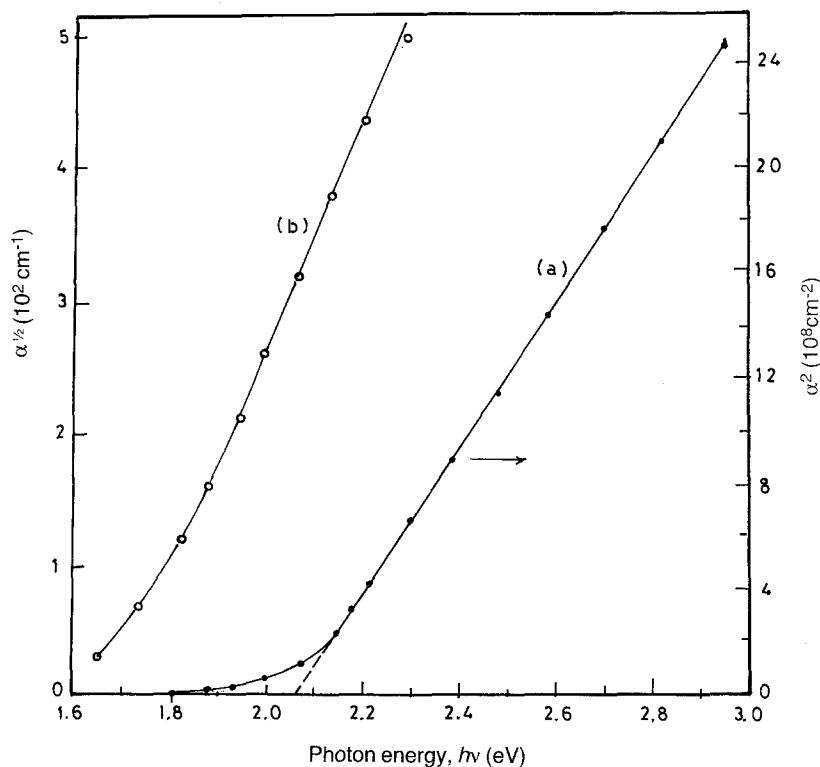


Figure 16 The dependence of the absorption coefficient, α , on the photon energy, $h\nu$; (a) α^2 against $h\nu$ and (b) $\alpha^{1/2}$ against $h\nu$.

$h\nu$, yields a straight line above 2.15 eV (Fig. 16) indicating a direct allowed optical transition in accordance with Equation 5 where the direct energy gap $E_g^d = 2.065$ eV, in good agreement with the value 2.06 eV, and 2.0 eV [3] reported for thin films and crystalline bulk material, respectively.

Plotting $\alpha^{1/2}$ against $h\nu$ in the spectral region from 1.85 eV to 2.2 eV yields a straight line (Fig. 16) following Equation 6, indicating an indirect allowed transition with an energy gap $E_g^i = 1.69$ eV. This may be compared to a reported value of the indirect gap of 1.63 eV [7] for the crystalline bulk material and to the value of an indirect gap of 1.8 eV deduced for crystallized films resulting from annealing amorphous films under vacuum at 623 K for 3 h.

References

1. H. HAHN, G. FRANK, W. W. KLINGLER, A. STÖRGER and G. STÖRGER, *Z. Anorg. Allg. Chem.* **279** (1955) 241.
2. N. A. GORYUNOVA, V. I. KOTOVICH and V. A. FRANK-KAMENETSKII, *Dokl. Akad. Nauk SSSR* **103** (1955) 659.
3. J. A. BEUN, R. NITSCHKE and M. LICHTENSTEIGER, *Physica* **27** (1961) 448.
4. P. MANCA, F. RAGA and A. SPIGA, *Phys. Status Solidi (a)* **16** (1973) 105.
5. *Idem*, *Il Nuovo Cimento* **19B** (1974) 15.
6. F. FORTIN and F. RAGA, *Solid State Commun.* **14** (1974) 847.
7. J. FILIPOWICZ, Tagungsbericht des Kolloquiums 4 des Berg-und Hüttenmännischen Tages, Frieberg, July 1977, p. 204.
8. S. I. RADAUTSAN, A. N. GEORGOBIANI and I. M. TIGINYANU, *Progr. Cryst. Growth Charact.* **10** (1985) 403.
9. J. FILIPOWICZ, N. ROMEO and L. TARRICONE, *Solid State Commun.* **38** (1980) 619.
10. M. M. EL-NAHAS, H. S. SOLIMAN, N. EL-KADRY, A. Y. MORSY and S. YAGHMOUR, *J. Mater. Sci. Lett.* **7** (1988) 1050.
11. F. ABELE and M. L. THEYE, *Surface Sci.* **5** (1966) 325.
12. O. S. HEAVENS, "Optical Properties of Thin Solid Films" (Dover, New York, 1965) p. 55.
13. J. L. PANKOVE, "Optical Processes in Semiconductors" (Prentice-Hall, New York, 1971).

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