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Optical properties of evaporated $PbSnS_3$ thin films

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$PbSnS_3$ is a ternary sulfide semiconductor material which has been relatively little studied in the literature. Thin films of this material were deposited on glass substrates by a thermal evaporation process and their optical properties investigated. The optical parameters were determined from the analysis of measured transmission spectra, at normal incidence, from 400–1500 nm, at room temperature. The fundamental absorption edge is placed at 1.04 ± 0.05 eV and is forbidden in nature. Other absorption edges are obtained at 1.44 and 1.55 ± 0.05 eV, with a nearby direct one at 1.68 ± 0.05 eV. The peaks at 1.44 and 1.55 eV have been independently confirmed by the spectral photocurrent response of the films. © *1998 Kluwer Academic Publishers*

1. Introduction

Ternary and multinary semiconductors have, in the recent past, attracted much attention because of their potential application in photonic devices [1, 2]. Because of the difficulty of growing single crystals of these classes of semiconductors, many are often first prepared as amorphous or polycrystalline thin films. The unfolding knowledge of optical and electrical transport processes in these films has led to the conception and development of improved devices, for example, absorber layers of solar cells, light-emitting diodes and thin-film transistors [3]. Unlike the I–III–VI_2 and I–IV–V_2 ternaries, the optical properties of thin films of the II–IV–VI_3 group of compounds, particularly the sulfide semiconductors, are rare in the literature. Single crystals of $PbSnS_3$, a member of this group, has been cursorily examined [4]. Its fundamental optical edge is placed at 1.04 eV, which makes it attractive for possible photovoltaic application. In addition, thin films are better suited for the study of optical properties of a material intended for thin-film devices.

In this work, we have therefore evaporated thin films of the material by a thermal evaporation process. The absorption spectra have been obtained from room-temperature transmission measurements. The spectra were analysed using both transmission ratio and Swanepoel's techniques [5]. Apart from the derivation of the optical edge, the refractive index, n, and the extinction coefficient, k, have also been calculated from the derived spectra. The photoresponse spectra of the films has equally been measured to determine the optical edge by an independent method.

2. Experimental procedure

Polycrystalline ingots of $PbSnS_3$ were directly synthesized from a stoichiometric mixture of its constituent elements in a vacuum-sealed quartz ampoule. Details of the synthesis and X-ray powder data are as detailed elsewhere [6]. The films were evaporated from pulverized ingots in a resistively heated quartz boat placed in an Edwards High Vacuum system pumped down to a pressure of 10^{-5} torr (1 torr = 133.322 Pa). About 5 at% excess sulfur was added to the starting mixture to prevent losses during evaporation. The films were deposited on cleaned Corning 7059 glass substrates placed at a distance of about 9.0 cm above the source.

Film thickness was determined with a tallystep (Technicor Instruments model 100) and deposition rate was subsequently estimated as 1.5 $\text{nm}\,\text{s}^{-1}$. The optical transmission of these films was taken at room temperature with a Varian 2390 double-beam spectrophotometer through the wavelength range 400–1500 nm. For photocurrent response, a monochromator was interposed between a Phillips 100W (tungsten–halogen) lamp and the film. The current was measured with a (Leybold–Heraeus 53200) current amplifier.

3. Analysis of measured transmission spectra

The measured transmission spectra of typical $PbSnS_3$ thin film is as shown in Fig. 1, for a film 0.5 μm thick. Two regions are indicated in the figure. The strong

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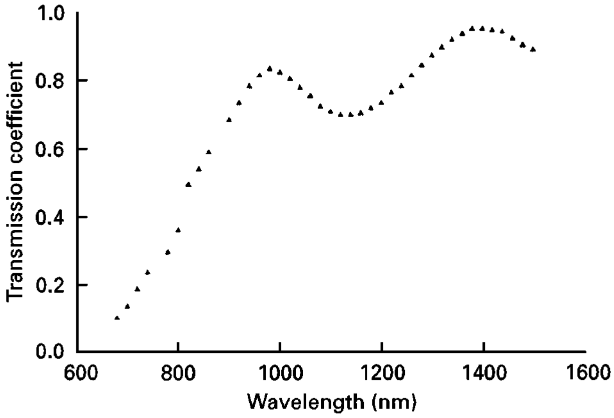

Figure 1 Transmission spectra of 0.5 μm thick thin film of $PbSnS_3$.

absorption region where transmittance decreases monotonically with wavelength and the weak absorption region showing characteristic interference effects are both shown.

The strong absorption region is regarded as between 400 and 750 nm, as indicated in the figure. To obtain the absorption coefficient, α, in this region, the transmittance of two films T_1 and T_2, of different thicknesses, d_1 and d_2 were measured, while α is derived from Equation 1 as [7]

$$\alpha = \frac{1}{\Delta d} \ln \frac{T_1}{T_2} \tag{1}$$

where $\Delta d = (d_2 - d_1)$.

In the weakly absorbing region (regarded as 800 to above 1500 nm), the measured transmittance was analysed following Swanepoel's method [5]. In this region, T is a function of α, n, k and d and may be expressed as

$$T = \frac{Ax}{B - Cx\cos\varphi + Dx^2} \tag{2}$$

where the terms A, B, C and D are expressed in terms of n and k, $x = \exp(-\alpha d)$ and $\varphi = 2\pi nd/\lambda$. Equation 2 is a transcendental equation and therefore multivalued. However, at the exterma, φ assumes a value of $\pm\pi$, giving

$$T_{\mathrm{M}} = \frac{Ax}{B - Cx + Dx^2} \tag{3}$$

and

$$T_{\mathrm{m}} = \frac{Ax}{B + Cx + Dx^2} \tag{4}$$

where T_{M} and T_{m} are the maximum and minimum values of the envelope enclosing the interference pattern of the transmission spectra (see Fig. 1). The difference of the reciprocals of Equations 3 and 4 yields

$$\frac{1}{T_{\mathrm{M}}} - \frac{1}{T_{\mathrm{m}}} = \frac{2C}{A} \tag{5}$$

substitution of the appropriate expressions for C and A in Equation 5 and rearranging, gives n as

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \tag{6a}$$

where

$$N = \frac{2s(T_{\mathrm{M}} - T_{\mathrm{m}})}{T_{\mathrm{M}} T_{\mathrm{m}}} + \frac{s^2 + 1}{2} \tag{6b}$$

and $s = 1.52$, the refractive index of the glass substrate. Calculation of n is straightforward once T_{M} and T_{m} have been defined from the transmission spectra. Having obtained n, x can be calculated from

$$x = \frac{E - [E^2 - (n^2 - 1)^3(n^2 - S^4)]^{1/2}}{(n - 1)^3(n - s^2)} \tag{7}$$

where

$$E = \frac{8n^2 s}{T_{\mathrm{M}}} + (n^2 - 1)(n^2 - s^2)$$

Then, α can also be obtained from

$$\alpha = \frac{1}{d} \ln \frac{1}{x} \tag{8}$$

and k from

$$k = \frac{\alpha\lambda}{4\pi} \tag{9}$$

4. Results and discussion

The combined absorption spectra calculated from the transmission spectra using Equations 1 and 7 is presented in Fig. 2. Three features can be observed in the figure. First, these equations give similar values of α in the energy range between 1.45 and 1.65 eV, where both absorption spectra overlap. Secondly, the spectra calculated from Equation 1 deviates fairly from that of Equation 7 between 1.3 and 1.45. The deviation arises because Equation 1 fails to account for the observed interference effects which set in just below 800 nm (see Fig. 1). Finally, beyond 1.6 eV, α exceeds $10^4\,\mathrm{cm}^{-1}$ and appears to be independent of film thickness, suggesting that the observed spectra is characteristic of evaporated $PbSnS_3$.

Near the absorption edge of the evaporated films, the spectra of Fig. 2 were analysed with Equation 10

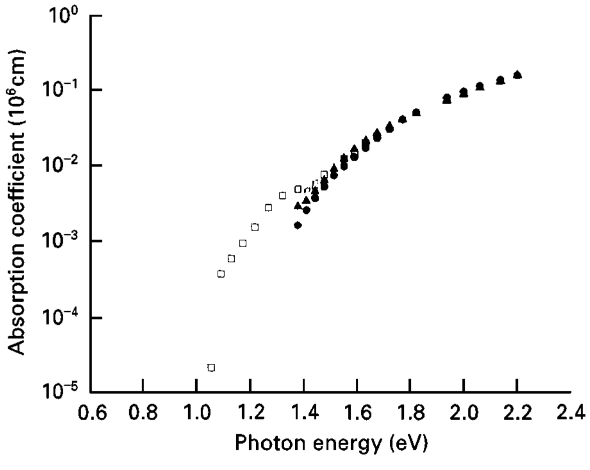

Figure 2 Composite absorption spectra of $PbSnS_3$ thin films. (□) Data from Swanepoel's calculation (Equation 7), (●, ▲) data using Equation 1 for films 300 and 500 nm thick, respectively.

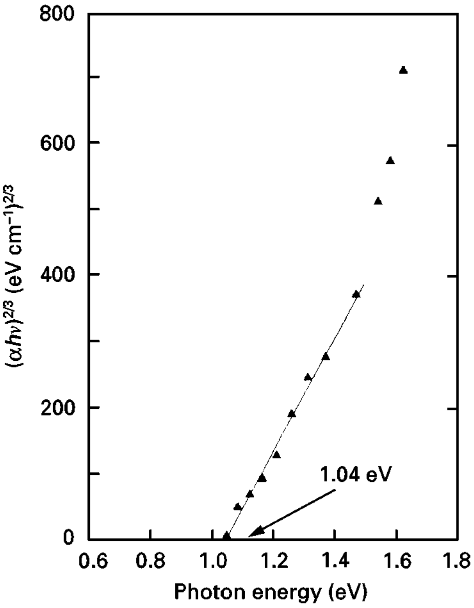

Figure 3 Analysis of the absorption spectra in the 0.8–1.4 eV energy range indicating a forbidden direct transition with the edge at 1.04 eV.

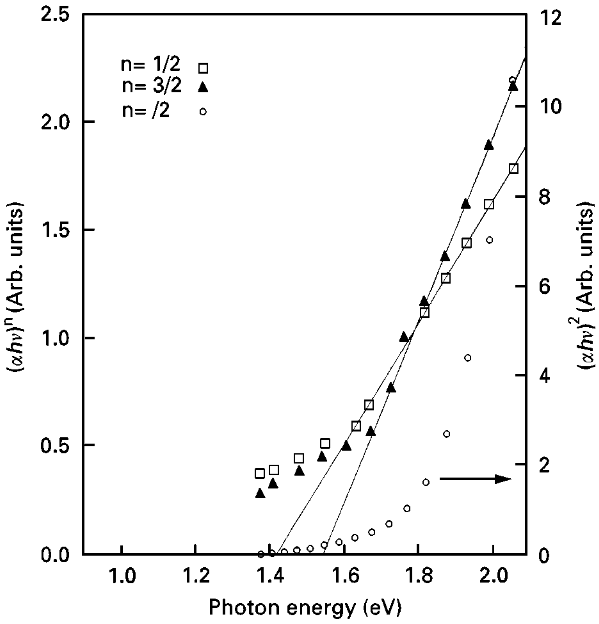

Figure 4 Analysis of the absorption spectra in the 1.4–2.0 eV energy range, indicating transitions for (□) indirect, (△) forbidden direct and (○) a nearby direct one.

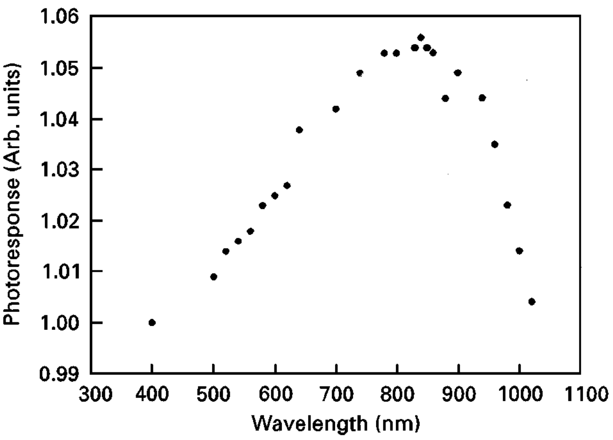

Figure 5 Spectral photoresponse of evaporated $PbSnS_3$ thin films.

expressed as [6]

$$\alpha h\nu = C(h\nu - E_o)^r \tag{10}$$

where E_o is the optical absorption edge and C a constant. By definition, the lowest optical energy gap in a material is referred to as the fundamental absorption edge and the nature of interband transition by the index r [7], where r can have the values 1/2, 2/3, and 2 for direct, forbidden direct and indirect transitions, respectively.

The analysis of the absorption spectra, therefore, commenced from the low-energy region (0.8–1.45 eV). The fitting curves give a very good fit for the value of $r = 2/3$, indicating a forbidden direct energy transition, with the edge at 1.04 eV as shown in Fig. 3. This value agrees quite well with that already reported for single crystals [3].

The fitting of the data at higher energy regions (1.4–2.0 eV) give transition energies at 1.44 and 1.55 ± 0.05 eV for indirect and forbidden direct transitions at these energies, as shown in Fig. 4. Also shown in Fig. 4 is the curve for direct transition, which tends asymptotically as $h\nu$ approaches the true optical edge which has been derived from the figure as 1.68 eV. This general behaviour is characteristic of forbidden direct materials [8].

Furthermore, the photoresponse spectra of the evaporated films gave an independent assessment of the energy and true nature of the optical gap in this high energy region. A typical spectra of these films is presented in Fig. 5. It shows a peak at 1.44 eV, and a shoulder at 1.55 eV which to a good extent support the optical edges obtained from the optical measurements.

At energies above the fundamental absorption edge, electronic transitions can occur at critical points in the band structure of any material. As a result, structures may be observed in the optical constants. Thus, different optical gaps observed for $PbSnS_3$ are not unique to the material. It has been observed in many binary, ternary and even quartenary compound semiconductors, for example, CdTe [9], $CuInSe_2$ [3], $CuGa_{0.5}In_{0.5}Se_2$ [10], $AgInSe_2$ [11], $CuGaTe_2$ [12], etc. Generally, this effect comes from the crystal field and spin orbit splitting of the valence orbitals of the respective materials at $k = 0$, to enhance transitions from such split levels to the conduction band minimum. Unfortunately, not much is known at present about the electronic structure of $PbSnS_3$, consequently, the assignment of the different transition energies will have to await detailed band structure studies for the material.

The spectral dependence of the refractive index, n, is shown in Fig. 6. n is observed to increase slowly from 2.17 at 1500 nm to about 2.2 at 1100 nm and peaks at 2.8 near 800 nm, indicating a dispersion region. Thereafter, n tends to decrease as shown by the dashed lines. The absorption region can also be seen in the spectral behaviour of k. In accordance with Equation 9, a steep increase in k gives a corresponding rise in α.

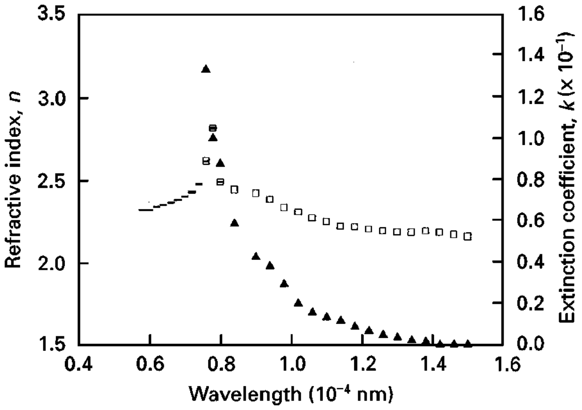

Figure 6 Wavelength dependence of (□) refractive index and (▲) extinction coefficient of $PbSnS_3$ thin films.

Acknowledgements

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