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Tin selenide (SnSe) thin films prepared by reactive evaporation

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Polycrystalline thin films of tin selenide have been prepared by reactive evaporation at substrate temperatures ranging from 473–600 K. Crystallites of the films prepared at substrate temperatures below 525 K are randomly oriented, while they have a strong preferred orientation on the substrate surface at higher substrate temperatures. Optical absorption studies indicate that the fundamental absorption starts at 1.21 eV and it is due to an allowed direct transition.

1. Introduction

Tin monoselenide (SnSe), whose band gap is about 1 eV, is a semiconductor with layer-type character and orthorhombic structure. Thin films of SnSe have received increasing interest because of its possible technical applications as memory switching devices [1] and as an efficient solar material [2–4]. Considerable attention has been devoted by various authors [5–11] to the preparation of tin selenide thin films by different methods and to the study of its electrical and optical properties. However, nobody has yet reported, to the best of our knowledge, the preparation of SnSe thin films by reactive evaporation.

The structure of the thin films, which strongly influences the electronic properties, is highly dependent upon the deposition conditions and the preparation technique employed. In view of this, we have undertaken the study of the structural and optical properties of reactively evaporated SnSe thin films and the results are reported here.

2. Experimental procedure

SnSe films were prepared by reactive evaporation, a variant of the three-temperature method, in which the individual elements were evaporated from separate sources and the compound films were deposited on the substrate, kept at an elevated temperature. It has been found [12, 13] that for many binary materials a stoichiometric interval exists with a limited degree of freedom in selecting the individual component fluxes and the substrate temperature.

Tin and selenium (purities, 99.999%) were used as evaporants. Tin was evaporated from a molybdenum boat and selenium from a conical quartz crucible with molybdenum wire windings. A detailed description of the apparatus and the deposition procedure are given elsewhere [14].

It has been found that good stoichiometric films of tin selenide are obtained with the following deposition parameters:

tin flux = 3.7×10^{14}–4.1×10^{14} atoms $\mathrm{cm^{-2}\,s^{-1}}$

selenium flux = 4.6×10^{14}–5.2×10^{14} atoms $\mathrm{cm^{-2}\,s^{-1}}$

substrate temperature = 473–600 K

The deposition rate of SnSe films was 0.2–0.3 nm $\mathrm{s^{-1}}$. Highly reproducible films were obtained under these conditions and these films had a metallic lustre. All the films used in this study were deposited on optically flat glass substrates.

Microstructural characterizations were carried out by X-ray diffraction using films with a thickness around 300 nm. Diffraction profiles were recorded on a chart recorder using $\mathrm{CuK_\alpha}$ radiation. The film thickness was measured by Tolansky's multiple beam interferometric method [15]. The optical properties were studied by taking the transmission spectra of the films using a Hitachi U-3410, UV-Vis-NIR spectrophotometer.

3. Results and discussion

3.1. Structural characterization

Fig. 1a shows a typical X-ray diffractogram of the film–substrate system prepared at a substrate temperature of 523 K. The corresponding (hkl) planes are also indicated. A similar diffraction pattern is also obtained for the films prepared at a substrate temperature of 473 K; however, the relative intensities of the reflections are slightly diminished. All the diffraction lines obtained are comparable with the standard pattern given for SnSe in the JCPDS card file. Because every line in the JCPDS card with moderate intensity could be identified, it must be concluded that the films prepared in this range of substrate temperatures are polycrystalline stoichiometric SnSe films with randomly oriented grains.

The X-ray diffraction pattern of the film prepared at a substrate temperature of 553 K is shown in Fig. 1b. In this pattern, only the (4 0 0) peak and its equivalents, (2 0 0), (6 0 0) and (8 0 0), were observed. The same

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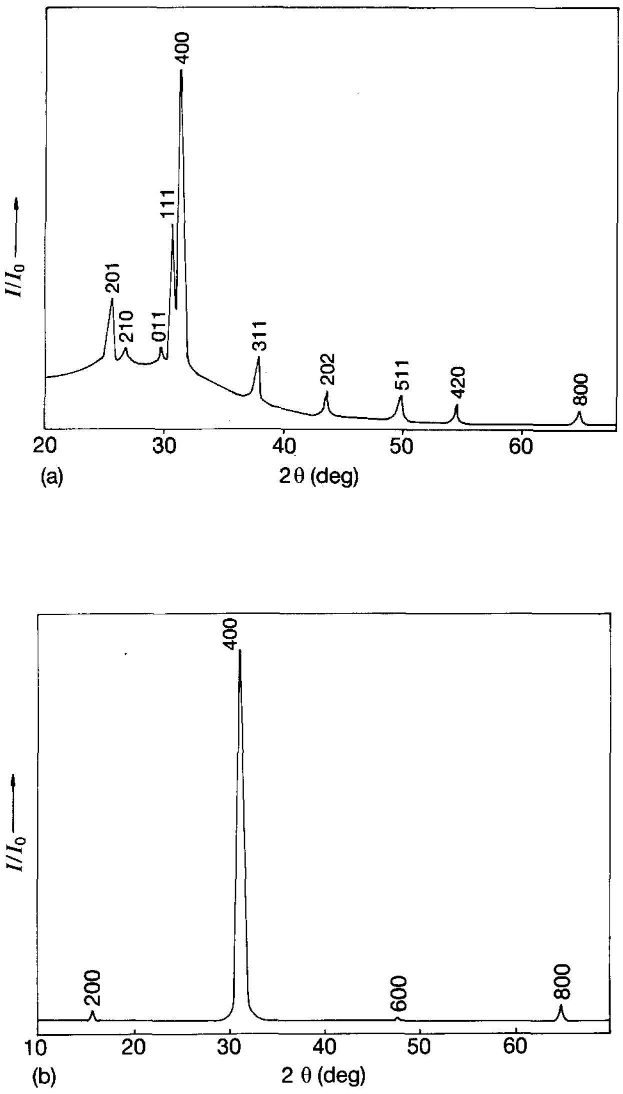

Figure 1 X-ray diffractograms of SnSe thin films prepared at different substrate temperatures: (a) 523 K and (b) 553 K.

patterns were obtained for the films prepared at still higher substrate temperatures. Hence we can conclude that the SnSe films prepared at higher substrate temperatures have a strongly preferred orientation and their crystallites are perpendicular to the (4 0 0) plane. It should be noted that this preferential orientation is similar to the orientation of the SnSe thin films synthesized by solid-state reactions [8] and is different from the (1 1 1) orientation of the SnSe films grown by hot-wall epitaxy [10].

3.2. Optical studies

The transmission, T, through a weakly absorbing film ($n^2 \gg k^2$) of refractive index n, absorption coefficient α, and thickness t, on a substrate of refractive index n_1, in a medium of refractive index n_0 is given by

$$T = \frac{16\, n_0 n_1 n^2}{(n_0 + n)^2\,(n_1 + n)^2}\exp(-\alpha t) \qquad (1)$$

The refractive index of the film was determined by the method given by Manifacier *et al.* [16]. Knowing the value of the refractive index, the absorption coefficient in the fundamental absorption region was calculated using Equation 1.

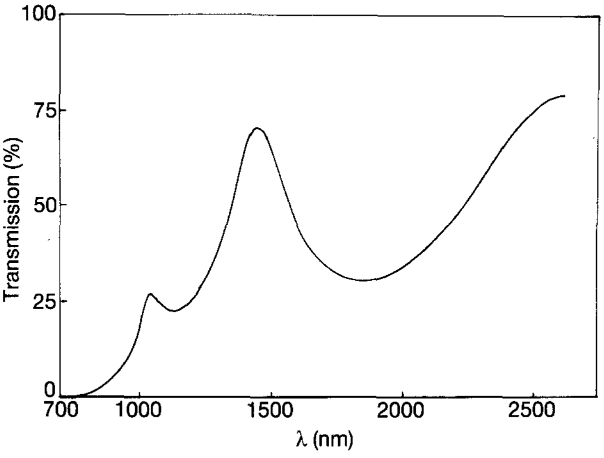

Figure 2 Transmission spectrum of a typical SnSe thin film.

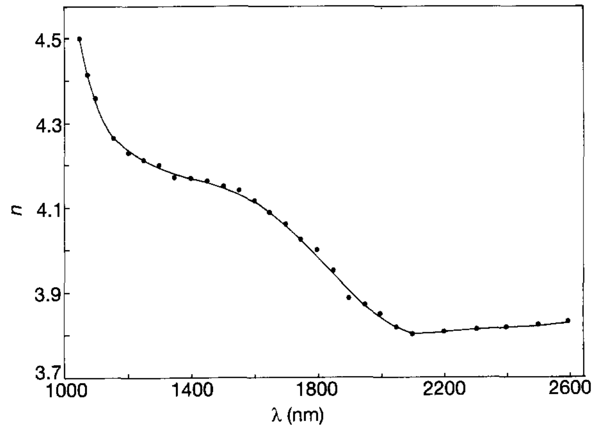

Figure 3 Variation of refractive index, (n), with wavelength, (λ).

A typical transmission spectrum of the SnSe film of thickness about 325 nm, prepared at a substrate temperature of 553 ± 2 K is shown in Fig. 2, from which the refractive index and absorption coefficient are determined.

The spectral dependence of the refractive index is shown in Fig. 3. The refractive index decreases with increasing wavelength up to 2100 nm, and beyond that it remains almost constant as the wavelength increases. A rapid increase of n occurs in the vicinity of the absorption edge and in this region its value is in agreement with the bulk value reported for single crystals [17].

Fig. 4 shows the variation of the absorption coefficient, α, as a function of photon energy, $h\nu$. The absorption has its minimum value at its low energy and increases with increasing optical energy in a similar manner to the absorption edge of the semiconductor.

The absorption coefficient data were analysed in terms of the theory of Bardeen *et al.* [18]. The theory predicts that $\alpha h \nu$ is proportional to $(h\nu - E_g)^x$, where x takes the value of 1/2 for direct allowed transitions, 3/2 for direct forbidden transitions, 2 for indirect allowed transitions, and 3 for indirect forbidden transitions. Fig. 5 shows $(\alpha h \nu)^2$ as a function of the photon energy in the vicinity of the fundamental absorption edge. The extrapolation of the graph gives a band gap

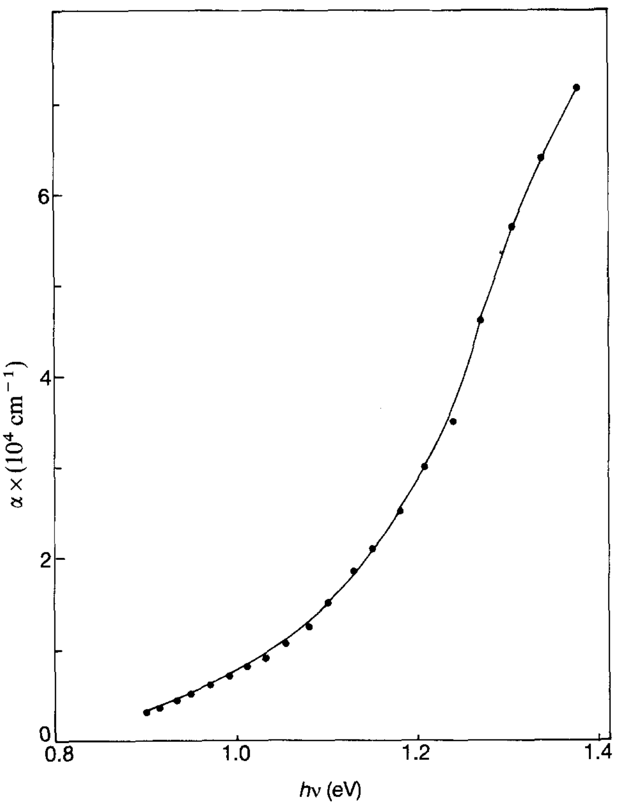

Figure 4 Variation of absorption coefficient, α, with photon energy, $h\nu$.

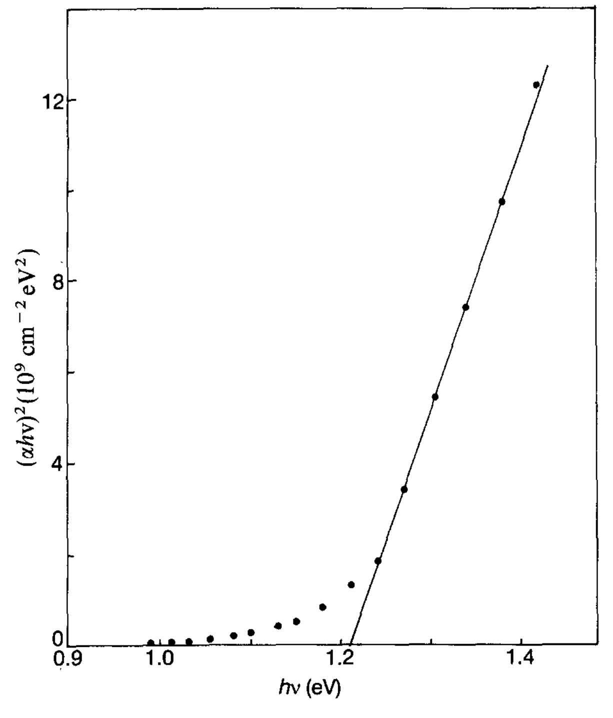

Figure 5 The absorption edge of SnSe film plotted as $(\alpha h\nu)^2$ against the photon energy, $h\nu$.

of (1.21 ± 0.01) eV, which is in good agreement with the reported value for SnSe thin films prepared by other methods [5, 8, 10]. The functional dependence also shows that the transition is a direct allowed one. Because the measurements were made at room temperature, exciton bands are not likely to be present. Moreover, from the value of $\alpha \simeq 10^4$ cm^{-1} it is reasonable to believe that the absorption is due to band to band transitions [19]. Hence, it is concluded that the absorption of reactively evaporated SnSe thin films is due to an allowed direct transition from the top of the valence band to the conduction band minimum at the centre of the Brillouin zone.

4. Conclusion

Polycrystalline stoichiometric SnSe thin films are prepared by reactive evaporation at substrate temperatures ranging from 473–600 K. The grains of the films prepared at substrate temperatures below 525 K have no preferred orientation, while the crystallites of the films prepared at higher substrate temperatures have a strongly preferred orientation on the substrate surface. Optical absorption studies show that the fundamental absorption starts at (1.21 ± 0.01) eV and the transition leading to this is a directly allowed one.

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