INFLUENCE OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF Sb_2S_3 THIN FILMS*

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Sb_2S_3 thin films were prepared by thermal vacuum evaporation technique. The substrate temperature was varied in the range 300-498 K and seems to be one of the most important parameters affecting the physical properties of the films. The structural investigations performed by means of X-ray diffraction (XRD) technique, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) showed that the films deposited at substrate $T_S < 498$ K have an amorphous structure, while those prepared at $T_S = 498$ K have a polycrystalline structure. The optical constants of the deposited films were obtained from the analysis of the experimental recorded transmission spectral data over the wavelength range 500–1400 nm. The values of some important parameters of the studied films (refractive index, n, absorption coefficient, α, and extinction coefficient, k) are determined from these spectra. It has been found that the refractive index dispersion data obeyed the single oscillator of the Wemple-DiDomenico model, from which the dispersion parameters and the high-frequency dielectric constant were determined. The low value of the extinction coefficient (in the order of 10^{-2}) as observed in our films is a qualitative indication of excellent surface smoothness of the films. An analysis of the optical absorption data of deposited films revealed on optical direct transitions with the estimation of the corresponding band gap values. A slight decrease in the direct optical gap from 1.95 eV to 1.77 eV as the substrate increases from 300 to 498 K was observed.

1. INTRODUCTION

Large area thin films semiconductors of antimony trisulfide (Sb_2S_3) can be deposited on metals and glass substrates by thermal vacuum evaporation technique. There are a number of reports on the properties of Sb_2S_3 thin films form prepared by various techniques such as spray pyrolysis [1], electrodeposition [2], chemical

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bath deposition [3–5] and successive ionic layer adsorption and reaction (SILAR) method [6]. However, the basic problem with Sb_2S_3 is to obtain uniformity over a large area and stoichiometry.

The thermal vacuum evaporation technique appears to be a relatively simple method to prepare homogeneous Sb_2S_3 thin films. Extensive research has been done on the deposition and characterization of Sb_2S_3 semiconducting thin films due to their potential application in the area of optoelectronic device fabrication and microwave [7–9]. Sb_2S_3 thin films have good optical transmittance, wide band gap and electrical properties suitable for their application to solar cell fabrication.

In a series of previous papers [10, 11], we have studied electronic transport and some optical properties of Sb_2S_3 thin films deposited at room temperature. In the present paper, the influence of substrate temperature on optical properties of Sb_2S_3 thin films is investigated.

2. EXPERIMENTAL

Antimony trisulfide thin films were deposited onto heated (300–498 K) glass substrate by thermal evaporation under vacuum of polycrystalline powder (purity 99.99 %) of the compound. The evaporation was performed in a vacuum better than 5×10^{-5} Torr, achieved using oil diffusion pump. The Sb_2S_3 compound was thermally evaporated from a quartz crucible, the mouth of which was covered by an insert-baffle containing perforations to prevent sputtering of the material at high evaporation rates. The quartz crucible loaded with Sb_2S_3 powder was thermally heated by activating the low voltage (30 V). The evaporation current ranges from 10 to 15 A. The films thickness was determined by an interferometric method using multiple-beam Fizeau fringe method at reflection of monochromatic light ($\lambda = 550$ nm) and for investigated samples ranged between 1.10 and 1.15 μm.

The structural investigations of the films were performed with a Dron-3 X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å) and means of transmission electron microscopy (TEM). Electron microscope Philips CM-120 operating at 100 kV was used. The surface structure was studied by scanning electron microscopy (SEM) using a Philips SEM 515 electron microscope operating at 30 kV.

Transmission spectra in the spectral domain 400–1400 nm were recorded using a double beam spectrophotometer PMQ II (Carl Zeiss Jena).

3. RESULTS AND DISCUSSION

The films deposited at substrate temperature 300 K up to 498 K showed an amorphous structure, while those deposited at 498 K have a polycrystalline orthorhombic structure by using X-ray diffraction analysis as shown in Fig. 1. The interplanar spacing, $d_{hk\ell}$, with the corresponding $(hk\ell)$ planes and the positions of the peaks are listed in Table 1. The lattice parameters of orthorhombic cell unit were calculated by using the relation

$$d_{hk\ell} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2} \right)^{-1/2} \tag{1}$$

where h, k, ℓ are the Miller indices.

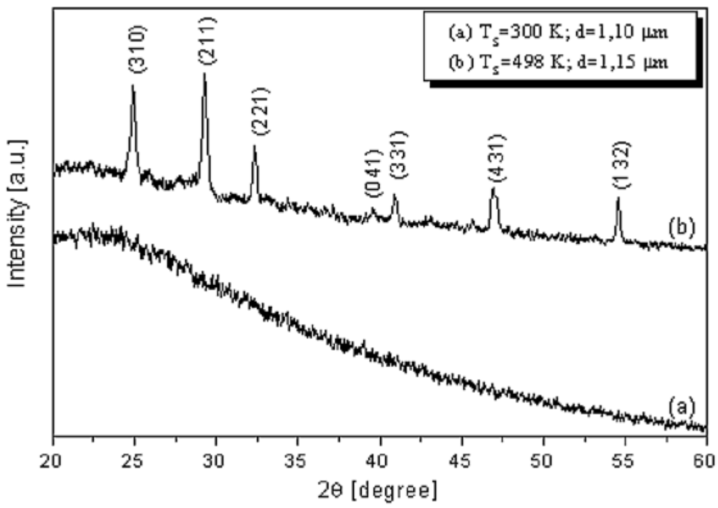

Fig. 1. – XRD patterns for Sb_2S_3 thin films deposited at: (a) T_S = 300 K, (b) T_S = 498 K.

Table 1

Comparison of XRD data for Sb_2S_3 thin film (T_S = 498 K) with standard values

$(hk\ell)$	2θ (deg.)	$d_{hk\ell}$ [Å] (XRD)	$d_{hk\ell}$ [Å] (ASTM)	I (%)
(310)	24.92°	3.554	3.558	100
(211)	29.18°	3.049	3.053	95.52
(221)	32.31°	2.757	2.764	61.03
(041)	39.54°	2.272	2.277	13.30
(331)	40.91°	2.201	2.185	29.77
(431)	46.94°	1.935	1.940	47.69
(132)	54.57°	1.687	1.691	48.88

The calculated lattice parameters are $a = 11.226$ Å, $b = 11.305$ Å and $c = 3.891$ Å. The results are in good agreement with the standard card (ASTM no. 6-674) and the previously reported data for Sb_2S_3 [12].

These results obtained by XRD were confirmed by electron diffraction. The selected area diffraction (SAED) patterns of Sb_2S_3 thin films deposited at 300 K and 498 K are presented in Fig. 2(a) and (b), respectively. The SAED pattern corresponding to the film deposited at 498 K indicates that the film has a polycrystalline structure and can be characterized as the Sb_2S_3 phase of orthorhombic cell unit type, which accords with its XRD pattern in Fig. 1(b).

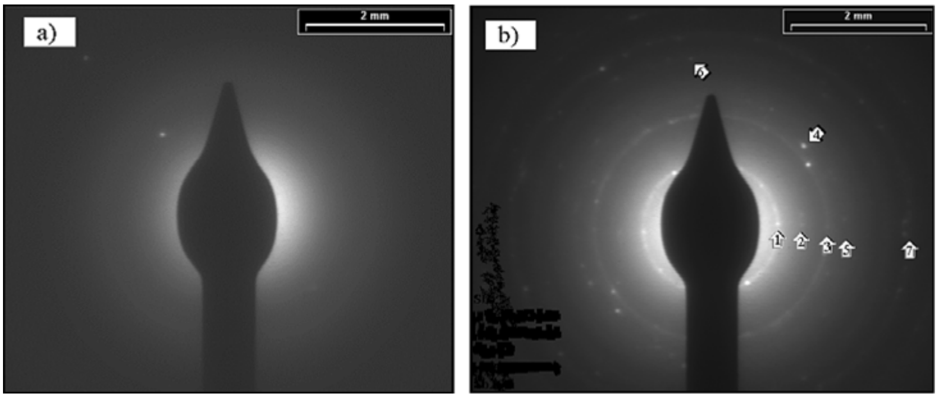

Fig. 2. – SAED patterns for Sb_2S_3 thin films deposited at: (a) $T_S = 300$ K, (b) $T_S = 498$ K.

Further characterization of Sb_2S_3 thin films using SEM proved that the morphologies of film prepared at 300 K and 498 K were amorphous and nanorods, respectively. The SEM micrographs of the Sb_2S_3 thin films are shown in Fig. 3. From the micrograph corresponding to the thin film deposited at 498 K, the average sizes of crystallites are found to be 68 nm.

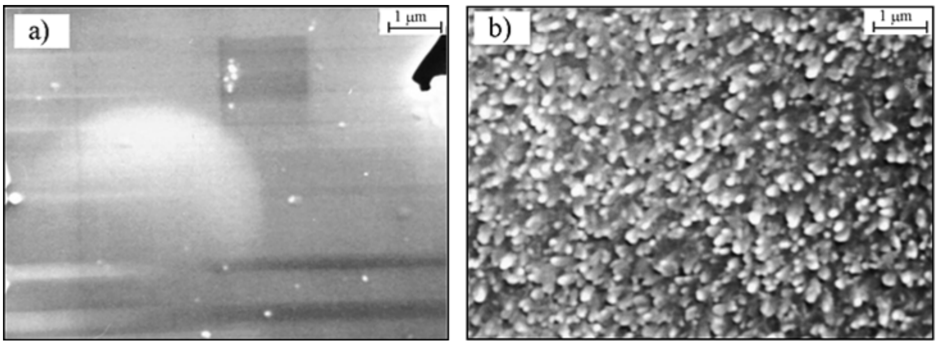

Fig. 3. – SEM micrographs of the Sb_2S_3 thin films deposited at: (a) $T_S = 300$ K, (b) $T_S = 498$ K.

Optical parameters of Sb_2S_3 thin films (refractive index, *n*, absorption coefficient, α, and extinction coefficient, *k*) were calculated from the transmission spectra using Swanepoel's method [13].

The optical transmittance spectra of Sb_2S_3 thin films were recorded in the wavelength range 500–1400 nm. The wavelength dependence of optical transmittance of investigated films deposited at different substrate temperatures is shown in Fig. 4. A shift in the optical absorption edge at low wavelength is apparent between the two curves of the transmission. When the substrate temperature is increased from 300 K to 498 K, the film with polycrystalline structure exhibited low transmittance due to scattering and reflection of light at the grain boundaries [14]. Interference maxima and minima due to multiple reflections on film surfaces can be observed. The appearance of interferences fringes is an indication of the thickness uniformity of the thin films.

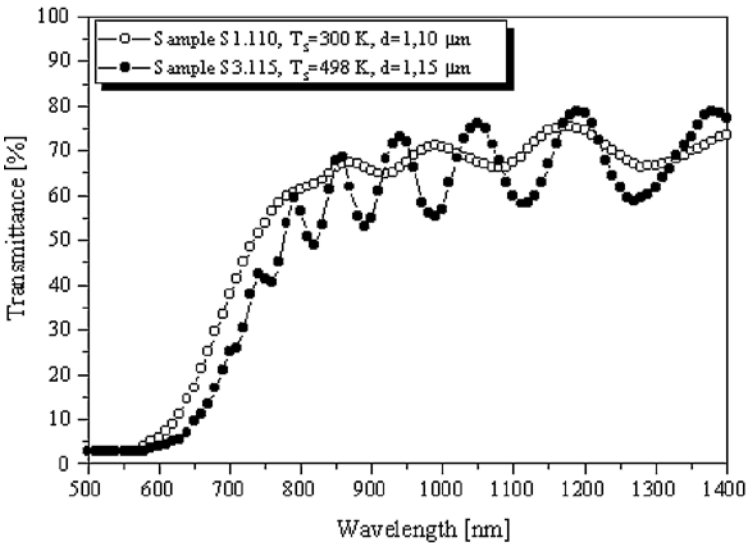

Fig. 4. – Variation of optical transmittance with substrate temperature.

The complex refractive index for the homogeneous film, with uniform thickness, *d*, is defined by the relation $n_c = n - ik$ [15].

The refractive index, *n*, was found from relation [13]

$$n = \left[N + \left(N^2 - n_s^2 \right)^{1/2} \right]^{1/2} \tag{2}$$

with

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \tag{3}$$

where n_s is the refractive index of glass substrate, T_M and T_m are the maximum and minimum values respectively of the transmittance at the same wavelength. The spectral dependence of refractive index, n, for Sb_2S_3 thin films is shown in Fig. 5.

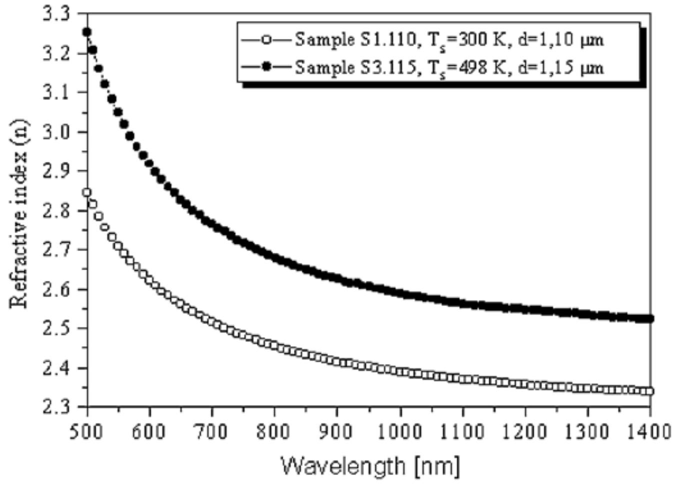

Fig. 5. – Spectral dependence of refractive index, *n*.

The refractive index of polycrystalline films (deposited at 498 K) is found to be higher than that of the amorphous film (deposited at 300 K), which may be due to the change in transmittance.

The absorption coefficient, α, was calculated from relation [13]

$$\alpha = -\frac{1}{d}\ln\left\{\frac{E_M - \left[E_M^2 - \left(n^2-1\right)^3\left(n^2-n_s^4\right)\right]^{1/2}}{\left(n-1\right)^3\left(n-n_s^2\right)}\right\} \tag{4}$$

where

$$E_M = \frac{8n^2 n_s}{T_M} + \left(n^2-1\right)\left(n^2-n_s^2\right) \tag{5}$$

Fig. 6 shows the variation of absorption coefficient with photon energy for amorphous and polycrystalline films of Sb_2S_3. The films possess the characteristic features of optical absorption edge of semiconductors. The absorption coefficient is slightly affected by the change of structure at lower energy values, while the change is observed at higher energy values. This behavior is probably due to the crystallized process of films deposited at 498 K. It is known that intercrystallite boundaries contain structural defects and impurities. These factors have a strong influence on the absorption processes. In

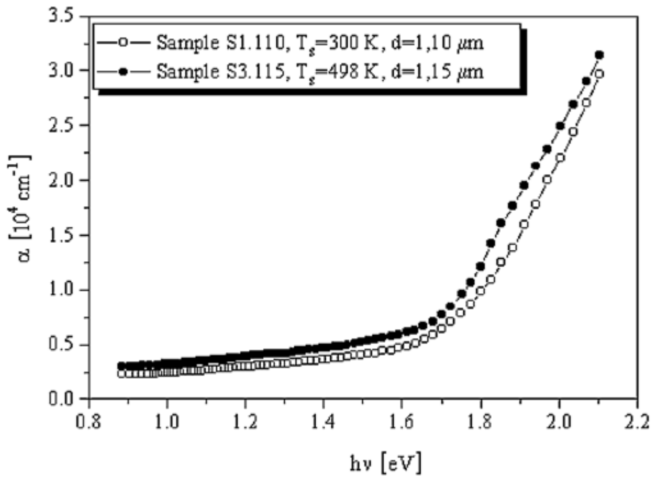

Fig. 6. – The dependence of absorption coefficient, α, on the photon energy, *h*ν.

the polycrystalline film, the intercrystallite boundaries play an important role in optical absorption [16].

The extinction coefficient, *k*, was calculated from relation [13]

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

The dependence of extinction coefficient, *k*, on wavelength, λ, is shown in Fig. 7. When the substrate temperature varies from 300 K to 498 K, the refractive index (at a wavelength λ = 800 nm) varies from 2.45 to 2.68 and the extinction coefficient (at 800 nm) increases from 2.73×10^{-2} to about 3.62×10^{-2}. The low value of extinction coefficient (in the order of 10^{-2}) in visible and infrared region is a qualitative indication of excellent surface smoothness of the Sb_2S_3 thin films [17].

According to a single-oscillator model (Wemple-DiDomenico model [18]), the relation between the refractive index, *n*, and photon energy, *h*ν, can be written as follows

$$n = \left[1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2}\right]^{1/2} \quad (7)$$

where *h* is the Planck constant, ν is the frequency, E_0 is the oscillator energy and E_d is the dispersion energy or the oscillator strength.

By plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ and fitting a straight line as shown in Fig. 8, E_0 and E_d can be determined directly from slope, $(E_0E_d)^{-1}$, and the intercept

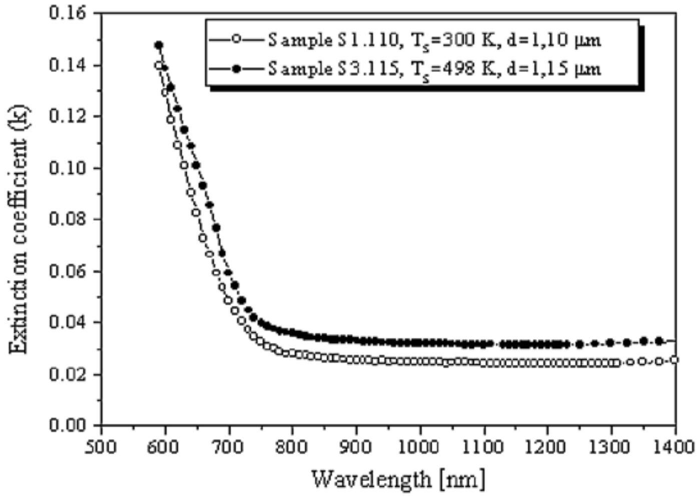

Fig. 7. – Wavelength dependence of extinction coefficient, k.

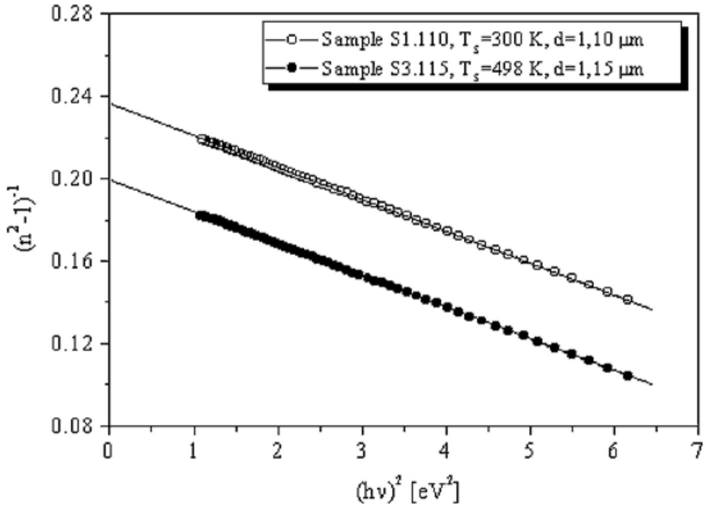

Fig. 8. – Plot of $(n^2 - 1)^{-1}$ against $(h\nu)^2$.

E_0/E_d, on the vertical axis. The oscillator energy, E_0, is an "average" energy gap and is related to the optical band gap, E_g, in close approximation by $E_0 \approx 2E_g$.

Table 2 summarizes the estimated values of the oscillator parameters, E_0, E_d and E_g, the values of refractive index, $n(0)$, for $(h\nu) \to 0$, extrapolated from the Wemple-DiDomenico single oscillator fit and the high-frequency dielectric constant $\varepsilon_\infty = n(0)^2$ [19]. A slight decrease in the direct optical band gap, E_g, from 1.95 eV to 1.77 eV as the substrate of the deposited films increases from 300 to 498 K.

Table 2

The estimated values of the oscillator parameters for Sb_2S_3 thin films

Sample	T_s [K]	d [μm]	E_0 [eV]	E_d [eV]	E_g [eV]	$n(0)$	ε_∞
S1.110	300	1.10	3.91	16.57	1.95	2.28	5.20
S3.115	498	1.15	3.57	18.09	1.77	2.45	6.00

The increased energy band gap of amorphous Sb_2S_3 thin films over those of polycrystalline films is supported by the difference existing in the spectral dependence which suggests that the density of states in the conduction band of the amorphous material is lower, or that the matrix elements for optical transitions are suppressed owing to the lack of long-range order which affect the sensitivity of allowed transitions. The shape and absorption edge depend very much on the conditions maintained during preparation of Sb_2S_3 thin films.

4. CONCLUSIONS

Structural and optical characteristics of Sb_2S_3 thin films prepared by thermal vacuum evaporation technique have been studied. The deposition parameters are optimized to yield uniform and well adhering films. The X-ray diffraction and electron diffraction reveal that the films prepared at 300 K possess an amorphous structure whereas the film prepared at 498 K exhibits a polycrystalline structure. SEM micrographs confirmed this amorphous and polycrystalline nature. The SEM micrograph of polycrystalline structure indicates that the grains are well distributed, homogeneous and finer.

The optical constants (refractive index, n, absorption coefficient, α, and extinction coefficient, k) of Sb_2S_3 thin films were determined by simple straightforward calculations using only the transmission spectra. A slight growth of absorption coefficient is observed when the substrate temperature increases from 300 to 498 K. We consider that the intercrystallite boundaries play a major role in optical absorption. The single oscillator parameters were calculated and discussed in terms of the Wemple-DiDomenico model. The results have shown that band gap energy, E_g, oscillator energy, E_0, and dispersion energy, E_d, are strongly dependent on the substrate temperature. The optical band gap energy of the films decreases from 1.95 eV to 1.77 eV as the substrate temperature varies from 300 to 498 K.

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