Substrate Temperature-Dependent Physical Properties of Thermally Evaporated $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ Thin Films

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Abstract In this work, the homogenous thin films of sulfosalt $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ were successfully synthesized by the thermal evaporation technique onto corning 7059 glass substrates heated at various temperatures in the range of 30–200 °C. The surface morphology and structural characteristics of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films were analyzed by atomic force microscopy, X-ray diffraction, and energy-dispersive X-ray, respectively. The X-ray diffraction analysis revealed that $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films crystallized in monoclinic structure according to a preferential direction ($\bar{6}$ 11). An improvement in the structural properties by increasing the substrate temperature was observed. The values of some important parameters such as absorption coefficient (α), band gap (E_g), refractive index (n), extinction coefficient (k), and dielectric constant (ϵ_∞) of thin film were determined. The absorption coefficient was larger than 10^5 cm^{-1} in the visible range. The electron transition of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films was direct allowed with the values that decreased (2–1.69 eV) by increasing substrate temperature from 30 to 200 °C. The dispersion data obeyed the single oscillator relation of the Wemple–DiDomenico model and Cauchy model. The electrical free carrier susceptibility and the carrier concentration of the effective mass ratio were estimated according to the model of Spitzer and Fan.

KEY WORDS: Thin film; Thermal evaporation technique; X-ray diffraction; Optical parameters

1 Introduction

$\text{Sn}_x\text{Sb}_y\text{S}_z$ sulfosalt has recently attracted a great deal of attention as low-cost alternatives to conventional photovoltaic materials [1, 2]. $\text{Sn}_x\text{Sb}_y\text{S}_z$ combines many advantageous characteristics for optoelectronic applications, such as a suitable band gap (1–1.5 eV), a high optical absorption coefficient (up to 10^5 cm^{-1}), abundant elements, and a

relatively low toxicity. In addition, $\text{Sn}_x\text{Sb}_y\text{S}_z$ films have promising thermoelectric properties [1, 3, 4] and present particular interest as phase-change memory devices [1, 5]. Semiconducting band gaps of sulfosalt were reported by Abdelkader et al. [6], Fadhli et al. [7], Dittrich et al. [2], Boldish et al. [8], and Lomelino [9]. Fadhli et al. [7] have prepared $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films by thermal evaporation and studied the effect of heat treatment in air on the properties of this material. They have shown that the as-deposited $\text{Sn}_2\text{Sb}_2\text{S}_5$ sample is crystallized in spite of low substrate temperature (room temperature) and the optical properties are strongly improved. Numerous sulfosalt compounds are studied and have band gaps close to the optimum value of 1.4 eV for single-junction energy conversion from the solar spectrum [2] indicating a possible application of sulfosalt in thin-film solar cells. The solar cells were prepared using the standard $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cell process, i.e.,

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Mo back contact, *p*-type Sn–Sb–S sulfosalt absorber layer, CdS buffer layer, and *n*-type ZnO window layer. Sulfosalt materials were prepared by adopting various methods such as sonochemical synthesis [10], radio frequency (RF) sputtering [1], sputtering + therm. ann. CBD [2], pulsed laser deposition [11], spray pyrolysis [12], and vacuum evaporation [7, 13]. In our previous researches [6, 7, 13], we have succeeded to synthesize SnSb_4S_7 , SnSb_2S_4 , $\text{Sn}_3\text{Sb}_2\text{S}_6$, $\text{Sn}_2\text{Sb}_2\text{S}_5$, $\text{Sn}_2\text{Sb}_6\text{S}_{11}$, and $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films by single-source thermal vacuum evaporation. $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ is an alternative ternary sulfosalt with high potential for photovoltaic. The aim of this work is to study the effect of substrate temperature on the structural and optical properties of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films grown by vacuum evaporation. In addition, it is intended to establish the optimized experimental substrate temperature to prepare $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ samples with high crystallinity, to assess the potential of this compound and to be used as solar cell absorber. To the best of our knowledge, no report devoting to the preparation of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ with different substrate temperatures has been published to date.

2 Experimental

2.1 Thin Films Preparation

The vacuum thermal evaporation method was used to deposit $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ film on corning 7059 glass substrates (10 mm × 20 mm × 1 mm). In our previous researches [6, 7, 13], stoichiometric amounts of the elements of 99.999% purity Sn, Sb, and S via Bridgman method have succeeded the synthesis of $\text{Sn}_x\text{Sb}_y\text{S}_z$ sulfosalt ingots materials. Crushed powders of these ingots were used as a raw material for the thermal evaporation. Thin films of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ were sublimated by conventional thermal evaporation technique using high vacuum coating system (Model Alcatel). The evaporator system utilizes two pumps to evacuate the high vacuum chamber, which was made of an enclosed bell jar. Powder of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ was used as the evaporation source material. The substrates were placed directly above the source at a distance of 15 cm. The vacuum chamber was evacuated to 1.33×10^{-4} Pa (10^{-6} Torr) before the source was heated. The molybdenum boat was heated using 40 A direct current for 10 s to melt the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$. The current was increased slowly to 90 A until all of the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ evaporated. The films were removed after waiting for a few hours for the chamber to cool down. The films were deposited onto clean corning 7059 glass substrates for optical measurements; the corning 7059 glass substrates were carefully cleaned by chromic acid for 15 min and then rinsed by deionized water. The

material was sublimated from a heated molybdenum boat in a vacuum of 1.33×10^{-3} Pa (10^{-5} Torr). The substrate temperature controlled by a chromel–alumel thermocouple was varied from 30 to 200 ± 5 °C. Substrate heating was performed by an electrical heater. The optimized deposition parameters such as molybdenum boat–substrate distance (10 cm) and evaporation time (20 min) were kept constant. In the end of the evaporation process, the heater was slowly closed, and the glass substrates were given up cooling for 1 h in vacuum. For each substrate temperature, the structure, morphological, and optical properties of the produced films were investigated.

2.2 Experimental Techniques

The crystal structures of the samples were analyzed using a Philips X'Pert X-ray diffractometer in Bragg–Brentano geometry ($\theta/2\theta$) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm and 40 kV, 30 mA) in the range $2\theta = 20^\circ\text{--}70^\circ$. The surface morphology of the films was investigated using the atomic force microscopy (AFM, Veeco model D 3100). The transmittance $T(\lambda)$, the reflectance $R(\lambda)$, and the spectra of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films were measured at normal incidence of light in the spectral range 300–1800 nm using a double-beam spectrophotometer (SHIMDZU model UV 3100S). An uncertainty of 1% was given by the manufacturer for measurements obtained by this spectrophotometer. A glass substrate, such as that used for thin film deposition, was used as a reference for transmittance and reflectance scan. Film thickness was calculated from the positions of interference maxima and minima of reflectance spectra using a standard method [14]. The film thickness was controlled and monitored during the evaporation process by using a quartz crystal sensor (Model, TM-350 MAX-TEK, Inc., USA). The deposited films have a thickness in the wavelength range 400–540 nm.

3 Results and Discussion

3.1 Energy-Dispersive X-ray Analysis

Energy-dispersive X-ray (EDX) analysis was used to determine the elements composition in typical $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin film. The result is shown in Fig. 1. The spectrum of the film deposited at $T_s = 30$ °C shows only S, Sn, and Sb elements, indicating the purity of the synthesized film. This result provides the elemental composition and the average atomic percentage of the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ film deposited at $T_s = 30$ °C, showing a high average atomic percentage of S (54.4%) compared to both Sn and Sb (12.8% and 32.8%).

Fig. 1 EDX measurements of the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at 30 °C

3.2 Structure and Morphologies

3.2.1 Powder X-ray Diffraction

The powder profile of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ material is shown in Fig. 2. The pattern exhibits well sharp and intense peaks, which is a signature of crystalline phase of prepared $\text{Sn}_4\text{Sb}_6\text{S}_{13}$. The powder X-ray diffraction data are indexed to be a monoclinic crystal system. The lattice parameters a , b , c , and β are calculated by using the following relation:

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl}{ac}\cos(\beta)\right)\frac{1}{\sin^2(\beta)} + \frac{k^2}{b^2}}}. \quad (1)$$

The corresponding lattice cell parameters are evaluated: $a = 2.438$ nm, $b = 0.392$ nm, $c = 2.288$ nm, and $\beta = 91.19^\circ$. These results are in good agreement with those in JCPDS Card No. 74-0676 ($a = 2.431$ nm, $b = 0.391$ nm, $c = 2.349$ nm, and $\beta = 94.05^\circ$). The peak

Fig. 2 X-ray diffraction patterns of standard and as-synthesized $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ powder

positions shown in Fig. 2 match well with those in the standard pattern (JCPDS Card No. 74-0676).

3.2.2 X-ray Diffraction of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ Films

Figure 3 shows the XRD patterns of a $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin film at various substrate temperatures. The reflections illustrate a strong peak of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$, corresponding to the $(\bar{6}11)$ plane. The weak $(\bar{4}02)$ diffraction peak of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ appeared at a substrate temperature of 100 °C, and no other peak was detected. Usually, semiconductor materials deposited by thermal evaporation method at room temperature present dominant amorphous component. Figure 3 presents an extraordinary result of the deposited $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ film crystallized in spite of low substrate temperature (room temperature 30 °C). Similar results were also observed by other researchers [6, 7]. All films are preferentially oriented along $(\bar{6}11)$ plane. It is obvious that the intensity of the peak corresponding to $(\bar{6}11)$ plane increases with the rise in the substrate temperature. This behavior shows that with heated substrates the crystalline quality of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ layers is enhanced. To get more structural information by exploiting X-ray diffraction patterns of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ compound, the microstructural parameters, i.e., crystallite size, lattice strain, and dislocation density, have been estimated. The average crystallite size of synthesized samples was calculated by applying the Scherrer's formula:

Fig. 3 X-ray diffraction patterns of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited on glass substrates heated at different temperatures

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where k is a constant (a shape factor whose value is about 0.9), λ is the wavelength of X-ray radiation (0.15405 nm) used, β is the full width at half maximum (FWHM) intensity of the diffraction line, and θ is the diffraction angle. By increasing substrate temperature from 30 to 200 °C, we note that the crystallite sizes of the samples increase from 20 to 48 nm and the FWHM of the ($\bar{6}11$) diffraction peak of samples decreases from 0.41° to 0.17°. This implies that the crystallization degree is improved and indicates that the prepared $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ material contains nano-crystallites. The increase in the grain size is related to the arrangement and coalescence of small grains at low substrate temperature, and because of their limited mobility, the adatoms remain in the substrate where they form smaller nuclei. With increasing substrate temperature, atoms become more mobile, which leads to obtain larger grain size [15]. The lattice strain ε is defined as the disarrangement of lattice created during deposition process and was determined by using the Scherrer's relation [16]:

$$\varepsilon = \frac{\beta}{4 \tan \theta}. \quad (3)$$

The lattice strain values were in the range of 6.38×10^{-4} – 2.65×10^{-4} . We remark that the micro-strain decreases with increasing substrate temperature. This change may be explained by the decrease in concentration of lattice imperfections related to the growth in the grain size.

The dislocation density (δ) is defined as the length of dislocation line per unit volume of crystal. It was calculated from the formula [17]:

$$\delta = \frac{1}{D^2}. \quad (4)$$

The calculated dislocation density varied in the range of 25×10^{14} – 4.33×10^{14} (lin. m⁻²) and is decreasing with increasing substrate temperature. This result indicates that the layers become more relaxed due to reduction in defects in the structure. This suggests the improvement in film crystallinity by increasing substrate temperature. The number of crystallites per unit area can then be evaluated using the following relation [18]:

$$N = \frac{t}{D^3}. \quad (5)$$

where t is the film thickness. The estimated number of crystallites per unit area is varied between 67.2×10^{15} and 3.6×10^{15} per unit area with substrate temperature. This increase can be attributed to grain agglomeration. First, at low substrate temperature, the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films are composed of large number of small grains. Then, by

increasing substrate temperature the small grains become greater. The calculated values of microstructural parameters are summarized in Table 1. It is clearly observed that substrate heat treatments improve the crystallinity of films.

3.2.3 AFM Analysis

Figure 4 shows two-dimensional (2D) and three-dimensional (3D) surface morphology images of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at different substrate temperatures. The scanning area was $1.0 \mu\text{m} \times 1.0 \mu\text{m}$ in tapping mode. The root-mean-square roughness (RMS) and the grain size were determined by using standard software (WS × M 5.0 software) [19]. It is clearly observed that the films deposited at various temperatures showed different surface roughnesses. The films deposited at room temperature and at 60 °C show a dense and smooth surface due to poor crystallinity. However, at substrate temperature higher than 100 °C the surface becomes homogeneous and constituted of densely packed grains. The crystallites have spherical form and uniform distribution. The AFM measurements indicate that the RMS of all samples increases from 2.81 to 8.23 nm. This is caused by the rise in substrate temperature from 30 to 200 °C (Table 1). The surface roughness of the films was also evaluated by using an optical method based on the spectrophotometric data following this formula ($\sigma \ll \lambda$) [20]:

$$\frac{R_S}{R_T} = \exp \left[- \left(\frac{4\pi\sigma}{\lambda} \right)^2 \right] + \left[1 - \exp \left[\left(\frac{4\pi\sigma}{\lambda} \right)^2 \right] \right] \times \left[1 - \exp \left[- \left(\frac{\beta\pi\sigma}{u\lambda} \right)^2 \right] \right]. \quad (6)$$

where R_S is the specular reflection, R_T is the total reflection of the films, and σ , μ are the average roughness of the irregularities, respectively, the highest and the lowest. The total reflection R_T equals the sum of R_S and R_{diff} (diffuse reflection). The diffuse and the specular reflection data of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films were measured by a UV–visible–NIR spectrophotometer in the spectral range of 300–1800 nm. Equation (6) is formed by two terms. The first defines the coherent part of reflection, while the second term represents the incoherent part. If the second term is negligible, a new expression of the relation (7) is obtained [21]:

$$\ln \left(\frac{R_S}{R_T} \right) = - \frac{(4\pi\sigma)^2}{\lambda^2} + A. \quad (7)$$

where A is a constant from the spatial fluctuations of the optical constants. Thus, by plotting $\ln(R_S/R_T)$ versus $\frac{1}{\lambda^2}$, the RMS values of the surface roughness of layers were calculated. The obtained values are given in Table 1. It is observed

Table 1 Structural parameters and surface roughness of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films deposited at different substrate temperatures

T_s (°C)	FWHM (°)	Crystallite size, L (nm)	Strain $\varepsilon \times 10^{-4}$	Number of crystallites per unit area (10^{15} N)	Dislocation density $\delta \times 10^{14}$ (lin. m^{-2})	Roughness (nm)	
						AFM	Optical
30	0.41	20	6.38	67.2	25.00	2.81	4.08
60	0.36	22	5.62	37.9	19.15	3.76	4.36
100	0.35	23	5.50	35.9	18.53	4.53	4.77
140	0.29	28	4.55	16.8	12.54	5.84	6.30
170	0.29	29	4.40	18.4	12.05	6.95	7.21
200	0.17	48	2.65	3.6	4.33	8.23	8.43

Fig. 4 2D and 3D AFM micrographs ($1 \mu\text{m} \times 1 \mu\text{m}$) of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited on glass substrates heated at different temperatures

that the estimated value of the surface roughness from both methods increases with increasing heating substrate. Thus, with increasing substrate temperature, the defects decrease and grain sizes become larger so crystallinity is improved. This result agrees with the XRD observation.

3.3 Optical Studies

3.3.1 Optical Transmittance and Reflectance Spectra

Figure 5a, b shows the typical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films grown at

different substrate temperatures in the wavelength range of 300–1800 nm. It is clear that all films exhibit two distinct slopes. The first one (900–1800 nm) is commonly named the transparency zone in which multitude interference fringes are seen showing fairly homogenous films. In this region, all films exhibit a good transparency (70%–80%) in the visible and infrared regions. However, a small decrease in the transmission by increasing the substrate temperature was observed in the spectral range 900–1800 nm. The second region (300–900 nm) is well known by the zone of high absorption. In this spectral region, the signal is strongly reduced at the band edge, especially at 200 °C. In

Fig. 5 Optical transmission **a** and reflection **b** spectra of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited on glass substrates heated at different temperatures

this spectral range, an increase in the rate values of reflection of 30% for substrate temperature of 200 °C was also observed, which can be explained by a decrease in the absorption phenomena reducing the performance of this material in this region.

3.3.2 Absorption Coefficients, Energy Gap, and Refractive Index

The optical absorption coefficient was evaluated from the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ data by using the following formula [22, 23]:

$$\alpha = \frac{1}{d} \ln \left(\frac{(1-R)^2}{T} \right). \quad (8)$$

where d is the film thickness. Figure 6 shows the dependence of the absorption coefficient on photon energy for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films deposited at different substrate temperatures. It can be seen that all the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films have relatively high absorption coefficients which are higher than 10^5 cm^{-1} in the visible and the near-IR spectral regions. This result is very important because the spectral dependence of the absorption coefficient affects the solar cell conversion efficiency in photovoltaic applications. The dependence of the absorption coefficient on photon energy is analyzed in the high absorption regions to achieve detailed information about the energy band gaps. The absorption coefficient and photon energy can be related by applying the model postulated by Tauc [24], Davis and Mott [25] independently:

Fig. 6 Absorption coefficient α of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited on glass substrates heated at different temperatures

$$(\alpha h\nu)^n = A(h\nu - E_g). \quad (9)$$

where A is a constant, E_g is the optical band gap, h is the Planck constant, and n is an index that characterizes the optical absorption process. In theory, n equals 1/2, 2, 3, and 3/2 for indirect allowed, direct allowed, indirect forbidden, and direct forbidden transition, respectively. In Fig. 7, $(\alpha h\nu)^2$ versus $h\nu$ is plotted in order to extract direct band

gap values by extrapolating the linear regions of $(\alpha h\nu)^2$ to the horizontal photon energy axis. The direct band gap energy tends to decrease from 2.03 to 1.69 eV with increasing substrate temperature. Figure 8 shows the variation of optical band gap E_g versus substrate temperature. The decrease in E_g to 1.69 eV by increasing substrate temperature may be explained by the enhancement of crystallite size and the decrease in defects [2]. This result was proved by many other studies of $\text{Sn}_3\text{Sb}_2\text{S}_6$, SnSb_4S_7 , and $\text{Sn}_2\text{Sb}_6\text{S}_{11}$ deposited by the same technique and in the same condition [26, 27]. Due to the existence of the interference patterns, this exhibits several maxima and minima as the wavelength increases, and the method of Swanepoel [28, 29] was used to calculate the refractive index n . The method is based on the approach of Manifacier et al. [30]. This approach offers a creation of upper and lower envelope for transmission spectrum beyond the absorption edge. The refractive index can then be calculated from the relation [28, 29]:

$$n = \left\{ N + (N^2 - n_s^2)^{1/2} \right\}^{1/2}. \quad (10)$$

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2}. \quad (11)$$

where n_s is the refractive index of glass substrate. T_M and T_m are the values of the envelope at the wavelengths where the upper and lower envelopes and the experimental transmittance spectrum are tangential, respectively. The variations of refractive index n versus wavelength of the $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films deposited at different substrate temperatures are shown in Fig. 9. As observed, the refractive index is influenced by

Fig. 7 Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited on glass substrates heated at different temperatures

Fig. 8 Variation of band gap energy E_g versus substrate temperature for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films

substrate temperature and shows normal dispersion behavior. Indeed, n decreases with increasing wavelength of incident photon and tends to be constant at higher wavelengths. The dispersion spectra of refractive index were fitted using the Cauchy formula [31]:

$$n(\lambda) = n_0 + \frac{A}{\lambda^2} + \frac{B}{\lambda^4}. \quad (12)$$

where A and B are the Cauchy's parameters and λ is the wavelength of light used. For $\lambda \rightarrow \infty$, the significance of the n_0 appears immediately as n_∞ . Figure 9 shows the variation of n with Cauchy fitting for as-deposited $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films at different substrate temperatures. It is clear that the values of n for all the investigated samples obey the Cauchy law. The values of fit parameters and n_0 are presented in Table 2. There is a good correlation between refractive index and optical band gap of semiconductors, where typically, n increases as E_g decreases. The same result is obtained by others study of SnSbS thin films grown by vacuum evaporation method [7]. Since E_g decreases with substrate temperature, the temperature dependence of n arises from the variation of E_g with the substrate temperature which can be correlated to the improvement in film crystallinity. Therefore, energy band gap decreases and refractive index increases with decreasing substrate temperature, which can be related to the film crystallization [32]. The refractive index dispersion has an important role in the research for optical materials due to a significant factor in optical communication and in designing devices for spectral dispersion. The dispersion

Fig. 9 Variation of refractive index n vs wavelength and the fit with Cauchy's formula for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at different substrate temperatures

Table 2 Results concerning Cauchy parameters and refractive index $n(0)$ at zero photon energy

T_s (°C)	A (nm^{-2})	B (10^{12} nm^{-4})	n_0 (Cauchy)	$n_{\text{(H-V)}}$
30	-119,842	0.36	2.59	2.58
60	-772,309	1.05	3.18	3.04
100	-1,268,800	1.38	3.54	3.24
140	-1,501,720	1.41	3.90	3.53
170	-792,455	2.23	3.38	3.39
200	-958,282	1.48	3.50	3.33

was analyzed using the model of single oscillator and can be expressed by the Wemple–DiDomenico relationship as follows [33, 34]:

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (13)$$

where $h\nu$ is the photon energy, n is the refractive index, E_0 is oscillator energy, and E_d is the dispersion energy. E_d allows evaluating the average force inter-band optical transition. Wemple and DiDomenico have related this parameter to the coordination number for anion and the valence electron number per anion. E_0 and E_d values are obtained from the intercept E_0/E_d and the slope $(E_0 E_d)^{-1}$ by extrapolating the curve representing the plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ (Fig. 10). The refractive index $n(0)$ at zero photon energy, which is defined by the infinite wavelength dielectric constant, can be deduced from the dispersion

Fig. 10 Plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at different substrate temperatures

Fig. 11 Plot of ϵ_r versus λ^2 for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at different substrate temperatures

relationship by extrapolation of the linear part $(n^2 - 1)^{-1}$ versus $(h\nu)^2$. The values of n_0 found by the Cauchy fitting and the Wemple–DiDomenico model are in good agreement. Dielectric constants are linked to the refractive index n and allow us to further analyze the optical properties of samples. The dependence of refractive

index n on the real dielectric constant is expressed by the Spitzer–Fan model [35]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{\pi c^2 m^*} N \lambda^2. \quad (14)$$

where ε_∞ is the high-frequency dielectric constant in the absence of any contribution from free carriers, N/m^* is the ratio of the carrier concentration to the effective mass, c is the speed of light, and e is the electronic charge. ε_∞ and N/m^* were deduced from plotting ε_r versus λ^2 (Fig. 11) and fitting to a straight line. It is important to compare the values of ε_∞ achieved from the Wemple–DiDomenico model (Fig. 10) with that obtained from the Spitzer–Fan model (Fig. 11). Indeed, the two models show satisfactory agreement. On the other hand, the electrical susceptibility χ_e owing to the inter-band transitions of free carriers can be obtained from the optical constants and is determined as:

$$\frac{e^2}{\pi c^2 m^*} N \lambda^2 = -4\pi\chi_e. \quad (15)$$

Plots of $-4\pi\chi_e$ versus photon energy λ^2 for the deposited $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films are shown in Fig. 12. The figure depicts that χ_e increases in magnitude with the wavelength and becomes sufficiently large to reduce the refractive index and dielectric constant in the near-infrared region. A good fit to a straight line is seen from which the free carrier susceptibility values at the extremes of the investigated range were estimated. All the results determined from the two models for both samples are summarized in Table 3.

4 Conclusion

$\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films were successfully evaporated on heated glass substrate by vacuum evaporation method. The substrate temperatures were varied in the range of 30–200 °C. From the powder X-ray diffraction study, it was observed that prepared material belongs to monoclinic crystal system and the corresponding lattice cell parameters are evaluated: $a = 2.438$ nm, $b = 0.392$ nm, $c = 2.288$ nm, and $\beta = 91.19^\circ$. X-ray diffraction analyses showed that the as-deposited $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films have a polycrystalline structure. All films are oriented along the $(\bar{6}11)$ plane, and the corresponding peak becomes more intense and very sharp by increasing the substrate temperature. Optical absorption measurements indicate that the absorption mechanism is due to direct transitions for the as-deposited films. The corresponding values of optical energy gap (E_g) are decreased from 2 to 1.69 eV with increasing substrate temperature from 30 to 200 °C. Also, the absorption coefficients are higher than 10^5 cm^{-1} in the visible range. In this work, the results have shown that the optical parameters E_d , E_0 , n_0 , ε_∞ , N/m^* , χ_e , and Cauchy parameters A , B are influenced by substrate temperature change. This confirms the effect of substrate temperature on the density of localized states and microstructure of the tested $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ films.

Fig. 12 Plot of $-4\pi\chi_e$ versus λ^2 for $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films deposited at different substrate temperatures

Table 3 Values of the dispersion energy (E_d), oscillator energy (E_0), ratio of the carrier concentration to the electron effective mass (n/m^*), the lattice dielectric constant (ε_∞), and electrical susceptibility χ_e as a function of substrate temperature of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ thin films

T (°C)	E_0 (eV)	E_d (eV)	E_0/E_g (eV)	N/m^* (10^{18} cm^{-3})	ε_∞^S	ε_∞^W	$-\chi_e$ (10^{-2})
30	2.15	10.16	1.06	3.24	7.56	5.72	1.19–07.40
60	1.91	12.35	0.96	4.17	10.30	7.46	1.51–09.71
100	1.86	13.03	0.99	2.31	11.22	8.00	0.87–05.41
140	1.85	13.8	1.01	1.14	12.72	8.45	0.55–02.46
170	1.48	10.69	0.83	6.70	13.34	8.22	4.29–14.96
200	1.74	12.70	1.00	5.91	12.27	8.29	3.18–13.37

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