Determination and Analysis of Optical Constant of Annealed $\text{Sn}_2\text{Sb}_2\text{S}_5$ Thin Films

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Abstract The effects of annealing on structural, optical and electrical properties of $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films were studied. $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films were deposited on no-heated glass substrates by single source vacuum evaporation method. The as-deposited films were annealed in air for 1 h at 100, 200 and 300 °C. XRD study shows that annealed films are crystallized according to the preferential orientation (602). Optical measurements show that the thin films have relatively high absorption coefficients in the range of 10^5 – 10^6 cm^{-1} in the energy range of 2–3.25 eV. It is also found that $\text{Sn}_2\text{Sb}_2\text{S}_5$ exhibit two optical direct transitions. The models of Wemple–DiDomenico and Spitzer–Fan were applied for the analysis of the dispersion of the refractive index and the determination of the optical and dielectric constants. The electrical resistivity measurements are recorded, and two activation energy values are determined. The layers annealed at 200 and 300 °C exhibit a resistive hysteresis behavior. The properties reported here offer perspective to $\text{Sn}_2\text{Sb}_2\text{S}_5$ for its application in many advanced technologies.

KEY WORDS: $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films; Optical constants; Electrical properties

1 Introduction

Solar energy becomes a promising source of energy nowadays. Thin films play a vital role in photovoltaic applications due to its potential reduction in costs. In fact, its material consumption is low in comparison with silicon wafer technology [1]. For the last few years, sulfosalts thin films are found to be interesting candidates for solar cells. They are good absorber, abundant, cheaper and comparatively less toxic, and they have favorable band gap and high absorption coefficient [2–4]. Recently, many studies were reported and considerable efforts have been done to gain better understanding of the structural, optical and

electrical properties of the Sn–Sb–S ternary compounds [5–9] which have interesting optoelectronic characteristic that can also be used in thermoelectric energy conversion [4]. Among these compounds, the material $\text{Sn}_2\text{Sb}_2\text{S}_5$ in the thin films was prepared by sputtering [10] and thermal evaporation [11] and showed interest physical properties.

This work deals with the study of the dispersive optical constants and electrical properties of $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films deposited by thermal vacuum evaporation in terms of air annealing.

2 Experimental

The initial ingot of the material $\text{Sn}_2\text{Sb}_2\text{S}_5$ was prepared by the horizontal Bridgman method [11]. The thin films were deposited onto no-heated glass substrates from $\text{Sn}_2\text{Sb}_2\text{S}_5$ powder by vacuum evaporation. The pressure during evaporation was maintained at 10^{-4} Pa. The as-deposited films were annealed in air for 1 h at 100, 200 and 300 °C.

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The annealing process was done in a programmable furnace (Nabertherm–Allemagne).

The crystalline phase and crystal orientation of the prepared films were examined using Phillips X'Pert X-ray diffractometer with CuK_α radiation ($\lambda = 0.154056 \text{ nm}$). Optical transmittance and reflectance spectra were measured at room temperature and at normal incidence with UV–VIS–NIR Shimadzu 3100S spectrophotometer in the wavelength range 300–1800 nm. Film resistance was measured using gold contact. The type of conductivity was determined by the hot probe method [12].

3 Results and Discussion

3.1 Structural Study

Figure 1 shows the X-ray diffraction (XRD) patterns of $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films before and after annealing at different temperatures. As seen in Fig. 1, the as-deposited film reveals an amorphous nature whereas the films annealed are polycrystalline having the orthorhombic structure. It is confirmed by comparing the peak positions (2θ) of the XRD pattern of the films with the standard X-ray powder diffraction data file (JCPDS 44-0829). For higher annealing temperatures, the peak (602) attributed to $\text{Sn}_2\text{Sb}_2\text{S}_5$ became sharp, which proves a good crystallinity. Indeed, the crystallinity of the films increases with the increase in annealing temperature. This result was confirmed by others researchers for this material and others compounds [13–15]. Figure 1 also shows the presence of (002) line characteristic of the Sb_2O_4 oxide [16].

The crystallite sizes of the thin films were calculated from the most intense broadening of the (602) peaks using Scherrer's formula [17]:

Fig. 1 XRD patterns of $\text{Sn}_2\text{Sb}_2\text{S}_5$ films as-deposited and annealed at different temperatures

$$D = 0.9\lambda/(\beta \cos \theta), \quad (1)$$

where λ is the X-ray wavelength, β is the full-width at half-maximum (FWHM) measured in radian, and θ is Bragg angle.

The lattice strain ε was calculated by using the Scherrer's relation [17]:

$$\varepsilon = \beta/(4 \tan \theta). \quad (2)$$

The origin of the strain is probably related to the lattice imperfections which decrease when the grains sizes rise [18]. The dislocation density (δ) defined as the length of dislocation lines per unit volume of the crystal was evaluated by the formula [19]:

$$\delta = 1/D^2. \quad (3)$$

The microstructural parameters have been given in Table 1. It is well known that the particle size depends on evaporation conditions like evaporation pressure, deposition time, substrate temperature, film thickness and annealing temperature [20]. From Table 1, it can be observed that the average grain size values increase with annealing temperature to improve the crystallization of the thin films. This result was proved by many other studies [21, 22]. Nevertheless, both the crystal strain and the dislocation density decrease with increasing the annealing temperature from 100 to 200 °C. For the film annealed at 300 °C, the decrease in the grain size is probably due to the presence of secondary phase which in turn increases the internal strain and the dislocation density [23].

3.2 Optical Properties

3.2.1 Transmittance and Reflectance Spectra

Figure 2a and b show the typical transmittance and reflectance spectra of the films before and after annealing in air, in the wavelength range 300–1800 nm. The thin films show a highly optical transparency. The maximum amplitude of the transmittance is about 80%. It is noted that the transmittance decreases for the annealing temperatures 100 and 200 °C and then it rises which is probably related to the presence of the secondary phase Sb_2O_4 .

Table 1 The estimated values of the microstructural parameters of $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

T (°C)	D (nm)	ε	δ (10^{-16} m)
As-deposited	16	0.35	35.46
100	40	0.06	6.09
200	41	0.05	5.72
300	35	0.08	8.02

Fig. 2 Transmittance **a**, reflectance spectra **b** of $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

$\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films exhibit interference pattern in the spectral region of low absorption with a sharp fall in transmittance at the fundamental absorption band edge. This sharp edge corresponds to electron excitation from the valance band to the conduction band and is interrelated to the nature and value of the optical band gap.

3.2.2 Absorption Coefficient and Energy Band Gap

The optical absorption coefficient α of the investigated films is evaluated from the experimental data of transmittance and reflectance in strong absorption region using the relation [24]:

$$\alpha = (1/d) \ln[(1 - R)^2 / T], \quad (4)$$

where α is the absorption coefficient and d is the film thickness, R and T are the reflection and transmission coefficients, respectively.

Figure 3 shows the absorption coefficients versus the photon energy for the thin films annealed at different temperatures. It can be seen that the films have relatively high absorption coefficients with maximum values in the range 10^5 – 10^6 cm^{-1} in the visible and near-IR spectral range. This result is very important because it is known that the spectral dependence of the absorption coefficient affects the solar conversion efficiency [25]. The absorption coefficient α can be related to the energy gap E_g by applying the model postulated by David and Mott [26]:

$$(\alpha h\nu) = A(h\nu - E_g)^q, \quad (5)$$

where A is a constant, h is the Planck constant, ν is the frequency of the incident beam, and n is equal to $1/2$ to a direct gap. Plotting of $(\alpha h\nu)^2$ versus photon energy $h\nu$ yields a straight line indicating direct optical transition (Fig. 4).

Fig. 3 Absorption coefficient spectra of $\text{Sn}_2\text{Sb}_2\text{S}_5$ films as-deposited and annealed at different temperatures

The energy gap values E_g are in the range 1.29–1.79 eV. This result was found by others researchers [10, 11]. It can be seen in Fig. 5 that another optical direct transition was found for the annealing temperature 300 °C which corresponds to the Sb_2O_4 phase [16].

3.2.3 Refractive Index

Due to the existence of the interference patterns, the method of Swanepoel was used to calculate the refractive index n from the relation [27, 28]:

$$n_c = \sqrt{N + \sqrt{N^2 + n_s^2}}, \quad (6)$$

$$N = 2n_s(T_m - T_m)/T_m T_m + (n_s^2 + 1)/2, \quad (7)$$

here n_s is the refractive index of the glass substrate. T_m and T_m are the values of the envelope at the wavelengths where

Fig. 4 Plot of $(\alpha hv)^2$ versus $h\nu$ for $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

Fig. 5 Plot of $(\alpha hv)^2$ versus $h\nu$ for the Sb_2O_4 phase for the $\text{Sn}_2\text{Sb}_2\text{S}_5$ film annealed at 300 °C

the upper and lower envelopes and the experimental transmittance spectrum are tangential. The spectral distribution of refractive index is shown in Fig. 6. The refractive index has been found to decrease with the increase in the wavelength. This decrease may be correlated with the increase in the transmittance and decrease in the absorption coefficient. The refractive index n is found to rise by increasing the annealing temperature from 100 to 200 °C. This result is probably due to the increase in the compactness and the crystallite size of the films [29]. For 300 °C, the refractive index decrease because of the formation of the Sb_2O_4 oxide.

3.2.4 Evaluation of Material Characteristic Energies

The dispersion refractive index was analyzed using the model of the single oscillator of Wemple–DiDomenico [30]:

Fig. 6 The variation of the refractive index, n with the wavelength λ for $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

$$n^2(h\nu) = 1 + [E_o E_d / (E_o^2 - (h\nu)^2)], \quad (8)$$

where $h\nu$ is the photon energy, E_o is the oscillator energy, and E_d is the dispersion energy. E_d is a measure of the average strength of the interband optical transitions. E_o defines the average energy gap usually considered as the energy separation between the centers of both the conduction and the valence bands. The values of E_d and E_o are obtained from the intercept and the slope resulting from the extrapolation of the curve of Fig. 7 representing plots of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$. It is noticed that E_o decreases by increasing the annealing temperature from 100 to 200 °C (Table 2). The variation of this parameter is usually associated with the evolution of the thin film microstructure such as it is related to the coordination number for anion and the valence electron number per anion [31].

Fig. 7 Plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

Table 2 The estimated values of the optical parameters of Sn₂Sb₂S₅ films annealed at different temperatures

T (°C)	E_{g1} (eV)	E_{g2} (eV)	E_0 (eV)	E_d (eV)	ε_∞	N/m^* (10^{48} cm ⁻³)
As-deposited	1.72	1.99	2.66	11.11	6.51	4.61
100	1.62	2.01	2.76	12.27	9.79	3.17
200	1.29	1.60	1.88	14.92	11.72	0.47
300	1.79	2.07	2.55	12.34	7.18	2.26

3.2.5 High-Frequency Dielectric Constant and Carrier Concentration

The dependence of the refractive index n on the real dielectric constant is given by the Spitzer–Fan model [32]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_\infty - (Ne^2\lambda^2/\pi c^2 m^*), \quad (9)$$

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. The values of ε_∞ and N/m^* were deduced from the extrapolation of the plots of ε_r versus λ^2 to $\lambda^2 = 0$ and from the slope of the graphs (Fig. 8).

It is noted that when the annealing temperature increases from 100 to 200 °C, ε_∞ increases then decreases for 300 °C. All the results determined from the optical models are summarized in Table 2.

3.3 Electrical Properties

3.3.1 Resistance Measurements

The electrical properties of the thin films are required for the optimization of the preparation conditions to use the material as an absorber in solar cell. Electrical

characterization of Sn₂Sb₂S₅ films annealed in air at different temperatures was carried out using gold contact. The type of electrical conduction is verified using the hot probe method. All films were highly compensated. The variation of resistivity as a function of temperature during annealing indicated that the films annealed at the temperatures lower than 200 °C have a high resistivity and no phase transition occurs between the measured temperatures intervals. For the temperatures 200 and 300 °C, Fig. 9a and b show the resistivity–temperature curve of the Sn₂Sb₂S₅ thin films. It can be clearly seen that an extremely sharp insulator (I) to semiconductor (SC) phase transition occurred between two critical temperatures T_I and T_{II} . This transition is characterized by a high resistivity ratio and a rectangular shape hysteresis loop [33]. It is associated with a change in the microstructure parameters specially an increase in strain and also with a variation in optical properties. It is also noticed that the transition width ($T_{II}-T_I$) decreases with increasing annealing temperature. This result is probably due to the presence of the Sb₂O₄ oxide.

3.3.2 Activation Energy

Due to polycrystalline nature, Sn₂Sb₂S₅ thin films annealed in air at various temperatures generally have a number of lattice defects such as interstitials and vacancies which influence the performance quality of the absorber.

The analysis of the defects in Sn₂Sb₂S₅ thin films was carried out by an examination of activation energies obtained using the relation [34, 35]:

$$\sigma(T) = \sigma_0 \exp(-\Delta E/kT), \quad (10)$$

where σ_0 is a parameter depending on the semiconductor nature, k is the Boltzmann constant, and ΔE is the thermal activation energy. The electrical conductivity as a function of inverse of temperature of annealed samples is given in Fig. 10a and b.

There are two linear regions in the plots. The corresponding activation energies ΔE_1 related to the intrinsic region and ΔE_2 which corresponds probably to the impurity scattering region [36] are determined. Table 3 shows that the annealing temperature affects the activation energies values. This result is found by others researchers [37, 38]. This fact is probably due to the alteration of the distribution of trapping sites caused by the presence of oxygen [39].

Fig. 8 Plot of ε_r versus λ^2 for Sn₂Sb₂S₅ films annealed at different temperatures

Fig. 9 Variation of the resistivity with the annealing temperatures for the $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at 200 °C **a**, 300 °C **b**

Fig. 10 Plots of $\ln \sigma$ versus $10^3/T$ for the $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at 200 °C **a**, 300 °C **b**

Table 3 The estimated values of the activation energies of $\text{Sn}_2\text{Sb}_2\text{S}_5$ films annealed at different temperatures

T (°C)	ΔE_1 (eV)	ΔE_2 (eV)
200	0.07	0.75
300	0.10	0.80

4 Conclusions

$\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films were deposited by the vacuum evaporation method. The thin films were annealed in air at the temperatures in the range 100–300 °C. Their crystallinity was shown to improve considerably through annealing. The analysis of the optical absorption spectra revealed two direct allowed transitions. The E_{g1} and E_o values decreased whereas the refractive index n of the films increased by increasing the annealing temperature from 100 to 200 °C. The layers annealed at the temperatures

greater than 100 °C exhibit a resistive hysteresis behavior characterized by a sharp and rapid phase transition, a high electrical resistance ratio between the insulating and the semiconductor phase and a rectangular shape hysteresis loop. We have noted that the temperature of annealing can be used to modify the properties of $\text{Sn}_2\text{Sb}_2\text{S}_5$ thin films because they depend on the deposition parameters.

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