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Optical and dispersion parameters of co-evaporated $SnS_{0.7}Se_{0.3}$ thin films

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ABSTRACT

Tin sulfoselenide ($SnS_{1-x}Se_x$) is a novel ternary semiconductor that belongs to the IV – VI group of compounds. It possesses the properties of both SnS and SnSe, which are proved as good absorber materials for solar cell fabrication. In the present work, $SnS_{0.7}Se_{0.3}$ thin films were deposited by vacuum co-evaporation technique at four different substrate temperatures (T_s), 200 °C, 250 °C, 300 °C and 350 °C. The optical properties of as-deposited $SnS_{0.7}Se_{0.3}$ films were analyzed using optical measurements. From the optical transmittance and reflectance data, the band gap energy of the layers was determined that varied in the range, 1.59–1.46 eV. The other optical parameters such as skin depth, refractive index, extinction coefficient, optical conductivity and dielectric constant of $SnS_{0.7}Se_{0.3}$ layers were determined and discussed as a function of substrate temperature. Moreover, the dispersion parameters of the layers were also evaluated using Wemple – DiDomenico (WDD) single oscillator model. The dispersion energy (E_d) and oscillator energy (E_o) of the films were evaluated and varied in the range, 2.19–2.38 eV and 7.55–9.52 eV respectively. Moreover, the optical dispersion moments (M_{-1} and M_{-3}) were also calculated that were varied from 0.25 to 0.29 and from 2.76×10^{-3} to 5.08×10^{-3} respectively.

Selection and peer-review under responsibility of the scientific committee of the 3rd International Conference on Solar Energy Photovoltaics.

1. Introduction

Tin chalcogenide semiconductors of IV-VI group have attracted considerable interest of researchers because of their distinct properties suitable for wide range of applications in optoelectronics, photovoltaics, storage devices and other semiconductor devices, since its constituent elements are abundant, inexpensive and less toxic [1]. Among various tin chalcogenide materials, tin sulfoselenide (SnSSe) has received more attention recently, due to its tunable physical properties. SnSSe is a p-type semiconductor mostly crystallizes in orthorhombic structure and its band gap energy can be varied in the range, 1.0 – 1.5 eV for absorbing a major portion of solar energy [2]. Therefore, SnSSe is perceived to be a promising candidate as a light absorbing material for the development of polycrystalline thin film solar cells [3]. In the present work, $SnS_{1-x}Se_x$ ($x \sim 0.3$) thin films were deposited on glass substrates using thermal co-evaporation method at different substrate temperatures, 200–350 °C. The structural, surface morphological, optical and other physical properties of as-deposited films with respect to substrate temperature were reported elsewhere [4,5]. The effect of substrate temperature on the optical and dispersion properties of as-deposited films was studied in detail and discussed in this paper.

2. Experimental details

$SnS_{1-x}Se_x$ thin films were deposited by thermal co-evaporation technique (using HHV BC 300 model box coater), a suitable technique to prepare compound or alloy films. For deposition of $SnS_{1-x}Se_x$ films, 0.1 gm of SnS (Alfa Aesar, 99.5%) and 0.05 gm of elemental Se (Sigma Aldrich, 99.99%) were taken as source materials and were simultaneously evaporated onto pre-heated soda lime glass substrates at a rate of 20 Å/s under vacuum of 5×10^{-5} mbar. The films were deposited at different substrate temperatures ranging from 200 °C to 350 °C, while the thickness of the films was monitored and maintained as ~ 1 μm during deposition using quartz crystal thickness monitor (model CTM 200). The optical as well as dispersion properties of as-deposited films were studied in detail using Photon RT spectrophotometer measurements.

3. Results and discussion

The as-grown films were uniform and pin-hole free as noted by the visual observation. The EDS composition analysis indicated

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x = 0.3 in $SnS_{1-x}Se_x$ layers. Hence, the optical properties of $SnS_{0.7}Se_{0.3}$ films were investigated in this work and given below.

3.1. Optical properties

The optical absorption coefficient (α) of $SnS_{0.7}Se_{0.3}$ films was calculated using both transmittance (T) and reflectance (R) data by following the relation, $\alpha = -\frac{1}{t}\ln\left(\frac{\sqrt{(1-\boldsymbol{R})^4+4\boldsymbol{T}^2\boldsymbol{R}^2}-(1-\boldsymbol{R})^2}{2\boldsymbol{T}\boldsymbol{R}^2}\right)$, where t is the film thickness (~1 μm) [5]. Fig. 1 shows the variations in absorption coefficient with respect to incident photon energy ($h\nu$) of $SnS_{0.7}Se_{0.3}$ films deposited at different substrate temperatures (T_S = 200–350 °C). From the figure, the absorption coefficient of the films is > 10^4 cm^{-1} in the visible region and is supporting the direct allowed transition in the films. It is also noticed from the figure that the absorption coefficient of the films deposited at T_S = 350 °C is low compared to other films. This is because of the presence of secondary SnS phase (not shown here) in the layers [4] that led to form more localized states in the film [6]. The optical band gap energy (E_g) of the films can be determined using the absorption coefficient data by following the relation, $(\boldsymbol{\alpha h\vartheta})^2 = \boldsymbol{A}(\boldsymbol{h\vartheta} - \boldsymbol{E_g})$, where A is a constant. The Tauc plots of the films are shown in inset of Fig. 1. The E_g values determined at fundamental absorption edge are 1.59 eV, 1.56 eV, 1.53 eV and 1.46 eV for the films deposited at T_S = 200 °C, 250 °C, 300 °C and 350 °C respectively. The band gap energy of the layers is decreased with increase of substrate temperature due to improved crystalline quality of the layers [7].

The skin depth or penetration depth (δ) is an important parameter that gives information about the travelling distance of light photons inside the material before being absorbed and is associated with the absorption coefficient of the material. It can be evaluated using the relation, $\delta = 1/\alpha$. Fig. 2 shows the variations of skin depth as a function of photon energy of as-deposited $SnS_{0.7}Se_{0.3}$ films. The skin depth in $SnS_{0.7}Se_{0.3}$ layers is decreased with increase of photon energy, indicating strong absorption of high energy photons, while the low energy photons are passed through the layers.

3.2. Optical and dielectric constants and optical conductivity

The optical constants, extinction coefficient (k) and refractive index (n) of $SnS_{0.7}Se_{0.3}$ films were evaluated using appropriate formulae reported in literature [8] and their variation with wavelength is shown in Fig. 3 (a and b). From the figure, the decrease in extinction coefficient with increase of wavelength refers to the minimized light absorption loss in the layers, whereas the decrease in refractive index against the wavelength indicates the normal dispersion of light in the layers.

The dielectric constant is one of the intrinsic properties of a material, which is directly proportional to the polarizability of that

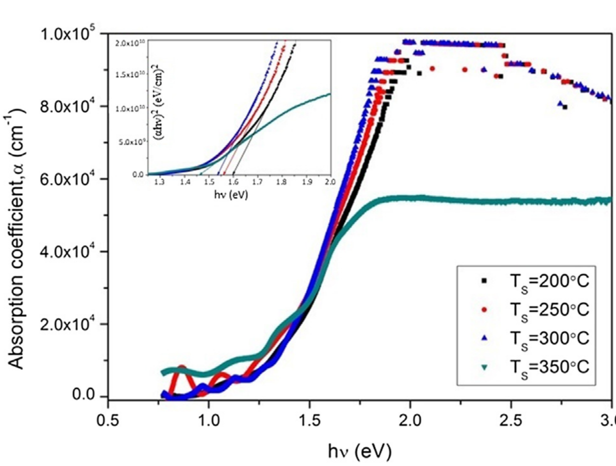

Fig. 1. Plot of α versus $h\nu$ and Tauc plots (inset) of $SnS_{0.7}Se_{0.3}$ films.

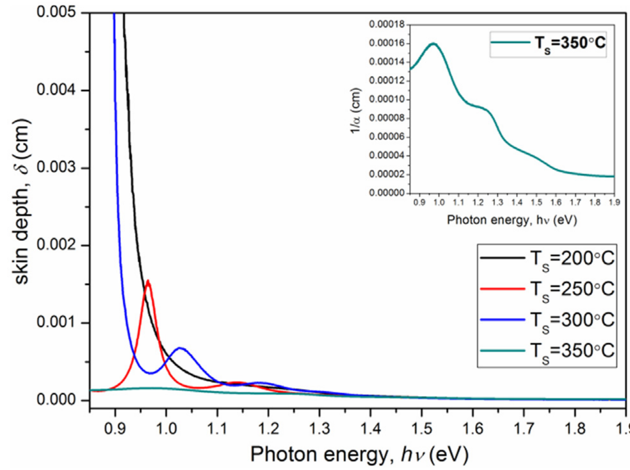

Fig. 2. Plot of δ versus $h\nu$ of $SnS_{0.7}Se_{0.3}$ films.

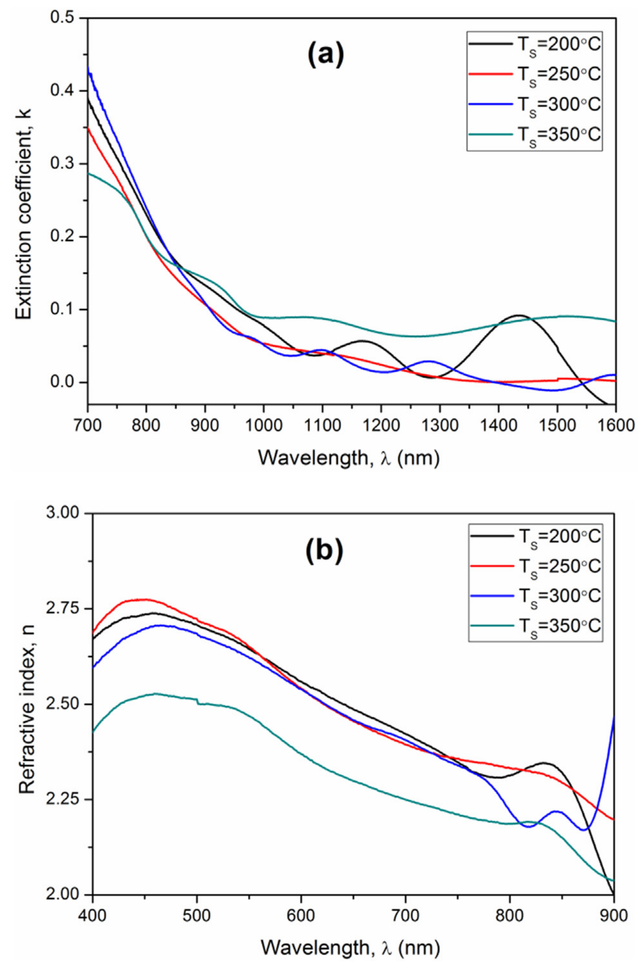

Fig. 3. Variation of (a) extinction coefficient and (b) refractive index with wavelength of $SnS_{0.7}Se_{0.3}$ films.

material. The real (ε_r) and imaginary (ε_i) parts of dielectric constant can be determined using n and k values following the relations, $\varepsilon_r = n^2 - k^2$ and $\varepsilon_i = 2nk$ respectively [8]. Fig. 4 (a and b) shows the plots of real and imaginary parts of dielectric constant of $SnS_{0.7}Se_{0.3}$ layers, which were decreased with increase of substrate temperature. Further, the ratio of imaginary to real parts of dielectric constant gives information about the energy dissipation in the material and is called as dissipation factor (tan δ). Fig. 5 shows the dielectric loss factor of $SnS_{0.7}Se_{0.3}$ films as a function of wavelength, which was also decreased with increase of T_S.

The optical conductivity (σ_{opt}) is an optical response of a material to the incident photon energy. It directly depends on both absorption coefficient and refractive index of that material. It can be determined using the relation, $\sigma_{opt} = \frac{\alpha n c}{4\pi}$, where c is the velocity of light and has dimension of frequency [9]. The variations in optical conductivity of $SnS_{0.7}Se_{0.3}$ layers as a function of photon energy is shown in Fig. 6. A sharp increase in optical conductivity is observed after ~ 1.4 eV for all the films under investigation, which is attributed to the high optical absorption of $SnS_{0.7}Se_{0.3}$ films in the high photon energy region.

3.3. Dispersion properties

The single oscillator model proposed by Wemple – DiDomenico (WDD) was applied to $SnS_{0.7}Se_{0.3}$ layers to analyze various dispersion parameters. The dispersion energy (E_d) and oscillator energy (E_o) of $SnS_{0.7}Se_{0.3}$ films were determined using the WDD relation (1) and given in Table 1

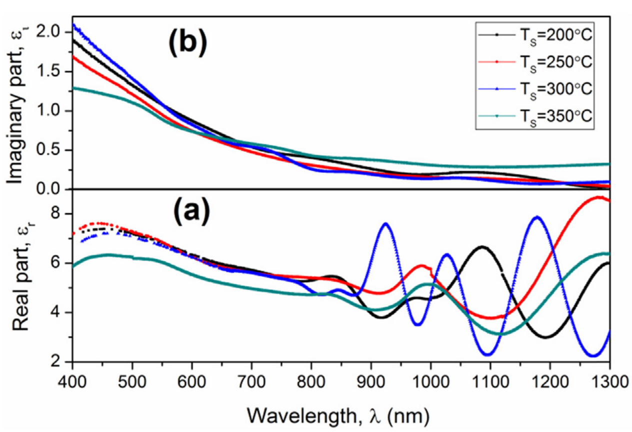

Fig. 4. Plots of (a) ε_r vs. λ and (b) ε_i vs. λ.

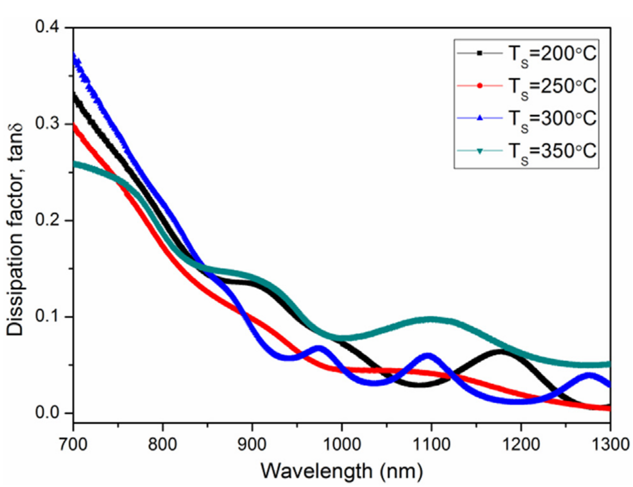

Fig. 5. Plot of tan δ vs. λ.

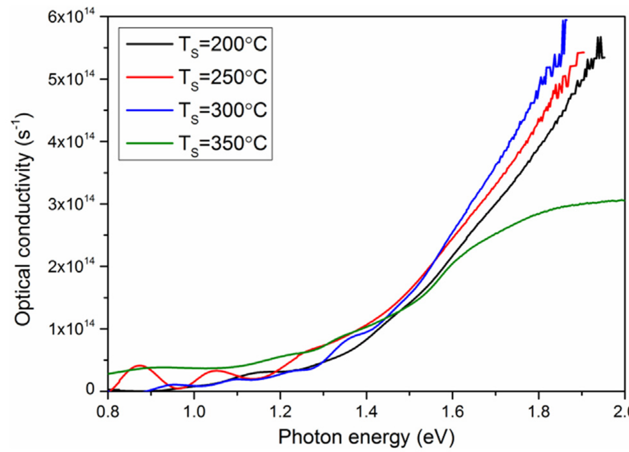

Fig. 6. Variation of optical conductivity with photon energy of $SnS_{0.7}Se_{0.3}$ films.

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\vartheta)^2} \tag{1}$$

where n is refractive index and hν is photon energy. Fig. 7 illustrates the plot of $(n^2\text{-}1)^{-1}$ as a function of $(h\nu)^2$ and fitted it to straight line, the values of E_d and E_o can be determined directly from the intercept on vertical axis (E_o/E_d) and slope $(E_d.E_o)^{-1}$ of the plot respectively. Further, the static refractive index (n_o) and static dielectric constant (ε_o) were also evaluated using the follow-

Table 1
Dispersion parameters and moments of $SnS_{0.7}Se_{0.3}$ films deposited at different T_S values.

T_S (°C)	200	250	300	350
E_o (eV)	2.38	2.34	2.29	2.19
E_d (eV)	9.52	9.36	9.16	7.55
n_o	2.24	2.23	2.23	2.11
ε_o	5.01	4.97	4.97	4.45
M_{-1}	0.25	0.25	0.25	0.29
$M_{-3} \times 10^{-3}$	2.76	2.85	2.97	5.08

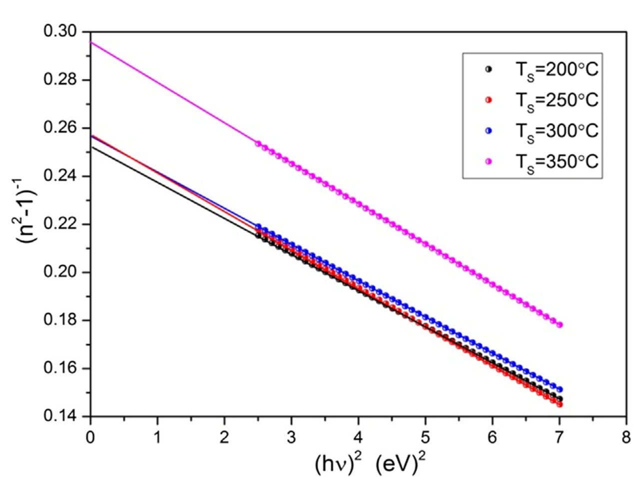

Fig. 7. Plot of $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$ of $SnS_{0.7}Se_{0.3}$ films.

ing equation (2) [8]. The calculated values of dispersion parameters are also listed in Table 1 and found to decrease with increase of T_S.

$$n_o^2 = \varepsilon_o = 1 + \frac{E_d}{E_o} \quad (2)$$

The moments of optical dispersion spectra, M_{-1} and M_{-3} can be evaluated using the relations (3) and (4), where E_o and E_d retains their usual meanings [10]. In contrast to other dispersion parameters, the optical dispersion moments of $SnS_{0.7}Se_{0.3}$ layers were slightly increased with T_S (see Table 1).

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (3)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (4)$$

4. Conclusions

The optical and dispersion characteristics of thermally co-evaporated $SnS_{0.7}Se_{0.3}$ thin films deposited at different substrate temperatures (200–350 °C) were studied. The band gap energy of as-deposited layers were evaluated that varied in the range, 1.59–1.46 eV with increase of substrate temperature. The skin depth and optical constants of $SnS_{0.7}Se_{0.3}$ films were also evaluated using the optical absorption data. The real and imaginary parts of dielectric constant were calculated. The optical conductivity of layers was found to be of the order of 10^{14} s^{-1}. Further, the dispersion parameters were analyzed by applying Wemple – DiDomenico single oscillator model and observed that the parameters were strongly dependent on substrate temperature. The results of above analysis suggested the potential use of $SnS_{0.7}Se_{0.3}$ layers in photovoltaic applications.

CRediT authorship contribution statement

K. Saritha: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft. **S. Rasool:** Resources, Validation, Visualization. **K.T. Ramakrishna Reddy:** Supervision, Project administration. **M.S. Tivanov:** Investigation, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] A. Le Donne, V. Trifiletti, S. Binetti, New earth abundant thin film solar cells based on chalcogenides, Front. Chem. 7 (2019) 297.
[2] W. Albers, C. Haas, H. Ober, G.R. Schodder, J.D. Wasscher, Preparation and properties of mixed crystals $SnS_{(1-x)}Se_x$, J. Phys. Chem. Solids 23 (1962) 215.
[3] H. Kafashan, Comparison the effects of Se and Te inclusion on the physical and electrochemical properties of SnS thin films, Mater. Sci. Semicond. Process. 88 (2018) 148.
[4] K. Saritha, S. Rasool, K.T. Ramakrishna Reddy, A.M. Saad, M.S. Tivanov, S.E. Tikoto, O.V. Korolik, V.F. Gremenok, Substrate temperature dependent physical properties of $SnS_{1-x}Se_x$ thin films, Appl. Phys. A 125 (2019) 704.
[5] K. Saritha, S. Rasool, K.T. Ramakrishna Reddy, M.S. Tivanov, A.M. Saad, A.V. Trofimova, V.F. Gremenok, Optical and electrical properties of thermally co-evaporated $SnS_{1-x}Se_x$ alloy films, Mater. Res. Express 6 (2019) 106439.
[6] U. Chalapathi, S. Uthanna, V. Sundara Raja, Structural, microstructural and optical properties of Cu_2ZnSnS_4 thin films prepared by thermal evaporation: effect of substrate temperature and annealing, Bull. Mater. Sci. 40 (2017) 887.
[7] L. Zhao, Y. Di, C. Yan, F. Liu, Z. Cheng, L. Jiang, X. Hao, Y. Lai, J. Li, In situ growth of SnS absorbing layer by reactive sputtering for thin film solar cells, RSC Adv. 6 (2016) 4108.
[8] H.N. Desai, J.M. Dhimmar, B.P. Modi, Optical and dispersion analysis of zinc selenide thin film, Materials Today: Proc. 3 (2016) 1650.
[9] P. Sharma, S.C. Katyal, Determination of optical parameters of a-(As2Se3) 90Ge10 thin film, J. Phys. D: Appl. Phys. 40 (2007) 2115.
[10] R. Hamrouni, N.E.H. Segmane, D. Abdelkader, A. Amara, A. Drici, M. Bououdina, F.C. Akkari, N. Khemiri, L. Bechiri, M. Kanzari, J.C. Bernede, Linear and nonlinear optical properties of Sb_2Se_3 thin films elaborated from nano-crystalline mechanically alloyed powder, Appl. Phys. A 124 (2018) 861.