

## STUDY OF $\text{Sb}_{28.47}\text{Sn}_{11.22}\text{S}_{60.32}$ COMPOUND AS THIN FILM FOR PHOTOVOLTAIC APPLICATIONS

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2  $\mu\text{m}$  thin elemental film is deposited by sputtering techniques and the sulphurization of the film was done inside vacuum thermal coater. The annealing of the film was carried out inside quartz ampoule at 475°C. EDS and XRD give the elemental and phase study while photoconductivity spectrometer was used for quantum efficiency measurement. The optical properties were measured via variable angle spectroscopic ellipsometry techniques.

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### 1. Introduction

Thin film photovoltaics have revolutionized most of the research worldwide due to the forthcoming energy crisis. The people are busy globally to investigate new materials for solar cells. Polycrystalline thin films which have been extensively studied are based on CdTe, CIGS, GaAs and ZnTe as absorber layer [1]. These ternary and quaternary polycrystalline thin films provide much contribution in the solar cell technology. Besides their good conversion efficiencies and ease of fabrication, the toxicity and material cost of these materials compel us to think for new materials for solar cell technologies. The preparation and characterization of metal chalcogenide thin films is one way to contribute this area [2]. Dittrich et al. studied different materials for photovoltaics and suggested Sulfosalts to be a new absorber for solar cell applications [3]. Presently  $\text{Sb}_2\text{S}_3$ , SnS, Copper Zinc tin sulphide (CZTS) sulfosalts have been used as an absorbing layer for solar cells [4, 5, 6]. Sulphide materials have potential as semiconductor materials whose properties match best in solar cell applications. Low band gap ( $\approx 1.2\text{eV}$ ) is required for trapping maximum number of photons for free exciton conversion and sulphur is a useful contingent in reducing energy gaps. The non toxic, abundant and cheap metal based sulphide thin films can be the desired material for this technology. SnSbS thin films are also a potentially stable sulfosalts which has not been studied in detail yet. Therefore we have made an attempt to study the structural and optical properties of SnSbS thin film annealed under argon atmosphere at 475°C.

### 2. Experimental

DC sputtering technique was used for the depositions of metallic SnSb thin film. The target to substrate distance was fixed to 10cm and the quartz crystal monitor was used to control the thickness of the metallic film. 1.5  $\mu\text{m}$  thick film was used in the current study.

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The SnSb sputtered films were deposited on soda lime glass substrates and then sulphurized in a vacuum chamber by thermal evaporation techniques. After sulphurization of the SnSb thin film, the film was annealed in sealed quartz ampoule containing argon gas at low pressure for 1 hour at 475°C in tube furnace. The thermocouple inserted inside the furnace was used to measure the in situ condition of temperature.



*Fig. 1. Ampoule containing SnSbS thin film.*

### 3. Results and discussion

The elemental composition (shown in table-1) is confirmed by Energy Dispersive X-ray Spectroscopy (EDX).

*Table 1. Elemental composition*

Sn	Sb	S
11.22%	28.47%	60.32%

XRD in Fig. 2 shows the phase analysis. There are many phases of tin sulphide and antimony sulphide along with  $\text{SnSb}_2\text{S}_4$  phase. The crystal size was calculated by using Scherrer formula [7]

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

Where  $\beta$  is the full width at half maximum and  $\lambda$  is the wavelength of X-rays used in the analysis. The average grain size was found to be 60Å.

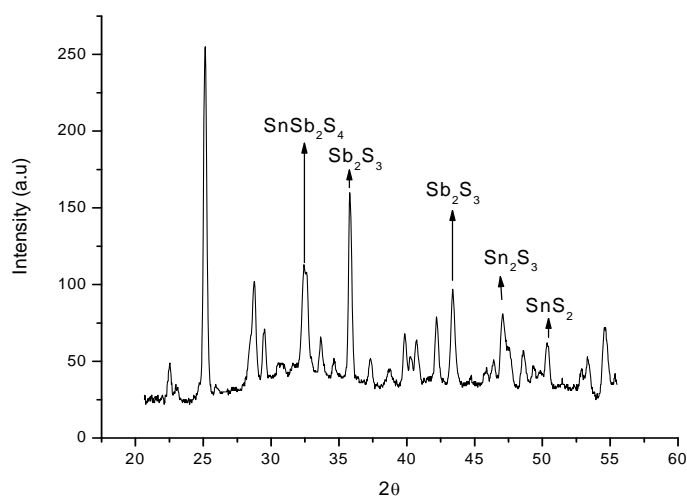


Fig. 2. XRD of  $\text{SnSb}_2\text{S}_4$  thin film.

The photoconductivity response of the sputtered thin film is shown in figure 3. The photoconductivity response lies in a wide spectrum, span from visible to far infrared region. This is a quite wide range of spectrum. This shows that sulphur might react with Sn and Sb at  $475^\circ\text{C}$  annealing and form a photoactive material.

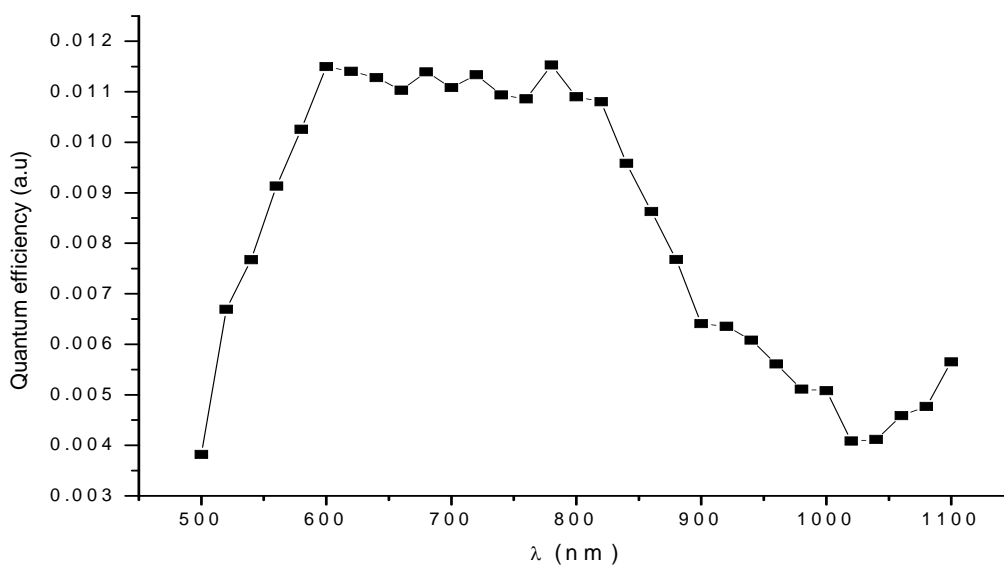
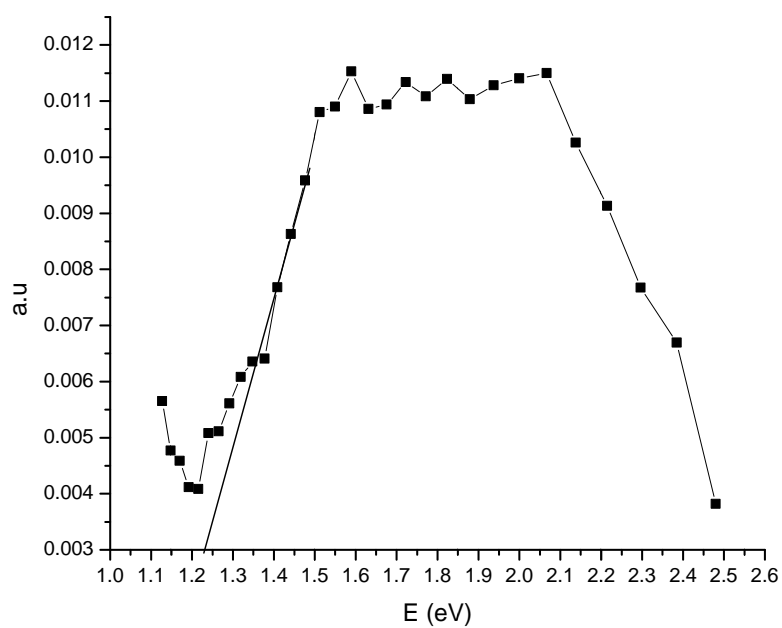
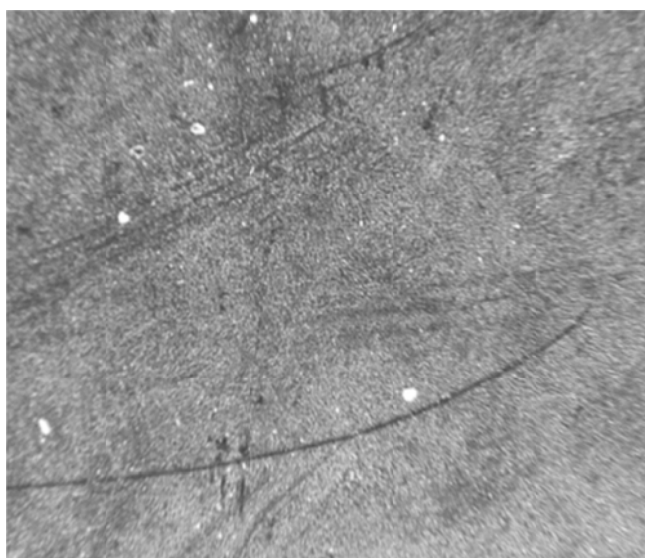


Fig. 3. Quantum efficiency of  $\text{SnSbS}$  thin film.

Fig 4 shows the band gap calculation for the film. The band gap for  $\text{SnSbS}$  is consistent with the literature. The band gap is found to be 1.23 eV which is the optimum value for an absorbing layer to be used in solar cells. The band gap is also calculated by the ellipsometric techniques and the band gap is found to be consistent by both methods.



*Fig. 4. Band gap calculation.*



*Fig. 5. SEM image of 475°C annealed film*

Fig. 5 represent the SEM images of Sn-Sb-S thin film sputtered library at 475°C annealed temperature. This shows that the sulphur is adsorbed fully in the metallic film and reacts with Sn and Sb for the formation of required phase.

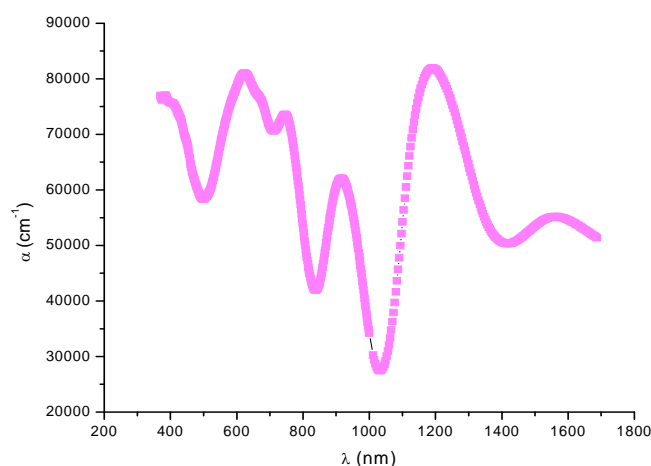


Fig. 6. Absorption coefficient of SnSbS thin film.

The absorption coefficient of thin annealed film is calculated by plotting  $\alpha$  ( $\text{cm}^{-1}$ ) vs.  $\lambda$  (nm). Where  $\alpha$  is the absorption coefficient of the film and is given by

$$\alpha = \frac{4\pi k}{\lambda}$$

where  $k$  is the extinction coefficient of the material obtained from variable angle ellipsometry. Figure 6 represents the absorption coefficient of the film in the range of  $3 \times 10^4$  -  $8 \times 10^4 \text{ cm}^{-1}$  which is the optimum value of absorption coefficient for absorbing layer [8].

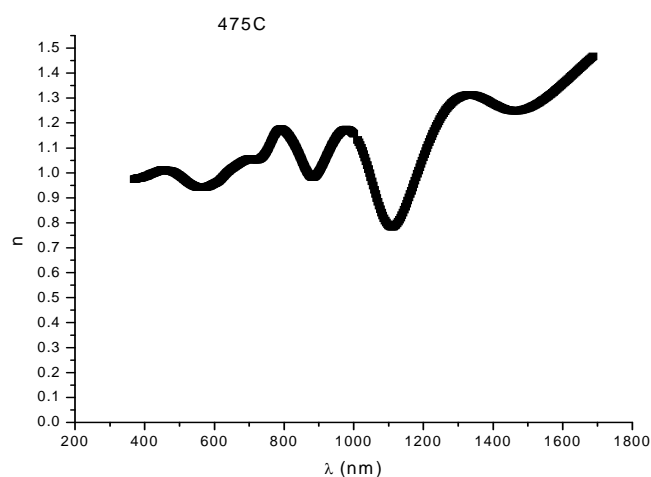


Fig. 7. Refractive index calculation.

The values of the refractive indices ( $n$ ) of the thin film were calculated by approximating the modeled ellipsometric data. The refractive index increases from 1 to 1.4 (Fig. 7). The refractive index is wavelength dependent and remains 1.1 in the visible spectrum which obey the Cauchy dispersion relation [9]

$$n = n_0 + a/\lambda^2 + b/\lambda^4 \quad (2)$$

For higher wavelength the refractive index increases in correspondence with the following dispersion relation [10]

$$n = A + B\lambda + C\lambda^2 + D\lambda^3 + E\lambda^4 \quad (3)$$

$\lambda$  is measured in  $\mu\text{m}$  and  $L=1/(\lambda^2-\lambda_0^2)$  and the coefficients for IR region are

$$A = 3.999, B = 3.3917, C = 0.1634, D = -0.000006, E = 0.000000053$$

Fig. 7 is in agreement with these dispersion relations. In the IR region the refractive index approaches to 1.4.

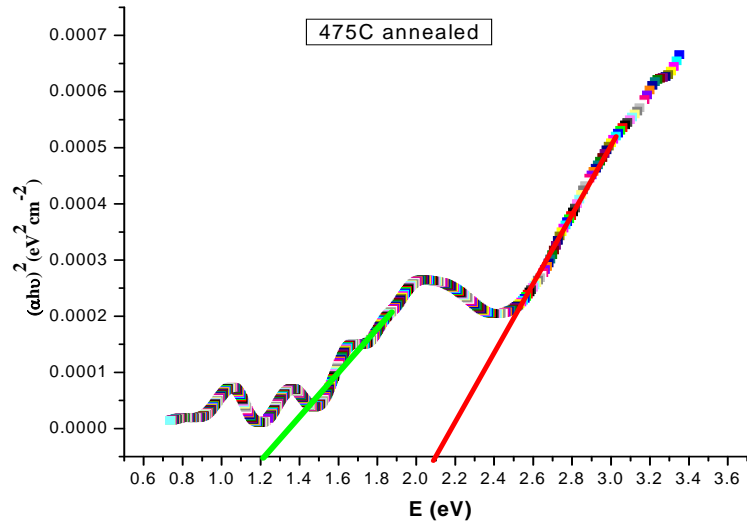


Fig. 8. Band gap calculations.

The band gap can be calculated by plotting  $(\alpha h\nu)^2$  Vs. the band gap energy  $E_g$  by interconnecting with the following equation [8]

$$\alpha h\nu = A (h\nu - E_g)^n \quad (4)$$

where  $h$  is Plank constant,  $A$  is a constant and  $n$  is  $\frac{1}{2}$  for a direct energy gap and 2 for indirect energy gap semiconductor materials. The band gap can be calculated by extrapolating the straight vertical section of the  $(\alpha h\nu)^2$  vs.  $h\nu$  curve to the horizontal energy axis [9]. The energy gaps were estimated from extrapolating the curve which corresponds to the valance-conduction band transition of 1.23eV as in figure 8. It is also observed from the optical properties that SnSbS has dual band gap characteristics and the 2<sup>nd</sup> energy band which is probably associated with valance band spilling through crystal field potential [10] is 2.1eV.

#### 4. Conclusion

This study tells us about the role of new absorber layer SnSb<sub>2</sub>S<sub>4</sub> thin film as a low cost material deposited by sputter coater for solar cells. The metallic thin film of SnSb was sputtered from tin and antimony targets (99.999% purity) on glass substrate via sputter coater. The film was sulphurized by thermal evaporation techniques by evaporating sulphur in vacuum chamber. The film was annealed at 475°C inside sealed quartz ampoule containing argon gas. The XRD study confirms the phase formation i.e. SnSb<sub>2</sub>S<sub>4</sub>. The photoconductivity measurement confirms the photo activeness of the material and lie in the spectrum range 500nm-1020nm. The band gap was calculated by fitting curve from photoconductivity data through horizontal photon energy axis as well as by ellipsometric techniques. From band gap measurement we found dual transition 1<sup>st</sup> at 1.23ev referred to the valance-conduction band transition while the 2<sup>nd</sup> (2.1ev) due to valance band spilling in the field of crystal potential. The refractive index was found to be 1.4 and have good absorption coefficient of the order of  $10^4 \text{cm}^{-1}$ .

## References

- [1] N. Koteeswara Reedy, K. T. Ramakrishna Reedy, Solid state electronics **49**, 902 (2005)
- [2] H. Maghraoui-Meherzi, T. Ben Nasr, N. Kamoun, M. Dachraoui, Physica B **405**, 3101 (2010)
- [3] H. Dittrich, D. J. Vaughan, R. D. A. Patrick, S. Graser, E. Makoviky et al. Cryst Res Technol **31**, 833 (1996)
- [4] A. Tanusevski, D. Poelman, Solar energy materials and solar cells **80**, 297 (2003)
- [5] H. Maghraoui-Meherzi, T. Ben Nasr, N. Kamoun, M. Dachraoui, Physica B **405**, 3101 (2010)
- [6] B. Li, Vardaan Chawla, and Bruce M. Clemens, Advanced Materials **24**, 6 (2012)
- [7] Gassoumi, M. Kanzari, Chalcogenide Letters v. **6**, 163 (2009)
- [8] S.M. Firoz Hasan, L. Quadir, Kh.S. Begum, M.A. Subhan, Kh.M. Mannan, Solar Energy Materials & Solar Cells **58**, 349 (1999)
- [9] D. H. Rank, H. E. Bennett and D. C. Cronmeyer, J. Opt. Soc. Am., **44**, 13 (1954)
- [10] M. Hertzberger and C. D. Salzberg, J. Opt. Soc. Am., **52**, 420 (1962)