



Influence of post-annealing in sulfur atmosphere on thermally evaporated β - In_2S_3 films

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ABSTRACT

Indium sulfide (In_2S_3) is an n-type semiconductor with wide bandgap energy (2.2–2.7 eV) and is currently used as buffer/window layer in thin film solar cells as an alternative to toxic CdS. In the present study, In_2S_3 thin films were deposited on soda lime glass substrates using thermal evaporation technique at different substrate temperatures, $T_s = 200$ °C–350 °C. Further, all the as-deposited films were annealed in sulfur ambient at 250 °C for 1 h. The structural, compositional and optical properties of annealed In_2S_3 films were analyzed using GIXD, EDS and Photon RT spectrophotometer respectively. All the annealed films exhibited polycrystalline nature with improved crystallinity and high optical transmittance in the visible region. Moreover, the as-deposited films were sulfur deficient whereas in annealed layers the S/In ratio was increased due to sulfur annealing. Therefore, annealing of In_2S_3 films in sulfur atmosphere enhanced the quality of the films. Among all the as-deposited and annealed films, the layers grown at $T_s = 300$ °C followed by annealing at 250 °C have shown better structural and optical properties than the other films.

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1. Introduction

Now-a-days, researchers are showing great interest on environmental friendly materials to develop low cost solar cells. In_2S_3 is a potential candidate for its use as a window/buffer layer in thin film solar cell applications due to its n-type conductivity, wide band gap energy (2.1–3.1 eV), good photoconductive response and less toxicity compared to CdS [1–3]. Generally, the properties of thin films can be enhanced by annealing, chemical treatment and doping or alloying processes. The main purpose of annealing is to improve the quality of thin films by enhancing the nucleation process, which consequently increases the grain size with reduced defects. In case of In_2S_3 films deposited at higher temperatures, the sulfur deficiency is a common phenomenon occurred due to re-evaporation of sulfur from the film surface owing to its high volatility and vapour pressure. To overcome this problem, sulfur annealing is an apt approach to maintain stoichiometric composition of In_2S_3 films. As per literature survey, despite the availability

of numerous reports on annealing effect on In_2S_3 films, a very few reports are available on the effect of sulfur annealing on In_2S_3 films [4,5]. Therefore in the present study, thermally evaporated In_2S_3 films were post annealed in sulfur atmosphere and the structural, compositional and optical properties of the layers were investigated using various techniques.

2. Experimental details

In_2S_3 thin films were deposited onto soda-lime glass substrates using thermal evaporation technique (Hind Hi Vac BC 300 box coater) at different substrate temperatures, $T_s = 200 - 350$ °C. In_2S_3 powder (Sigma Aldrich 99.999%) was used as source material and kept at a distance of 14 cm from the glass substrates. The powder was evaporated at a rate of 15 Å/s. The grown In_2S_3 films were of ~500 nm thick measured using a quartz crystal thickness monitor. Further, the as-deposited layers were annealed under sulfur atmosphere (2×10^{-2} mbar) using two zone tubular vacuum furnace at 250 °C for 60 min. The as-deposited as well as annealed In_2S_3 films were characterized using various techniques. The structural details of the films were investigated using Ultima IV X-ray

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diffractometer with Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) in grazing incidence X-ray diffraction (GIXD) geometry at 1 degree of grazing angle. The layer composition was analyzed by energy dispersive spectroscopy (EDS) with the aid of an INCA energy analyzer attachment (Oxford Instruments). The optical transmission and reflection spectra of the films were measured using Photon RT spectrophotometer (Essent Optics).

3. Results and discussion

3.1. Structural analysis

Fig. 1(a) and (b) shows the GIXD patterns of as-deposited and annealed In_2S_3 films. From Fig. 1(a), the films deposited at lower substrate temperatures ($T_s = 200^\circ\text{C}$ and 250°C) showed amorphous nature due to insufficient thermal energy provided to the substrate as a result the ad-atoms could not move freely on the substrate surface, which causes the growth of many nuclei without surface diffusion [6]. Further increase of T_s to 300°C and 350°C , the films exhibited polycrystalline nature with poor crystallinity and had mixed phases of cubic and tetragonal $\beta\text{-In}_2\text{S}_3$. The films changed from amorphous nature to polycrystalline with increase of T_s due to increase of ad-atom mobility that stimulated the growth of crystallites in different orientations. Moreover, the existence of mixed phases of cubic and tetragonal $\beta\text{-In}_2\text{S}_3$ is a common phenomenon observed in thin film formation irrespective of the deposition techniques used, which was reported in several works [7–9]. All as-deposited films required post-annealing treatment to improve the crystalline quality as well as other physical properties. Therefore, all the as-deposited layers were annealed at 250°C under sulfur ambient for 60 min. The annealed layers showed bet-

ter crystallinity than the as-deposited films and had only cubic phase of $\beta\text{-In}_2\text{S}_3$ (JCPDS 65–0459) (see Fig. 1(b)). Further, the size of coherent scattering region (L) and the lattice deformation (ε) of the films were calculated using the appropriate formulae as reported in the literature [10] and the obtained values were tabulated in Table 1. From Table 1, it is observed that 'L' value increased in annealed films, which might be due to the coalescence of smaller nuclei or neighboring smaller crystallites. The crystallinity of the films improved after annealing due to the sufficient thermal energy available for recrystallization and grain growth with reduced defects.

3.2. Composition analysis

Fig. 2 shows the variation of S/In ratio for as-deposited and annealed In_2S_3 films. It is observed that S/In ratio decreased from 1.21 to 1.01 with increase of substrate temperature (200°C – 350°C) in the as-grown films due to re-evaporation of sulfur from the films, owing to its high volatility and vapour pressure, whereas for annealed layers, the S/In ratio is increased and varied in the range, 1.53–1.66. The films deposited at $T_s = 300^\circ\text{C}$, after sulfur annealing showed S/In ratio of 1.53, which is close to bulk value (1.49) of In_2S_3 powder and the rest of the annealed films contained higher S/In ratio greater than 1.60. The increment of sulfur content in annealed films is due to rapid reaction of sulfur vapours with indium that led to the formation of stoichiometric $\beta\text{-In}_2\text{S}_3$ phase. A similar variation of S/In values was reported by Bouabid et al. for flash evaporated In_2S_3 films annealed at 300°C under sulfur atmosphere [4]. Moreover, the change in S/In ratio can affect the optical band gap and other properties of the In_2S_3 layers.

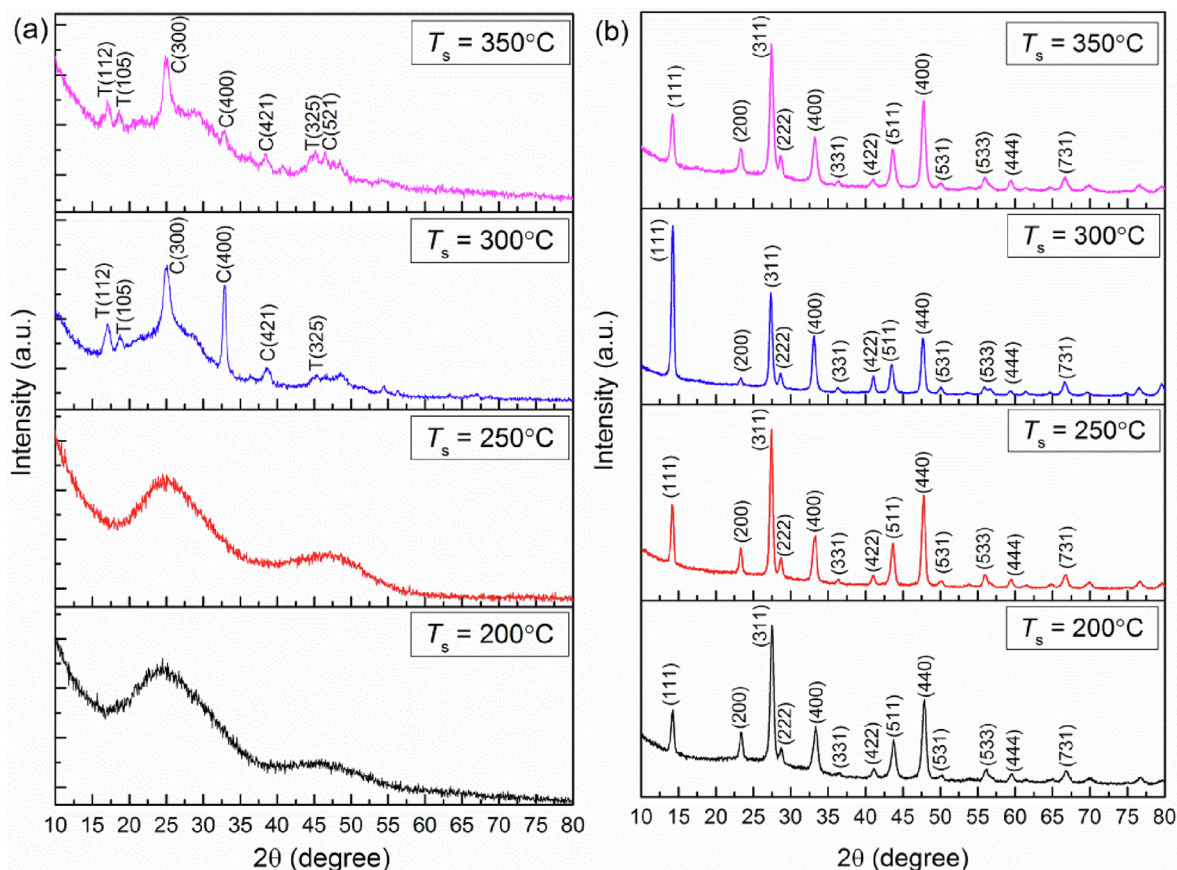


Fig. 1. GIXD patterns of In_2S_3 films (a) before and (b) after annealing at 250°C .

Table 1
Structural parameters of In₂S₃ films.

T_s (°C)	Before annealing				After annealing			
	200	250	300	350	200	250	300	350
(hkl)	-	-	(300)	(300)	(311)	(311)	(111)	(311)
L (nm)	-	-	3.0	8.7	13.7	15.0	15.2	12.7
$\epsilon \times 10^{-2}$	-	-	5.5	1.9	1.1	1.0	1.0	1.2

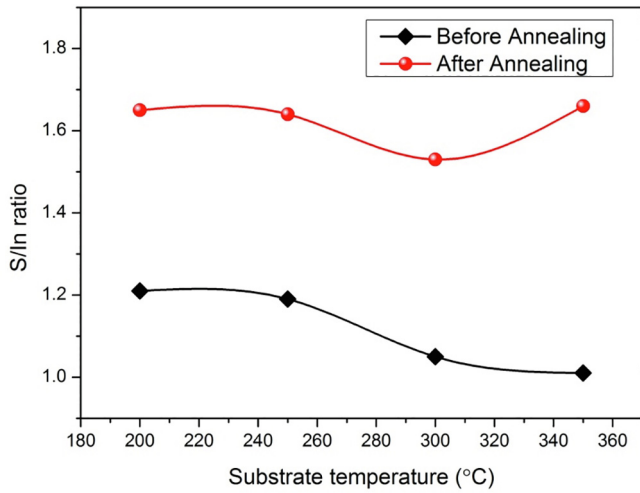


Fig. 2. Variation of S/In ratio with substrate temperature.

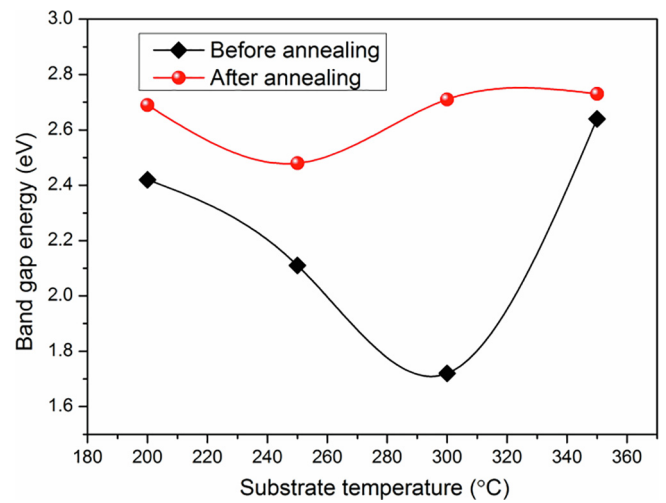


Fig. 4. Variation of band gap energy with substrate temperature.

3.3. Optical studies

Fig. 3(a) and (b) shows the transmission spectra of as-deposited and annealed In₂S₃ films. After annealing, all the films showed high transmittance (>60%) in the visible region compared to as-deposited layers and the interference fringes in the transmittance spectra indicates good homogeneity and uniformity of the films. The optical transmittance was improved for annealed films because of improved crystallinity.

The optical band gap energy of the layers was evaluated from the following Tauc relation for direct allowed transitions [6], where $h\nu$ is photon energy and A is a constant related to the effective mass of the material.

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

The evaluated band gap energy values of the as-deposited layers was initially decreased from 2.42 eV to 1.72 eV upto $T_s = 300^\circ\text{C}$ and then increased to 2.64 eV due to change in composition and structural defects of the layers, whereas for annealed layers, the band gap energy was higher than the as-deposited layers and varied in the range, 2.48 – 2.73 eV. The rise in band gap energy upon annealing was due to better stoichiometry, improved crystallinity and less defects of the layers compared to as-grown layers [11]. Fig. 4 shows the variations of band gap energy values of the layers with the substrate temperature.

4. Conclusions

In₂S₃ thin films were deposited at different substrate temperatures using thermal evaporation technique. Further, all the films

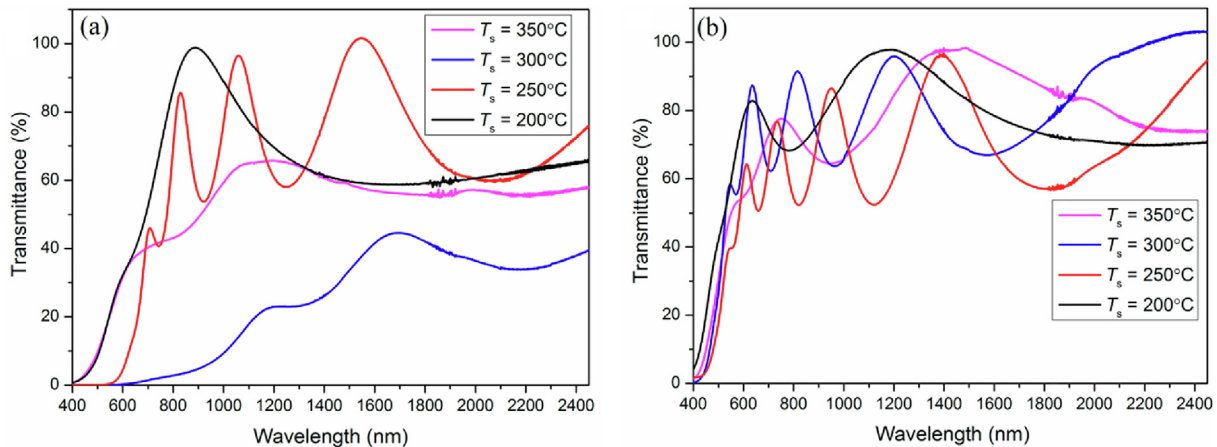


Fig. 3. Transmittance of In₂S₃ films (a) before and (b) after annealing at 250 °C.

were annealed at 250 °C in sulfur atmosphere. The structural, composition and optical properties of as-deposited and sulfur annealed films were investigated. From the results, it is concluded that the post-annealing treatment of the layers grown at 300 °C in sulfur ambient improved the physical properties of as-deposited films.

CRediT authorship contribution statement

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

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] M.A. Mughal, R. Engelken, R. Sharma, Progress in indium (III) sulphide (In_2S_3) buffer layer deposition techniques for CIS, CIGS and CdTe-based thin film solar cells, *Sol. Energy* 120 (2015) 131.
- [2] J. George, K.S. Joseph, B. Pradeep, T.I. Palson, Reactively evaporated films of indium sulfide, *Phys. Status Solidi A* 106 (1988) 123.
- [3] E.B. Yousfi, B. Weiberg, F. Donsanti, P. Cowache, D. Lincot, Atomic layer deposition of zinc oxide and indium sulfide layers for Cu(In, Ga)Se₂ thin-film solar cells, *Thin Solid Films* 387 (2001) 29.
- [4] K. Bouabid, A. Ihlal, Y. Amira, A. Sdaq, A. Outzourhit, G. Nouet, Effect of annealing on In_2S_3 thin films prepared by flash evaporation, *Eur. Phys. J. Appl. Phys.* 40 (2007) 149.
- [5] C. Sanz, C. Guillén, J. Herrero, Annealing of indium sulfide thin films prepared at low temperature by modulated flux deposition, *Semicond. Sci. Technol.* 28 (2013) 015004.
- [6] Z.Y. Zhong, E.S. Cho, S.J. Kwon, Effect of substrate temperature on evaporated In_2S_3 thin film buffer layer for Cu(In,Ga)Se₂ solar cells, 547 (2013) 22.
- [7] N. Revathi, P. Prathap, K.T. Ramakrishna Reddy, Thickness dependent physical properties of close space evaporated In_2S_3 films, *Solid State Sci.* 11 (2009) 1288.
- [8] J. Raj Mohamed, L. Amalraj, Effect of precursor concentration on physical properties of nebulized spray deposited In_2S_3 thin films, *J. Assian Ceram. Soc.* 4 (2016) 357.
- [9] M.G. Sandoval-Paz, M. Sotelo-Lerma, J.J. Valenzuela-Ja'uregui, M. Flores-Acosta, R. Ramirez-Bon, Structural and optical studies on thermal-annealed In_2S_3 films prepared by the chemical bath deposition technique, *Thin Solid Films* 472 (2005) 5.
- [10] S. Rasool, K. Saritha, K.T. Ramakrishna Reddy, M.S. Tivanov, A.V. Trofimova, S.E. Tikoto, L. Bychto, A. Patryn, M. Maliński, V.F. Gremenok, Effect of annealing on the physical properties of thermally evaporated In_2S_3 thin films, *Curr. Appl. Phys.* 19 (2019) 108.
- [11] S.P. Nehra, S. Chander, A. Sharma, M.S. Dhaka, Effect of thermal annealing on physical properties of evaporated In_2S_3 buffer layer for eco-friendly photovoltaic applications, *Mater. Sci. Semicond. Proc.* 40 (2015) 26.