Research Article

Growth of Polycrystalline In$_2$S$_3$ Thin Films by Chemical Bath Deposition Using Acetic Acid as a Complexing Agent for Solar Cell Application

G. R. Gopinath and K. T. Ramakrishna Reddy

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

Correspondence should be addressed to G. R. Gopinath; gopisiri07@gmail.com

In$_2$S$_3$ films have been successfully deposited on Corning glass substrates via chemical bath deposition (CBD) method using acetic acid as a novel complexing agent. The layers were grown by employing synthesis using indium sulphate and thioacetamide (TA) as precursors by varying TA concentration in the range of 0.1–0.5 M, keeping other deposition parameters constant. Energy dispersive X-ray analysis (EDAX) revealed an increase of S/In ratio in the films with the increase of TA concentration in the solution. The X-ray diffraction (XRD) analysis indicated a change in preferred orientation from (311) plane related to cubic structure to the (103) direction corresponding to the tetragonal crystal structure. The evaluated crystallite size varied in the range of 15–25 nm with the increase of TA concentration. Morphological analysis showed that the granular structure and the granular density decrease with the raise of TA concentration. The optical properties of the layers were also investigated using UV-Vis-NIR analysis, which indicated that all the In$_2$S$_3$ films had the optical transmittance >60% in the visible region, and the evaluated energy band varied in the range of 2.87–3.32 eV with the change of TA concentration. Further, a thin film heterojunction solar cell was fabricated using a novel absorber layer, SnS, with In$_2$S$_3$ as a buffer. The unoptimized SnS/In$_2$S$_3$/ZnO:Al solar cell showed a conversion efficiency of 0.6%.

1. Introduction

Indium sulphide (In$_2$S$_3$) is one of the potential materials for various device applications. This includes development of photovoltaic [1, 2], photoelectrochemical solar cells [3], electronic [4], optical, [1, 5] and acoustic [6] dry cells, [7] which are displayed [8, 9] as photocatalysts for dye degradation [10] and water splitting [11]. This is mainly due to its chemical stability, wide energy band gap, and controllable electrical properties [12]. In photovoltaic solar cells, indium sulphide has been proved to be a promising buffer layer in the fabrication of thin film solar cells due to its lower toxicity compared to that of CdS [13]. In$_2$S$_3$ is an *n*-type semiconductor that belongs to the III–VI group of compounds. Depending upon synthesis temperature and pressure, it exists in three crystallographic phases such as α, β, and γ. Among these phases, β-In$_2$S$_3$ is the most stable phase at room temperature [14].

In$_2$S$_3$ films have been elaborated using a variety of methods such as spray pyrolysis [15, 16], chemical bath deposition (CBD) [17, 18], atomic layer deposition (ALD) [19–21], atomic layer epitaxy [22], electrodeposition [23], ion layer gas reaction (ILGAR) [24], sulfurization [25], thermal treatment of electroplated indium in a flowing stream of H$_2$S [26], metal-organic chemical vapor deposition (MOCVD) [27, 28], physical vapor deposition (PVD) [29, 30], chemical vapor deposition [31], thermal evaporation [1], sputtering [32, 33], and spray ion layer gas reaction [24]. Out of these different methods used, CBD is a convenient, inexpensive, and simple method for the deposition of In$_2$S$_3$ thin films over a large area. Further, In$_2$S$_3$ deposited by CBD as a buffer layer in Cu (In,Ga) Se$_2$-based solar cells has shown solar conversion efficiencies > 15% [34]. Generally, most of the studies made on the CBD grown In$_2$S$_3$ films used indium chloride as source of indium so that the films had lots of chlorine as an impurity. Further, the process has created lots of surface defects,

leading to the degradation of the final device efficiency [35, 36]. Further, toxic reagents such as hydrazine hydrate and triethanolamine were used as complexing agents to deposit In_2S_3 films in CBD process. Moreover, the literature survey revealed that there was only one report on the synthesis of In_2S_3 films by CBD process using indium sulphate as the indium source [37]. Hence, an attempt has been made in this work to deposit In_2S_3 layers using indium sulphate as the precursor for indium with a novel and nontoxic complexing agent, acetic acid. The layers were formed by altering the thioacetamide concentration, and the chemical and the physical properties were investigated. A novel heterojunction was also fabricated using SnS as an absorber and In_2S_3 as a window layer, and the solar cell behavior was investigated.

2. Experimental Details

In_2S_3 thin films were deposited on Corning glass substrates using CBD method. The cleaned glass substrates were vertically immersed into a beaker containing aqueous solution of indium sulphate and thioacetamide (TA) and kept on a hot plate. In_2S_3 films were grown by varying the TA concentration from 0.1 M to 0.5 M, keeping the concentration of indium sulphate constant at 0.025 M. Acetic acid was used as the complexing agent. Appropriate quantities of the precursor solutions were taken in a beaker, so that the final volume of the reaction bath was 50 mL. The temperature of the reaction bath (T_b) was kept constant at $70°C$ using an oil bath. The deposition was carried out for 60 min. Initially, the color of the solution was lemon yellow that turned into bright yellow at the final stage of the film deposition. Finally, the films were removed from the solution and dried under nitrogen gas flow.

In order to check the suitability of the grown layers for solar cell application, a novel SnS-based solar cell was fabricated in this work. SnS absorber layer was deposited onto the Mo-coated glass substrates by thermal evaporation at a temperature of $350°C$. The details of SnS growth were reported elsewhere [38]. In_2S_3 layer was grown at the optimized TA concentration onto glass/Mo/SnS. Al-doped ZnO window layers were deposited by reactive DC magnetron sputtering in argon ambient. Finally, Cu/Al contact was made by thermal evaporation.

The as-grown layers were characterized to evaluate properties such as composition, crystal structure, grain size, morphology, optical transmittance, and energy band gap. The chemical composition of the deposited films was determined by energy dispersive X-ray analysis (EDAX) using Inca Penta FET x3 attached to scanning electron microscope (SEM). The structure of the grown films was examined using Seifert 3003 TT X-ray diffractometer (XRD) with CuK_α (λ = 1.542 Å) radiation source in the 2θ range, 10–60°. The surface morphology of the films was analyzed by using Carl Zeiss EVO MA15 SEM. The optical energy band gap was determined using the transmission versus wavelength data obtained from the Perkin Elmer Lambda 950 UV-Vis-NIR double beam spectrophotometer. The illuminated current density-voltage (J-V) characteristics of the preliminary unoptimized solar cell devices were measured using a
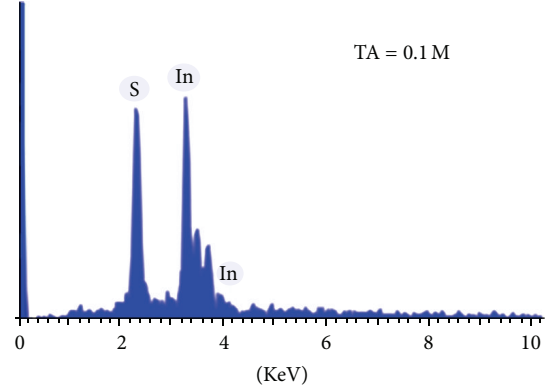

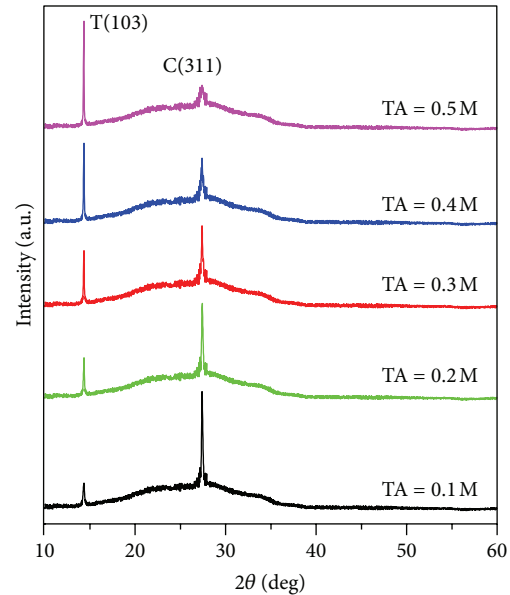FIGURE 1: EDAX spectrum of In_2S_3 film grown at 0.1 M TA concentration.

FIGURE 2: XRD spectra of In_2S_3 films grown at various TA concentrations.

Keithley 230 programmable voltage source and a Keithley 619 electrometer. A tungsten halogen lamp of 100 mW/cm^2 intensity at AM 1.5 condition was used as the illuminating source using evaporated Cu/Al as the top contact.

3. Results and Discussions

The as-deposited In_2S_3 films were uniform, pinhole free, and the color of the films changed from lemon yellow to bright yellow with the increase of TA concentration from 0.1 M to 0.5 M. Figure 1 shows the EDAX spectrum of In_2S_3 layer grown at 0.1 M TA concentration. The EDAX analysis revealed that the TA concentration had a significant influence on the stoichiometry of the grown layers. The spectra showed peaks related to the presence of In and S elements, and no other impurity peaks were found. The films formed at 0.1 M TA concentration were stoichiometric, and with the
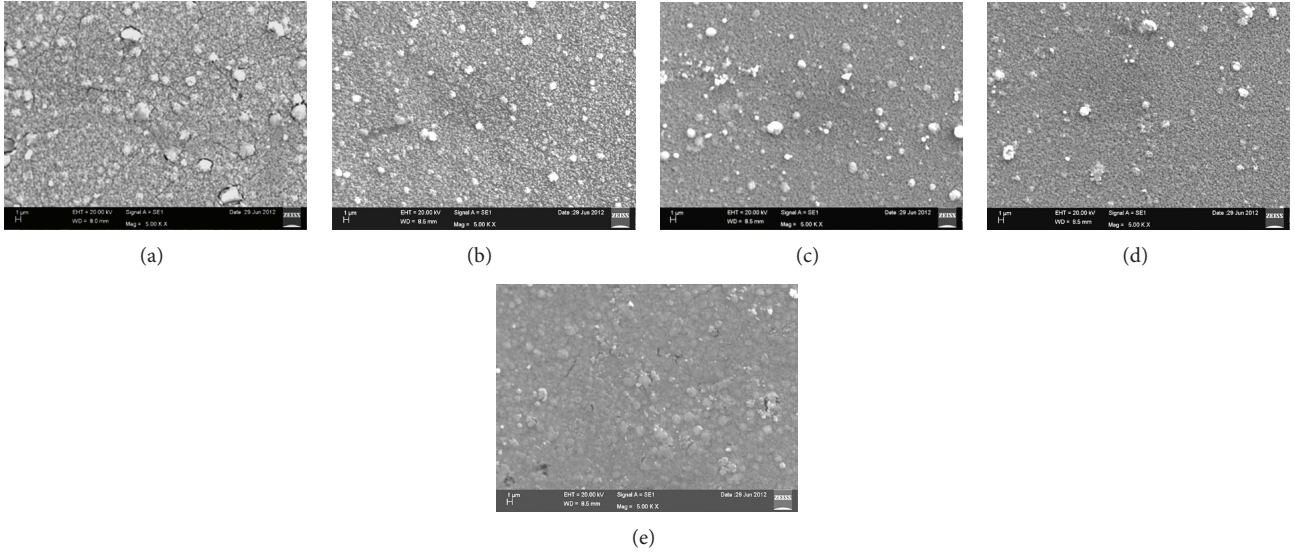
FIGURE 3: SEM images of the films grown at different TA concentrations (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, (d) 0.4 M, and (e) 0.5 M.
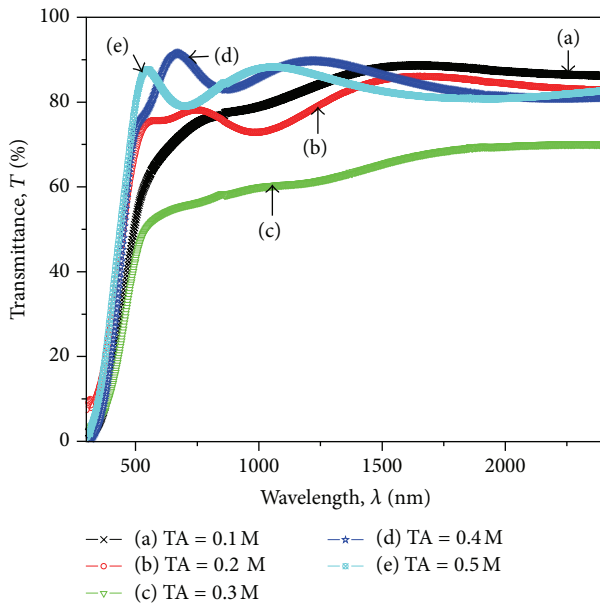

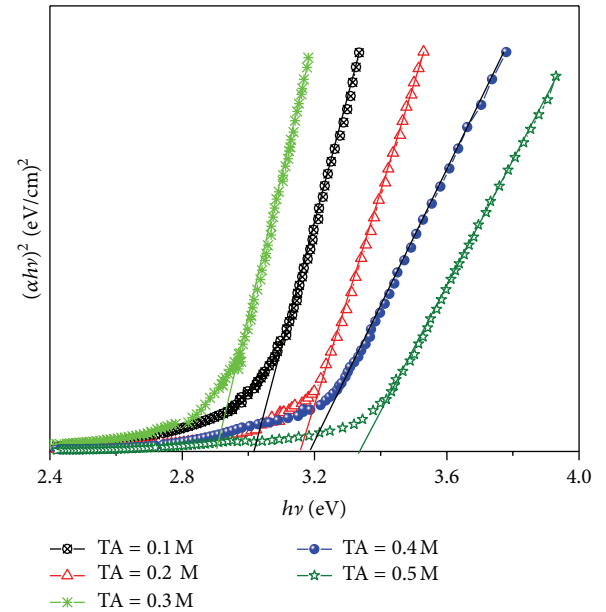FIGURE 4: Transmittance versus wavelength of In_2S_3 films.

FIGURE 5: $(\alpha h\nu)^2$ versus $h\nu$ plots of In_2S_3 films spectra grown at various TA concentrations.

further increase of TA concentration, the sulfur content in the grown layers increased. This might be due to more availability of sulphur content in the bath with the increase of TA concentration. Therefore, the S/In ratio in the films indicated a continuous increase with TA concentration from 1.49 to 1.61.

The X-ray diffraction patterns of as-grown films are shown in **Figure 2**. All the deposited films were polycrystalline in nature and exhibited two crystal structures. The layers grown at low TA concentration, 0.1 M, showed the (311) plane as preferred orientation with cubic crystal structure, and its intensity decreased with the increase of TA concentration, but the layers grown at higher TA concentration, 0.5 M, revealed the (103) plane as the prominent orientation, which

corresponded to the tetragonal structure, and its intensity increased with increase of TA concentration from 0.1 M to 0.5 M. This change in structure from cubic to tetragonal form with the increase of TA concentration might be due to structural reorientation that occurred in the film in order to minimize the interfacial energy. Therefore, the grains grew predominantly along the (103) crystal plane due to lower interfacial energy compared to the (311) growth direction. The presence of mixed phases of both cubic and tetragonal β-In_2S_3 was reported by Sandoval-Paz et al. in annealed In_2S_3 films prepared by chemical bath deposition [39]. Revathi et al. also reported a similar structural change from one crystal
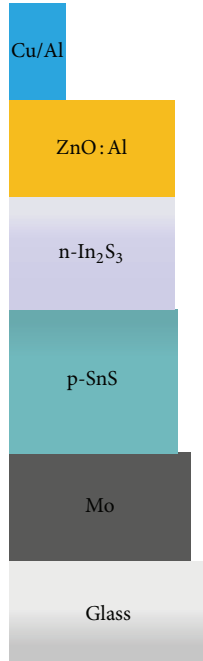
FIGURE 6: Structure of the SnS/In$_2$S$_3$ solar cell.
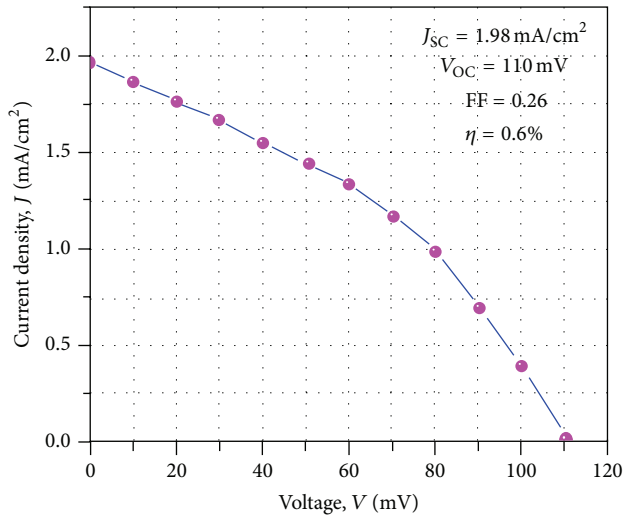
FIGURE 7: Illuminated J-V characteristics of the SnS/In$_2$S$_3$ solar cell.

structure to the other in In$_2$S$_3$ films formed by close spaced evaporation [40]. Peaks corresponding to other phases of indium sulphide or indium oxy/hydroxy sulphides were not observed in the XRD spectra. It was found that only the amorphous nature of the layers was reported by Lokhande et al., when the In$_2$S$_3$ films were formed on glass substrates using indium sulphate as indium source with triethanolamine and hydrazine hydrate as complexing agents [41], but in the present study, polycrystalline In$_2$S$_3$ films were formed by replacing the complexing agent with acetic acid. This indicates that acetic acid might have promoted the crystallinity in the films. The detailed analysis of the related growth mechanism is to be analyzed.

The average crystallite size "L" was calculated using the Scherrer formula [42]:

$$L = \frac{0.94\lambda}{\beta \cos \theta}, \tag{1}$$

where λ is the wavelength of X-rays used, β is the full width at half maximum in radians, and θ is the Bragg angle. The calculated crystallite size is found to vary in the range of 15–25 nm.

The surface morphological studies of In$_2$S$_3$ films were carried out using scanning electron microscopy measurements. The SEM images of In$_2$S$_3$ films are shown in **Figure 3**. The SEM studies indicated granular structure at lower TA concentrations that changed into smooth surface morphology at higher TA concentrations. The surface of the films grown at lower TA concentrations had high density of islands with only few grains developed on the island, only in certain regions. However, with the increase of TA concentration, the density of grains increased, leading to the agglomeration of grains. On increasing the TA concentration, the number of grains increased, and with the further increase in the TA concentration, the grains joined to form island structure which can be clearly seen in the increase of the grain size with TA concentration.

Figure 4 shows the dependence of optical transmittance, T, on wavelength for In$_2$S$_3$ films grown at different TA concentrations, measured in the range from 300 nm to 2400 nm. It can be observed that all the films showed a sudden fall in the transmittance near the fundamental absorption edge, indicating direct optical transition in the films. The films had an optical transmittance >70%, except for the films grown at a TA concentration of 0.3 M that had only 60% transmittance. This might be due to the coexistence of both cubic and tetragonal structures with approximately equal intensity in the layers as observed from the XRD measurements.

The optical absorption coefficient, α, of the experimental films was calculated using the formula:

$$\ln T = -\alpha d, \tag{2}$$

where T is the optical transmittance and d is the film thickness that varied in the range of 100–250 nm. The optical energy band gap, E_g, of the films was determined using the relation [43]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2}, \tag{3}$$

where A is constant depending on the transition probability.

Figure 5 shows $(\alpha h\nu)^2$ versus $h\nu$ plots of In$_2$S$_3$ layers grown at different TA concentrations. The energy band gap was obtained by extrapolating the linear portions of the plots onto $h\nu$ axis. The evaluated energy band gap varied in the range of 2.87–3.32 eV with the change of TA concentration. The value of energy band gap observed for In$_2$S$_3$ films grown in this study was high compared to the values reported in the literature [44, 45]. This might be attributed to the particle size confinement because of the lower crystallite size observed. A similar behavior of decrease of energy band gap with TA

concentration and vice versa was reported by John et al. [15] for indium sulphide films deposited by spray pyrolysis.

A thin film heterojunction solar cell was formed using In_2S_3 layers grown in this work in order to check the quality of the grown layers for device application. Thermally evaporated SnS films were used as the novel absorber layer to fabricate the junction. Figure 6 shows the structure of SnS/In_2S_3 solar cell device. The illuminated current density-voltage characteristics were measured to evaluate the device performance. Figure 7 shows the illuminated J-V plot of the device. An open circuit voltage of 110 mV, short circuit density of 1.98 mA/cm^2, and fill factor of 0.26 were observed for the unoptimized device that gave a solar conversion efficiency of 0.6%. The observed low efficiency might be due to the recombination of charge carriers at the interface due to lattice mismatch of a large conduction band offset at the interface because of the difference in electron affinity values of both the layers. A detailed analysis of the junction is required to find out the correct reason and is under progress. Although the observed efficiency value is low compared with the reported values obtained on SnS-based solar cells fabricated using other buffer layers [46–48], this study demonstrated the quality of the grown In_2S_3 films formed in the present work.

4. Conclusions

In_2S_3 films were grown by CBD process using indium sulphate and thioacetamide (TA) as precursors with a nontoxic complexing agent, acetic acid. The films were grown by varying the TA concentration in the range of 0.1–0.5 M. The S/In ratio was influenced significantly by the change of TA concentration. A change from cubic to tetragonal crystal structure was observed with the increase of TA concentration. A rough surface morphology is observed for the films grown at lower TA concentrations while those formed at higher TA concentrations indicated the smooth surface. The films had an optical transmittance >60%, and the evaluated energy band gap varied in the range of 2.87–3.32 eV. The higher value of energy band gap obtained is attributed to the particle size confinement. Novel thin film heterojunction solar cell was formed using In_2S_3 as the buffer and SnS as the absorber layer, and that showed a solar conversion efficiency of 0.6%.

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