

Compositional, structural and optical properties analysis of β - In_2S_3 Thin Films Prepared by Chemical Spray Pyrolysis and Electrochemical Deposition Techniques

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Abstract – An increased attention is devoted to interfacial In_2S_3 thin films because of their potential application as a new generation of buffer layer in copper indium gallium diselenide (CIGS)-based solar cells. In this paper, thin films of β - In_2S_3 were deposited by Chemical Spray Pyrolysis and Electrochemical deposition onto FTO Coated Glass Substrates. Characterization of the films was carried out by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS). Optical analysis to determine band gap gives band gap varying from 2.45 eV to 2.90 eV which are very close to the accepted values. The structural analysis reveals films with (0 0 12) as main peak for all samples in all case.

Key words : Indium sulfide, Buffer Layer, electrodeposition, Spray Pyrolysis, DMSO, FTO.

1. INTRODUCTION

Needless to say one of the crucial issues in recent decades has been the increasing energy needs. When facing, as we are to this problem, a transition out of the fossil civilization is necessary. A promising alternative source of energy is the use of solar cells. Finding viable alternatives also to silicon-based photovoltaics, through low-cost solution processable materials, is important. The international scientific community constantly fosters the development of innovative solar energy transducing devices. In the recent decade a large number of semiconductor materials have been studied for using in solar cells. Most promising materials for the use as light absorbers in thin film solar cells are chalcopyrites type semiconductors such as CIGS. CIGS absorbers need a buffer layer to form photovoltaic heterojunctions. Currently one of the best buffer materials for this purpose is a thin CdS film [1]. However, the use of cadmium in PV devices is undesirable from the view point of environmental safety [2]. Serious efforts have been made to substitute the CdS buffer layer by other non-toxic low-absorbing materials. Indium sulfide (In_2S_3) thin films as an n-type semiconductor have

recently attracted considerable attention because of their interesting physical properties, which are suitable for optoelectronic device fabrication. These films have a great potential for photovoltaic applications. In_2S_3 is one of the possible candidates to replace CdS as buffer layer. This compound can be found under three polymorphic forms. The cubic α form [3] is stable above 693 K and crystallizes in the defect spinel structure ($a = 10.77\text{\AA}$). The stable room temperature phase is β - In_2S_3 [4]. A third modification (γ - In_2S_3) with trigonal symmetry has been reported above 1047 K [5]. Depending upon the type and composition, the band gap reported for In_2S_3 compound varies between 2.0 and 2.45 eV [6]. Hetero-junctions as CIGS/ β - In_2S_3 [7] or CIS/ $\text{In}(\text{OH},\text{S})$ [8] have been built by CBD with conversion efficiencies of 15.7% and 11.4% respectively. Indium sulfide has elaborated using various techniques like Successive Ionic Layer Adsorption and Reaction (SILAR) [9], Thermal Evaporation (TE) [10], Atomic Layer Deposition (ADL) [11], Chemical Bath Deposition (CBD) [12] etc. It was noted that the quality of films depends strongly on growth technique. Electrodeposition and Chemical Spray Pyrolysis are also interesting for In_2S_3 synthesis. In the present work, we prepared β - In_2S_3 by two different ways: Chemical Spray Pyrolysis and Electrochemical deposition. The structure, morphology, optical properties and composition were studied and compared.

2. Experimental procedure

2.1. Preparation of thin films

Thin films of β - In_2S_3 were prepared by Chemical Spray Pyrolysis and Electrochemical deposition onto FTO Coated Glass Substrates.

Using Chemical Spray Pyrolysis, Indium sulfide (In_2S_3) thin films were prepared onto FTO (Fluorine Doped Tin Oxide) coated glass substrate from aqueous solution containing indium (III) chloride (InCl_3) (99.999%), thiourea ($\text{CS}(\text{NH}_2)_2$)

($\geq 99\%$) and alcohol (5% in volume) to reduce the surface tension. The concentration of indium chloride was fixed at 0.026M and the $[S]/[In]$ ratio was 3. The substrate temperature varied 250°C-277°C-300°C-330°C. The volume sprayed was 5mL, the spray rate 1.5mL/min, the air compressed pressure 0.7 bar and the distance between the glass substrate and nozzle was kept to 30 cm. Glass substrate were previously washed with HNO_3 and subsequently rinsed with water, ethanol and acetone.

Using electrodeposition, the In_2S_3 films were deposited by pulsed potentiostatic electrodeposition from a DMSO solution composed of 50 mM of sulfur (S8, Merck 99.8%), 40 mM indium perchlorate ($In(ClO_4)_3$, Aldrich 98%) and 10 mM potassium perchlorate ($KClO_4$, Aldrich >99%) as supporting electrolyte. The temperature of the electrolytic bath was 70°C. The working electrode substrates were glass plates coated with FTO ($SnO_2:F$). The electrodes were rinsed and subsequently cleaned in an ultrasonic bath with acetone and chemically treated in fresh 1 M nitric acid solution for 20 min at room temperature to improve the adherence of the films. Then, they were carefully rinsed with distilled water and dried with a nitrogen stream. The electrodeposition potentials were performed applying a pulsed E/t program using a three-electrode conventional arrangement. The counter electrode was a platinum wire (99.99%) and a $Ag/AgCl$ sat. ($E^\circ = +0.199$ V vs. NHE) was used as reference electrode, all the potentials reported in this work refer to this electrode. Electrochemical measurements were performed using an Ecochimie Potentiostat/Galvanostat, Autolab PGSTAT100 model.

2.2. Preparation of thin films

The surface morphology and microanalysis using Energy Dispersive X-ray Spectroscopy (EDS) of all the films were obtained on a Jeol-JSM6300. Structural properties were characterized by means X-ray diffraction (XRD) measurement with a Rigaku Ultima IV diffractometer using a parallel beam in grazing incidence. In this configuration the angle of the incident beam remains constant (θ_i) while the detector angle moves 2θ . The parallel beam was obtained by passing the $Cu-K\alpha$ radiation of an X-ray tube through a CBO module. The samples were scanned from $2\theta = 15$ to 60° in steps of 0.02° at a speed of $1^\circ/\text{min}$. Optical properties were monitored by transmittance using a Xe lamp in association with a 550 mm Yvon-Jobin Triax-550 spectrophotometer using a back-thinned CCD detector (Hamamatsu) optimized for the UV-VIS range.

3. Results and discussion

3.1 Structural properties

The Thin films Structural of $\beta - In_2S_3$ properties prepared by Chemical Spray Pyrolysis were characterized by means X-ray diffraction (XRD) measurement with a Rigaku Ultima IV diffractometer in the $\theta - 2\theta$ configuration and using $CuK\alpha$ radiation (1.5418\AA). Figure 1 shows the XRD patterns of thin films $\beta - In_2S_3$ prepared by Chemical Spray Pyrolysis at different substrate temperatures. All films deposited are polycrystalline with (0 0 12) as preferential direction perpendicular to substrate plan. others peaks appeared at $14.17^\circ - 22.30^\circ - 23.48^\circ - 27.54^\circ - 43.96^\circ$ and 48.06° corresponding to (103), (107), (116), (109), (1 0 15) and (2 2 12).

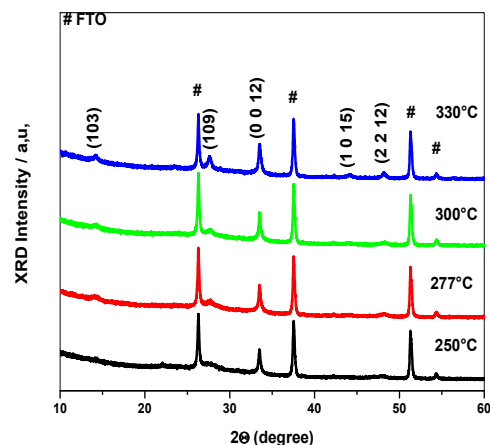


Fig-1: X-ray diffraction spectra for films deposited by Chemical Spray Pyrolysis at different FTO coated glass substrate temperatures

Fig- 2 shows the XRD pattern of a In_2S_3 thin film formed by electrochemical deposition at -1.125 V and recorded at grazing incidence for two different incident angles ($\theta_i = 0.4$ and 0.5°). indeed, grazing incidence measurements are performed at very low incident angles to maximize the signal from the thin layers. This is important when it is desired to attenuate the influence of the substrate. Dots correspond to FTO substrate Reference pattern JCPDS #25-0390 relates to a tetragonal structure. In this reference only XRD peaks with intensity higher than 15% have been plotted. All films deposited are also polycrystalline with (0 0 12) as preferential direction. The intensity of XRD peaks corresponding to FTO substrate (labelled with dots) decreases when the incident angle changes from 0.5 to 0.4° while the signal coming from the top layer remains constant. Some Peaks (103) and (109) are appeared only in films deposited by Spray Pyrolysis with high intensity and other

(118) (116) (419) appeared on those deposited by Electrodeposition . Comparing the X-ray diffraction spectra (Fig-1 and Fig-2), we notice that although the overall majority crystal structure appears identical. The mean crystallite size, D, has been determined from line width of the XRD patterns by using the Scherrer equation [15]:

$$D = \frac{K\lambda_x}{\beta \cos\theta}$$

where K is a constant close to 1 (K = 0.9 was used), λ_x is the X-ray wavelength whose value is 1.54\AA ($\text{CuK}\alpha$), β is the full width at half maximum (FWHM) of the peak corrected by the instrumental broadening, while θ is the Bragg angle at the center of the peak. The crystallite size D obtained from this equation corresponds to the mean minimum dimension of a coherent diffraction domain. When determining the crystallite sizes, the (0 0 12) diffraction peak has been used, because is the strongest one in all the samples, what leads to less uncertainty in broadening determination. According to this procedure, a crystallite size of about 25 nm has been roughly calculated for In_2S_3 films by Electrodeposition and 35 nm for those deposited by Chemical Spray Pyrolysis .

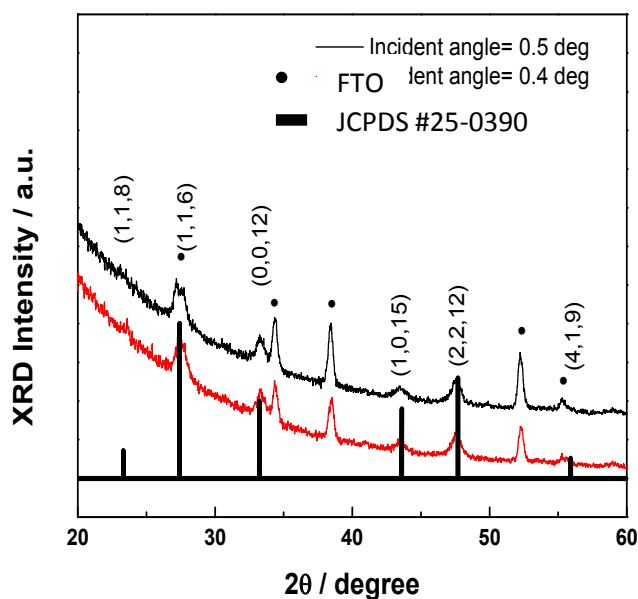


Fig-2: XRD pattern of electrodeposited In_2S_3 layers at -1.125V recorded under grazing incidence.

3.2. Surface morphology

Scanning Electron Microscopy (SEM) is a convenient method to study microstructure of thin films. It was utilized to study the surface morphology of indium sulfide thin films deposited by Chemical Spray Pyrolysis and Electrochemical deposition

onto FTO Coated Glass Substrates. Films deposited by Chemical Spray Pyrolysis were well-covered, homogeneous, dense, continuous and compact with no cracks neither voids. Grains are very small (Fig- 3).The small grain size results from the quick crystallisation between the precursors during the film drying. Otherwise grains size is big explaining by agglomeration of small grains to form big one. Debye Scherrer's formula derived to XRD confirms well those results.

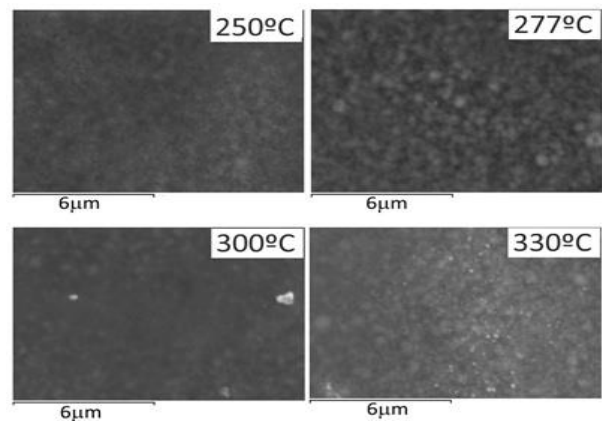


Fig-3: SEM micrographs of In_2S_3 thin films at different substrates temperatures

Fig- 4 shows typical SEM surface morphologies for three different In_2S_3 thin films electrochemically obtained onto FTO substrates in a potential interval comprised between -1.125 V and -1.175 V. The images show a uniform morphology with crystallites of very small size which agrees with the analysis of grazing XRD patterns. The morphologic characteristics are independent of the electrochemical potential employed in the synthesis. the predominant phases are In_2S_3 (tetragonal spinel $\beta\text{-In}_2\text{S}_3$). In fact, the morphological characteristic observed are entirely consistent with those obtained for In_2S_3 thin films formed in aqueous solution through of chemical bath deposition (CBD) [13,14]. Thus, all the samples show a cauliflower like morphology with aggregates .

In conclusion , all the films obtained by the two different ways show good uniformity and adherence.

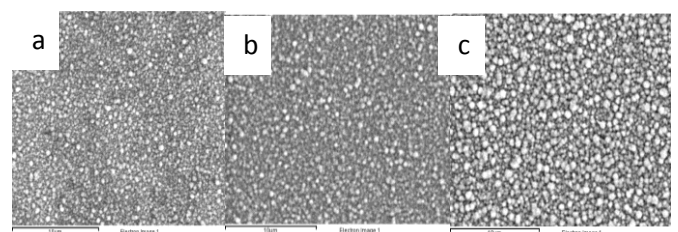


Fig-4: SEM micrographs for three typical In_2S_3 thin films electrochemically grown onto FTO substrates at: (a) -1.125 V, (b) -1.150 V and (c) -1.175 V respectively

3.3 Compositional Analysis

Energy Dispersive Spectroscopy (EDS) is a quantitative and qualitative tool to measure atomic concentration of elements present in sample after elaboration. Atomic concentration of In and S of samples obtained from EDS attached to SEM are given in Table -1 and Table -2. We notice that all samples elaborated have good stoichiometry.

Table -1: Composition of In_2S_3 /FTO glass substrate obtained EDS at different temperatures

Ts (°C)	at% S	at% In	Experimental Atomic Ratio S/In
250°C	59.69	40.31	1.48
277°C	59.00	41.00	1.43
300°C	57.55	42.45	1.35
330°C	54.25	45.75	1.18

Table -2: Composition of In_2S_3 /FTO glass substrate obtained EDS for three different In_2S_3 thin films electrochemically grown at different electrodeposition potential.

Ed/V (120s)	%at In	%at S	Experimental Atomic Ratio S/In
Theoretic values	40	60	1.50
-1.25	38.56	61.44	1.59
-1.50	39.21	60.78	1.55
-1.75	39.80	60.20	1.51

The EDAX analysis of In_2S_3 thin films electrochemically grown onto FTO substrates shows an appropriate composition with an atomic ratio very close to the theoretical values (see Table -2). The decreasing in the atomic ratio at more cathodic potential indicates that the films present a small indium excess.

We noted that all samples either elaborated by Chemical Spray Pyrolysis or Electrochemical deposition have good stoichiometry.

3.4. Optical properties

Optical studies of In_2S_3 films were carried out in the visible range using a spectrophotometer HR-4000 Ocean Optics. The transmittance T versus λ spectrum of films deposited by Chemical Spray Pyrolysis and Electrochemical deposition show that films have better transmittance. All the films show more than 55 % transmission for wavelengths longer than 500 nm (Fig- 5 and Fig- 7). The sharp rise in transmission near 500 nm is an identification of good crystallinity of films. Optical absorption spectra recorded in the wavelength region 250-1000nm in order to determine the optical band gap, graph was plotted with $(\alpha h\nu)^2$ against $h\nu$. Optical band gap was determined from this plot for all films by linear fit in the straight portion of the graph. For the thin film obtained by Electrochemical deposition, the band gap energy values decreasing from 2.80 eV to 2.45 eV (Fig- 8) after the heat treatment which is very close to the accepted value [16]. Films prepared Spray Pyrolysis have band gap larger (from 2.73 eV to 2.90 eV) (Fig- 6). The change in the band gap value can be correlated with possible nano-crystal sizes through the nano-crystal size effects, which agrees with the crystallite size found through the grazing XRD analysis.

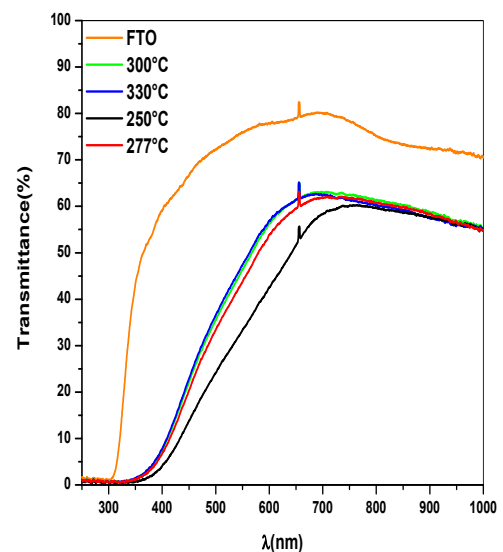


Fig-5: Transmittance spectra of samples at different substrate temperatures

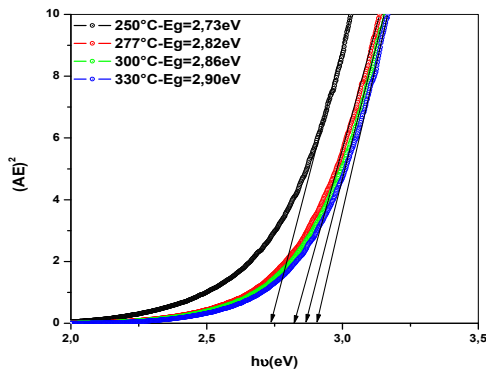


Fig-6: Band gap variation of samples at different substrates temperature

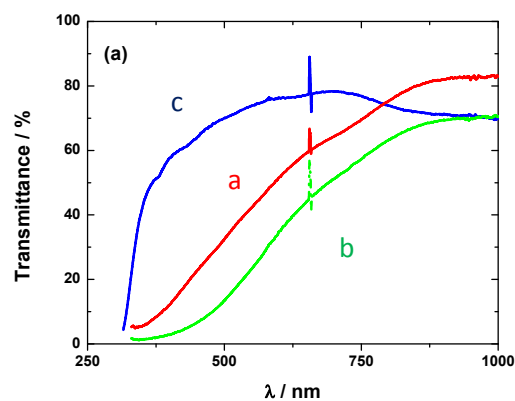


Fig-7: Transmittance of a In_2S_3 thin film electrochemically formed onto FTO substrate at 1.125 V, the figure show the spectral response (a) as grown and (b) after a heat treatment at 450°C for 30 min, the (c) represent the optical response of FTO substrate.

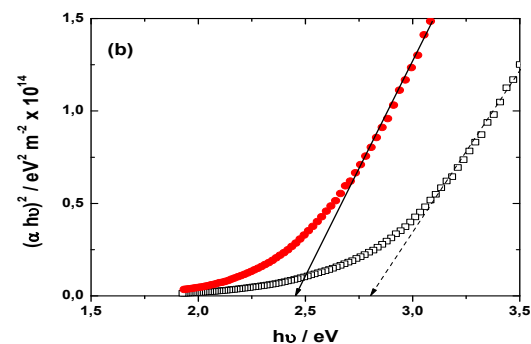


Fig-7: Determination of bandgap energy through the $(\alpha hv)^2$ vs $h\nu$ plot for the same sample (●) before and (◻) after heat treatment.

4. CONCLUSIONS

β - In_2S_3 thin films were fabricated by using two different ways :Chemical Spray Pyrolysis and Electrochemical deposition. Films grown by Electrochemical deposition have lower crystallinity than those grown by Chemical Spray Pyrolysis. All thin films show a similar X-ray diffraction pattern. Indeed, X-ray diffraction analysis reveal that all thin films are polycrystalline with (0 0 12) as main peak which has high intensity . XRD peaks located at 2θ angles of 27.47, 33.23, 43.60, and 47.70 are also clearly identified and match well with the JCPDS #25-0390 pattern corresponding to a tetragonal phase of In_2S_3 . SEM images revealed good substrate coverage and microstructure whereas EDAX analysis gave a stoichiometric composition very close to the expected. Optical measurements allowed to establish the band gap of In_2S_3 . The results reveal that the microstructure and the optical properties of the In_2S_3 films are highly dependent on the growth method. Films prepared Spray Pyrolysis have band gap larger (from 2.73 eV to 2.90 eV) and the band gap energy values decreasing from 2.80 eV to 2.45 eV(Fig- 8) after the heat treatment for the thin film obtained by Electrochemical. In all cases ,gap energy values of all the thin films ranges from 2.45 eV to 2.90 eV. This makes the films suitable for optoelectronic devices, for instance window layers in solar cells.

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