

Compositional, Structural and Optical Properties Analysis of β - In_2S_3 Thin Films Prepared by Chemical Spray Pyrolysis at Different Substrate Temperatures

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Abstract : In_2S_3 thin films were prepared using chemical spray pyrolysis technique. All films were deposited on FTO (Fluorine Doped Tin Oxide) coated glass substrate with different temperatures. The films obtained were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmission spectra, energy dispersive spectroscopy (EDS) and Atomic force microscopy (AFM). XRD studies have revealed that the samples are β - In_2S_3 . All the films grown exhibited transparency over 55% in the visible spectral region. According to SEM, the surface morphologies of the films were free of defects. The AFM micrograph show that the films adhered to the FTO substrate with a small grain size. The optical band gap energy varied from 2.73 eV to 2.90 eV.

Keywords: Indium sulfide; Buffer Layer ; Spray Pyrolysis ;FTO.

1. Introduction

Indium sulphide (In_2S_3) thin films have attracted research interest due to their potential use in the manufacturing of optoelectronic devices. It is an important material for photovoltaic applications [1, 2]. It can be used as an effective replacement for cadmium sulfide (CdS) in Cu(In, Ga)Se₂ based solar cells. It is nontoxic and almost transparent to visible light. It has stable optical properties and can grow under the low temperature. In_2S_3 has been used as a buffer layer for CuInS₂/In₂S₃/ZnO type solar cells in order to improve conversion efficiency[3]. A Cu(In, Ga)Se₂ based solar cell prepared with chemical bath deposited In_2S_3 as a buffer layer could reach efficiencies (15.7%) near to those obtained by devices made with a standard CdS buffer layer [4].

Indium sulfide (In_2S_3) is a III–VI compound originating from the II–VI semiconductor by replacing group II metals by group III elements [5]. In_2S_3 exhibits different polymorphic structures such as α , β and γ depending on the processing parameters[6]. The β - In_2S_3 phase was found to be the stable crystalline phase of indium sulfide at room temperature with tetragonal structure[7]. In_2S_3 films are prepared by various methods such as chemical bath deposition[8], thermal evaporation [9], electrodeposition[10], spray pyrolysis [11, 12, 13] radio-frequency (rf) sputtering [14, 15] and atomic layer epitaxy [16].

In this paper we report the preparation of β indium sulphide (β - In_2S_3) thin films using the chemical spray pyrolysis (CSP) technique at different substrate temperatures. The CSP method has been chosen because this method is economical, requires short processing time, and can be performed in atmospheric. A detailed study of the structural, optical

properties, and compositional analysis has been carried out for these films.

2. Experimental Details

Indium sulfide (In_2S_3) thin films were deposited on to FTO Coated Glass Substrates using an aqueous solution of indium (III) chloride (InCl_3) (99.999%), thiourea CS (NH_2)₂ (99%), and alcohol: isopropyl (5% by volume) to reduce the surface tension. The substrate temperature was kept at 250 °C, 277 °C, 300 °C, and 330 °C using a Proportional-Integral-Derivative (PID) system with a sensitivity of ± 0.1 °C. Before the deposition, the FTO substrates were cleaned using soapy deionized water and were put in to the ultrasonic bath for 5 min. Then the substrates were thoroughly rinsed with deionized water and different solvents in the following order: acetone and 2-propanol previously warmed in the ultrasonic bath during 5 min each.

The crystal structure of the sprayed films was characterized by X-ray diffraction (Rigaku Ultima IV). The surface morphology of the films was examined by scanning electron microscopy (JEOL-JSM6300) and by atomic force microscopy (Bruker Multimode 8 AFM Nanoscope V controller). The visible spectrophotometer (Yvon-Jobin HR460) is used to record the optical transmissions. Mole ratios of In and S atoms in films were measured by Energy Disperse Spectroscopy (EDS).

3. Results and Discussion

3.1 XRD analysis

Samples were prepared at different substrate temperatures in the range 250–330 °C. The XRD patterns are shown in Fig.

1. It indicate that In_2S_3 thin films have a preferential orientation along the (0 0 12) direction. The d values coincide with that of $\beta\text{-In}_2\text{S}_3$ in the standard JCPDS data card (25-390). As the temperature was increased from 250 to 330°C, the intensity of the peak corresponding to the (0 0 12) plane increased. The reflections (103), (107), (116), (109), (1 0 15) and (2 2 12) confirm the $\beta\text{-In}_2\text{S}_3$ phase (JCPDS#25-0390). According to the XRD study, phase composition of the sprayed films did not depend on substrate temperatures. All thin films show a similar X-ray diffraction pattern. the best substrate temperature is 330 °C with high intensity of main peak.

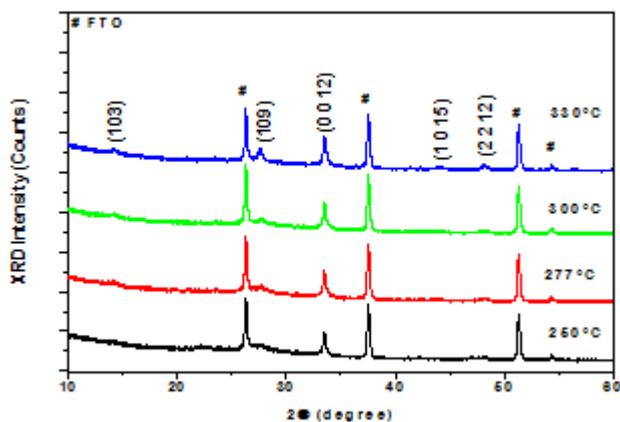


Figure 1: X-ray diffraction spectra for films deposited by Chemical Spray Pyrolysis at different FTO coated glass substrate temperatures

The mean crystallite size, D, has been determined from line width of the XRD patterns by using the Scherrer equation [17]:

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

where K is a constant close to 1 (K = 0.9 was used), λ 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. Details are shown in Table I . The grain size of the films increased from 33.47nm to 35.41 nm.

Table I: Grain size of $\beta\text{-In}_2\text{S}_3$ by Scherrer Formula method

Temperature (°C)	Grain size (nm)
250°C	33.49
277°C	35.41
300°C	34.61
330°C	33.47

3.2 Surface morphology

Scanning Electron Microscopy (SEM) was utilized to study the surface morphology of indium sulfide thin films. Figure 2 display the SEM micrographs of $\beta\text{-In}_2\text{S}_3$ prepared at different substrate temperatures. Films were well-covered, homogeneous, dense, continuous and compact with no cracks neither voids. Grains are very small. The small grain size results from the quick cristallisation betwween the precursors during the film drying. Otherwise the big grains size is explaining by agglomeration of small grains to form one more big.

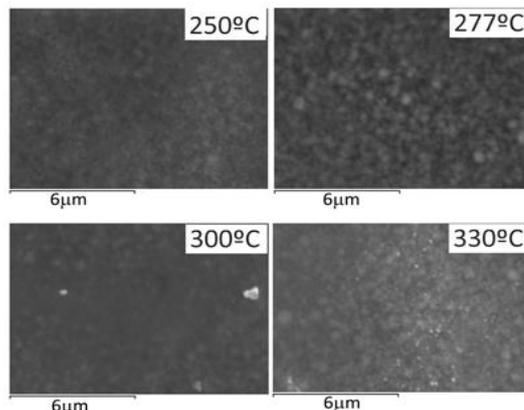


Figure 2: SEM micrographs of In_2S_3 thin films at different substrate temperatures

We used AFM in addition to SEM to characterize the surface morphology of the sprayed films. The AFM micrographs of In_2S_3 thin films with different substrate temperatures were

analyzed in an area of $3\mu\text{m} \times 3\mu\text{m}$ are shown in Figure 3. The deposited films are generally little rough. Their structure is uniformt with well defined grain boundaries and a few grains dispersed on the surface of the films. We noted a variation of grains size with substrate temperatures. we seen also that grain size measured with AFM are bigger compared to those measured with Debye Scherrer's formula. The difference between crytallite sizes calculated from Scherrer equation and grain sizes gives by AFM analysis is explained by the fact that Schrrer's formula gives the size of crystallites while AFM analysis gives grain sizes. However, one grain (as seen by AFM) contain several crystallites (as detected by XRD).

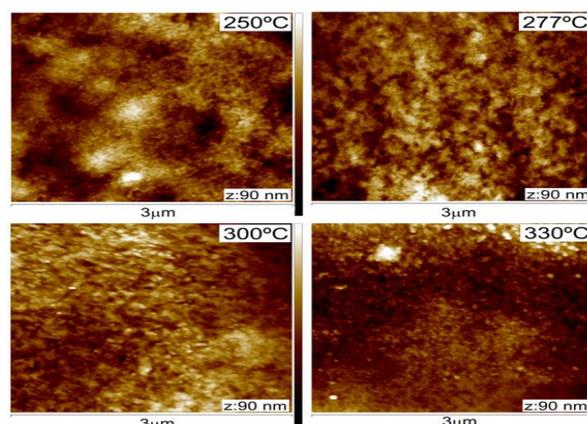


Figure 3: AFM micrographs of samples deposited by spray pyrolysis at different substrate temperatures

Table II: Surface roughness and grain size of samples giving by AFM analysis

Temperature (°C)	Mean Roughness (nm)	Grain size (nm)
250°C	6.67	106.25
277°C	7.29	126.40
300°C	9.58	102.53
330°C	9.92	87.40

3.3. Compositional Analysis

Energy Dispersive Spectroscopy (EDS) is a quantitative and qualitative tool to measure atomic concentration of elements present in sample. Atomic concentration of In and S of samples obtained from EDS are shown in Table III. In₂S₃ thin films are close to standard stoichiometric composition which indicates that films have a good crystallinity. The decreasing in the atomic ratio at high substrate temperatures indicates that the films present a small indium excess.

Table III: Composition of In₂S₃/FTO glass substrate obtained EDS at different temperatures

Temperature (°C)	at% S	at% In	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

3.4. Optical Studies

Figure 4 shows the optical transmission spectra of the sprayed In₂S₃ films grown at different substrate temperatures. The transmittance T with respect to spectrum of films deposited show that the films have a transmittance between 55% and 66% probably due to too thin thicknesses of samples. The lower optical transparency of thin films can be also a result of the increase in light scattering on rough surfaces. Otherwise transmittance increases with substrate temperature for all samples. However, the transmission spectra of the films obtained at 300 °C and 330 °C exhibited similar behaviour. The optical band gap values were determined from the transmission data. 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. Bandgaps of all samples increase with substrate temperatures. Eg values of sprayed In₂S₃ films deposited at temperatures between 250°C and 330°C were in the range of 2.73 eV – 2.90 eV which are very close to the accepted values. This makes the films suitable for optoelectronic devices, for instance window layers in solar cells.

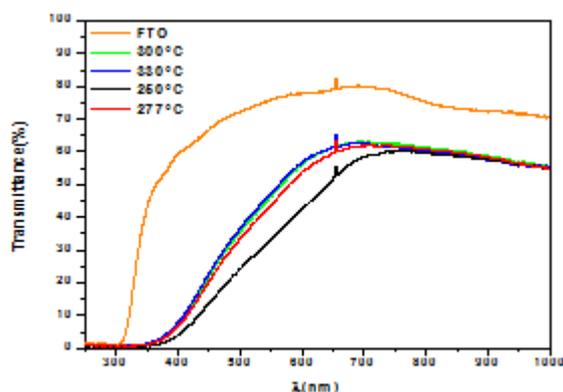


Figure 4: Transmittance spectra of samples at different substrate temperatures

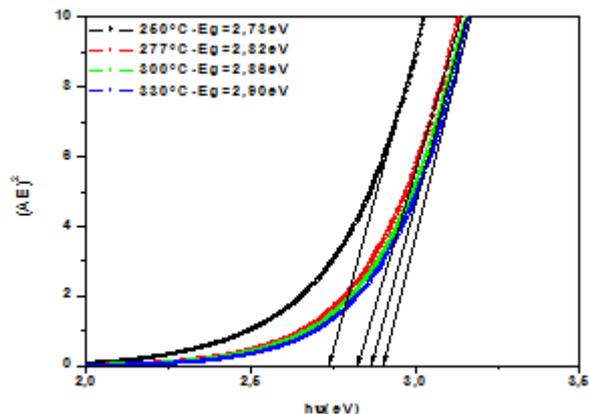


Figure 5: Bandgap variation of samples at different substrate temperatures

Table 4: Gap energy of samples at different substrate temperatures

Temperature (°C)	Bandgap (eV)
250°C	2.73
277°C	2.82
300°C	2.86
330°C	2.90

4. Conclusions

β-In₂S₃ thin films were prepared by using Chemical Spray Pyrolysis technique and using InCl₃, thiourea in aqueous and alcoholic solutions at different substrate temperatures. The effect of substrate temperatures on the formation of In₂S₃ thin films was investigated. Substrate temperatures have significant effects on the structure and the properties of films. X-ray diffraction analysis reveals that all films are polycrystalline with (0 0 12) as main peak which has high intensity at 330 °C. A SEM image shows films dense, compact, homogeneous, without voids. AFM analysis confirms the results of SEM analysis. The Eg increased with substrate temperatures from 2.73 to 2.90. optical transmittance of In₂S₃ films is over 55% in the visible region. In₂S₃ thin films are close to standard stoichiometric composition which indicates that films have a good crystallinity. This makes the films suitable for optoelectronic devices, for instance window layers in solar cells.

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