CONTRIBUTION TO THE STUDY OF In_2S_3 THIN FILMS PROPERTIES GROWN BY SPRAY PYROLYSIS

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Abstract

Polycrystalline In_2S_3 thin films were grown on glass substrates by means of chemical spray pyrolysis, using indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) as precursors. The deposits were performed under air atmosphere with substrates maintained at temperatures varying from 300 to 400°C. The optical and structural properties of the films were studied as a function of the deposition time and the substrate temperature.
X-ray diffraction has shown that the In_2S_3 material is the main phase present in these films and that the allotropic structure of this phase is affected by the substrate temperature and the deposition time. The optical transmittance of the In_2S_3 films varies in accordance with the substrate temperature. The average transmission in the visible region exceeds 70% and optical band gap of the films was found to vary from 2.47 to 2.53 eV.

Keywords: Thin films, In_2S_3, Spray pyrolysis, Raman

1. Introduction

The replacement of harmful heavy metals and even costly elements by non toxic and economically available materials is a major challenge in the field of photovoltaic devices research. In this economical point of view, thin film technology offers a considerable interest due to its versatility and its reduced budget in term of materials consumption and by-products production. Among various semiconductor compounds, Indium Sulphide (In_2S_3) has to be considered, as a promising candidate for optoelectronic and photovoltaic applications in accordance to its high stability, its photoconductive properties, its wide band gap and its high conversion efficiency [1,2]. It can be found in literature that its band gap varies from 2.0 eV [3] to 2.4 eV [4]. But larger values of In_2S_3 band gap have also been reported, for instance Lokhande et al. [5] have measured a value of 2.75 eV, and Yousfi et al. [6] an even higher value of 3.25 eV. In term of applications, In_2S_3 can be considered as a nontoxic substitute for cadmium sulphide (CdS) in copper indium gallium diselenide (CIGS) based solar cells. The thin films of this material can be grown by a variety of physical and chemical techniques [7].
In this work, we study the effect of substrate temperature and the deposition time on the physical and chemical properties of In_2S_3 thin films deposited by Spray Pyrolysis technique on Corning glass substrates.

2. Experimental details

Thin films of In_2S_3 were prepared from aqueous solutions containing indium chloride and thiourea and deposited by chemical spray pyrolysis (CSP) technique onto glass substrates using compressed air as carrier gas. The indium/ sulfur molar ratio (In/S) in the spray solution was varied from 1.4/3 to 2.8/3. This was achieved by varying the molarity of the precursors keeping the volume of solution fixed. The solution was sprayed in the air onto preheated glass substrates ($25\times25\times1$ mm^3) maintained at temperatures from 300 to 400 °C and using spray rate of 1 ml/min in various spray durations. The structural properties of these films were characterized by X-ray diffraction. XRD patterns in the 2 range 10-60° configuration with a step size of 0.067° were performed using Cu-Kα radiation of a copper anticathode (0.154 nm) and the generator settings were 40 mA, 45 KV. Spectral transmittance and reflectance were recorded in the wavelength range 300-2000 nm. The microstructure and the surface morphology were analyzed by JEOL scanning electron microscope (SEM). The elemental composition of In_2S_3 thin films was determined thanks to an energy dispersive spectrometer (EDS) connected to JEOL SEM. Raman spectroscopy was performed in retrodiffusion geometry with a LASER excitation line of 514.5 nm in a Jobin-Yvon T64000 setup. The optical head of the Raman

spectrometer was equipped with Olympus microscope lens with a 100x magnification, focusing the LASER beam to a spot diameter down to 1 µm. The LASER penetration depth is estimated to be close to 500 nm.

3. Results and discussion

3.1. Structural properties

Several crystalline phases (α, β, and γ) have been reported for In_2S_3 films deposited by several techniques, the tetragonal β phase being the most stable at room temperature. It is also the most common crystalline phase observed in In_2S_3 films. In this work, the β phase is observed for the films sprayed at substrate temperatures in the range of 300-400°C. Fig 1 shows the XRD patterns of In_2S_3 films sprayed at various substrate temperatures with the same deposition time of 15 mn. As we can see from the XRD patterns, the films show a good crystallization. The crystallization grows with the increasing temperature up to the value 350 °C and starts decrease after this value. The sharpness is clear for the (0012) peak which is located at 2θ = 33.62. The sharper peak obtained for the value 350°C indicates the best deposition condition in term of substrate temperature. Since the best substrate temperature in this work is found to be 350°C, we studied the evolution of XRD diagram for In2S3 thin films obtained at this temperature as a function of the deposition time ranging from 10 min up to 20 min by step of 5 min as shown in Fig 2. We can see that there is also a growth in the crystallization of In_2S_3 thin films with the increase of deposition time and the films are completely crystallized after 20 min.

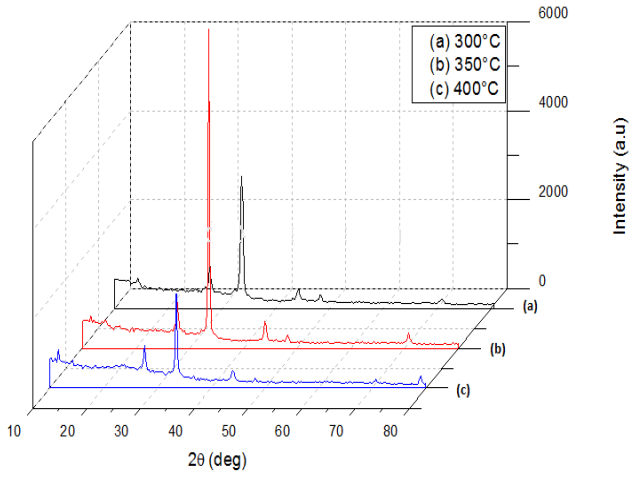

Fig.1.X-ray patterns of In_2S_3 thin films prepared at various substrate temperatures with 15mn deposition time.

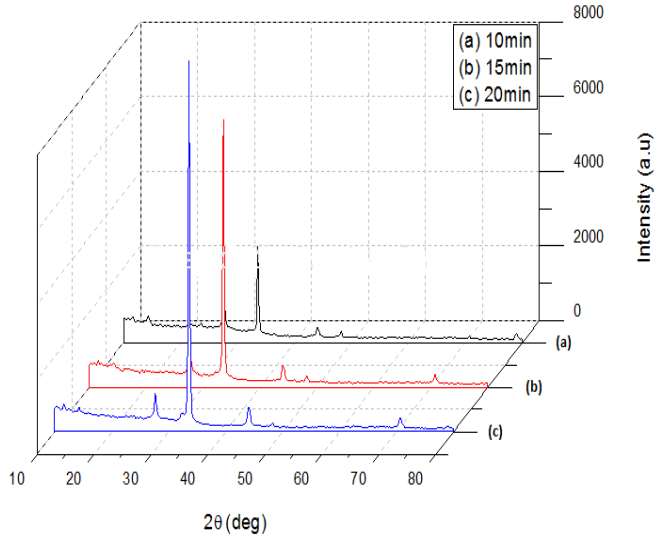

Fig.2. XRD spectra of In_2S_3 films grown at 350 °C with different deposition times.

The crystallite size of the In_2S_3 films prepared at different temperatures was calculated by using Scherrer's formula [8].

$$D_{hkl} = 0.94 \frac{\lambda_{hkl}}{\beta_{hkl} \cos(\theta_{hkl})}$$

Where D_{hkl} is the crystallite diameter, λ_{hkl} is the wavelength of the incident radiation (λ = 0,154 nm), β_{hkl} is the full width at half maximum (FWHM) of the peak corrected by the instrumental broadening. Expressed in radians, θ_{hkl} is the Bragg half-angle diffraction [9]. The results are reported in Table1. These results indicate that the values of the grain size increase from 28.22 to 34.97 nm with the increase in substrate temperature from 300 to 400°C. Generaly, the grain size increases with the increase in growth temperature due to the increase in ad-atom mobility and sticking coefficients of the deposited material.

Table 1: Crystallite size along prominent diffraction planes for In_2S_3 films prepared at 300°C, 350°C and 400°C

Samples	Temperature (°C)	Grains size (nm)
HFS44	300	28.22
HFS53	350	34.97
HFS62	400	34.97

3.2. Chemical Composition (EDX)

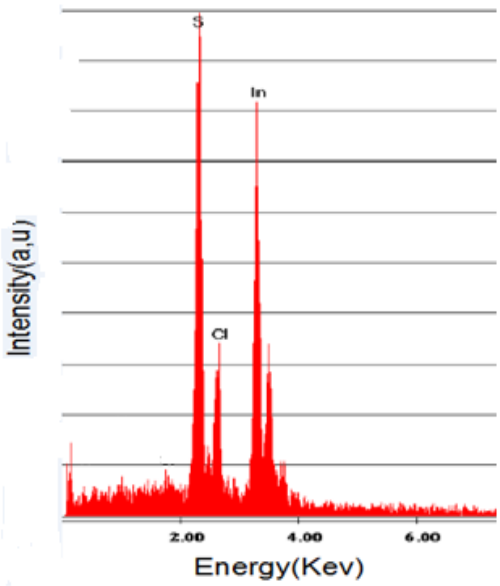

Fig.3.the typical EDAX spectra of In2S3 layers

The elemental composition of In_2S_3 thin films determined from EDS analysis for films deposited at various substrate temperatures are shown in Table 2.

Table 2: Analysis of the composition of thin films by EDS deposited in following conditions (300°C , 350°C and 400°C)

Temperature (°)	S(at %)	In (at %)
300	58.21	41.79
350	58.81	41.19
400	57.92	42.08

The EDS microanalysis revealed that the chemical composition of In_2S_3 thin films elaborated at all temperatures is close to the stoichiometry as we can see it in Table 2.

3.3. Optical properties

3.3.1. Transmission

Figure 3 shows the optical transmittance curves as function of the wavelength. The films present a high transmittance in the visible wavelength range, mostly in excess of 70%.

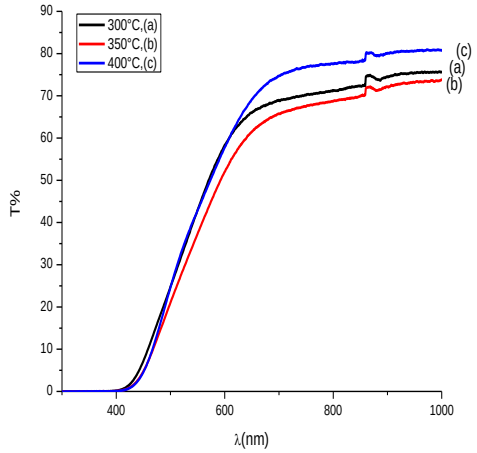

Fig. 4. Optical Transmission spectra at various substrate temperatures with a 20 mn deposition time.

From the transmission curves as a function of the wavelength, we can calculate the absorption coefficient for each wave length, and plot the variation of $(\alpha.h\upsilon)^2$ as a function of $(h\upsilon)$. The width of the band gap Eg of these films can be determined from the following equation [10].

$$(\alpha.h\upsilon)^2 = B\,(h\upsilon - Eg) = f\,(h\upsilon)$$

Where $h\upsilon$ is the energy of incident photons, Eg the optical gap and B is a constant

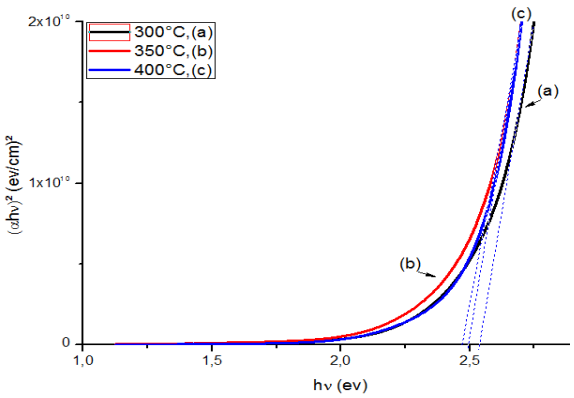

Fig.5. Determination of the energy gap by extrapolation method from the variation of $(\alpha.h\upsilon)^2$ according to $h\upsilon$ for a thin layer of In_2S_3

As shown in Fig 5, the values of energy gap Eg of the samples of In_2S_3 were obtained by extrapolating the linear part of the curves to the zero absorption.

The results show that the energy band gap decreases when the substrate temperature increases.

Samples	Eg(ev)
(a)	2.53
(b)	2.49
(c)	2.47

3.3.2. Raman spectroscopy

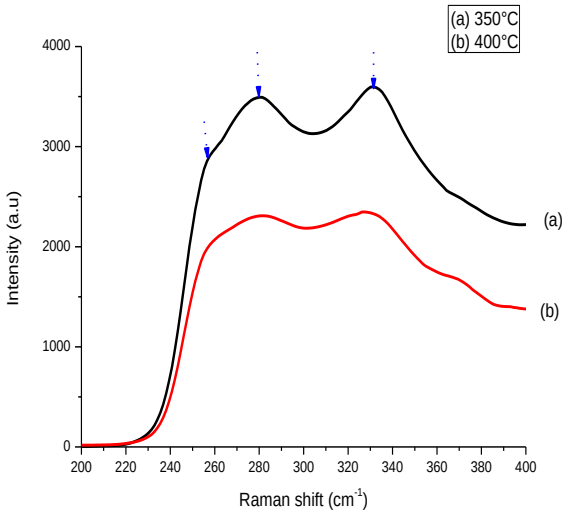

Fig.6. Raman analysis of In_2S_3 thin film prepared at various substrate temperatures

The Raman scattering strongly depends not only on the nature of the investigated system but also on the crystallographic form and crystallinity of the compound. Raman spectroscopy is a nondestructive and relatively fast experimental technique to determine the phase and the quality of the deposited films. As we can see in Fig.6, the Raman spectra of In_2S_3 films deposited at different substrate temperatures present bands at 256, 279 and 331 cm^{-1} indicating the presence of the β-phase in all the films [11,12]. The position and the half width of the Raman bands are affected by the degree of crystallinity of the medium. We did not observe any shape difference between spectra performed on films deposited at 350 and 400°C. It can be inferred that the dimension of the In_2S_3 crystallites do not change significantly in accordance to the substrate temperature in the range explored.

4. Conclusion

In this paper, we report the structural and optical properties of chemically deposited In_2S_3 polycrystalline films. We show also the modifications of their properties produced by the variation of substrate temperature and deposition time. The In_2S_3 layers were prepared by the CSP method and characterized by XRD and Raman spectroscopy. The XRD patterns showed that all the diffraction peaks can be indexed to the tetragonal β-In_2S_3. No other impurities were detected. The observation also revealed that the grown In_2S_3 films exhibit a preferential orientation along the (0012) direction. The square absorption coefficients spectra reveal that the energy band gap decreases when the substrate temperatures increase (2.47-2.53 ev). The Raman spectra reveal the presence of the β-phase. The active modes of β-In_2S_3 are present at 256, 279 and 331 cm^{-1}; their nanocrystalline nature is reflected in the broadening of the bands (mostly in the high frequency bands).

Acknowledges:

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