The effect of molarity on some physical properties of In_2S_3 thin films deposited by chemical spray pyrolysis technique

Nadir F. Habubi¹ Raid A. Ismail² Mahmood M. Abbod³

¹Physics Department, Education Faculty, University of Al- Mustansiriyah, Baghdad, Iraq

²Department of Applied Sciences, University of Technology, Baghdad, Iraq

³Physics Department, Education Faculty, University of Al- Mustansiriyah, Baghdad, Iraq

Corresponding author, E-mail:nadirfadhil@uomustansiriyah.edu.iq

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ABSTRACT. In_2S_3 thin films were grown by the chemical spray pyrolysis (CSP) method using indium chloride and thiourea as precursors at a different molar ratio (0.05, 0.1, 0.15 and 0.2)M. The deposition was carried out at 400 °C on glass substrates. The film thickness is about 0.4 μm . The X-ray diffraction analysis revealed that all the films were polycrystalline in nature with a strong (311) plane as the preferred orientation and consisted of cubic phases. The evaluated crystallite size varied in the range of (7.32–8.32)nm with the increase of molarity concentration. Morphological analysis showed that the granular structure and the granular density decrease with the raise of molarity concentration. The optical properties of the layers were also investigated using UV-Vis. analysis, which indicated that all the In_2S_3 films had the optical transmittance (60-85)% with increasing in molarity in the visible region, and the evaluated energy band varied in the range of (3.5–3.3)eV with the raise of molarity. The purpose of the preparation of a thin film of indium sulfide at several rates is to get thin films with a high degree of chemical balance (Stoichiometry) and a high degree of crystallization.

1. INTRODUCTION

Indium sulphide (In_2S_3) is one of the potential materials for various device applications; this is mainly due to its chemical stability, wide energy band gap, and controllable electrical properties [1]. This includes development of photovoltaic [2,3], electronic [4] and optical [1,5]. In_2S_3 is n-type semiconductor that belongs to the III–VI group of compounds. Indium sulfide (In_2S_3) is an important material for optoelectronic and photovoltaic applications and is a promising candidate for many technological applications due to its stability, wider band gap and photoconductive behavior [1]. In_2S_3 is a III–VI compound originating from the II–VI semiconductor by replacing group II metals by group III elements and exists in three crystallographic modifications α , β and γ [6]. The crystalline properties and composition of the films depend strongly on their growth technique. Thin films of In_2S_3 material have been successfully synthesized using numerous techniques like thermal evaporation [7], RF sputtering [8], atomic layer deposition (ALD) [9], metal organic chemical vapour deposition (MOCVD)[10], Chemical spray pyrolysis (CSP) [11,12], spray ions layer gas reaction (ILGAR)[4], spin coating [13] and chemical bath deposition (CBD)[14]. In this study, In_2S_3 films were formed on glass substrates by chemical spray method. The effect of molarity on the structural, morphological and optical properties was reported and discussed.

2. EXPERIMENTAL PART

In_2S_3 films were deposited on (1.5×1.5) cm^2 glass substrates by the spray pyrolysis technique. The In_2S_3 thin films were prepared by spraying an aqueous solution of indium chloride InCl_3 and thiourea $\text{CS}(\text{NH}_2)_2$ maintaining at different molarity concentration (0.05, 0.1, 0.15 and 0.2)M. The deposition conditions were optimized in order to obtain reproducible and good quality films. Compressed Nitrogen was used as the carrier gas, the gas pressure was kept at 10^5 N/m^2 . The nozzle to substrate distance was approximately 30 cm, and the spraying time period was 9 Sec with 1.5

min wait between the steps of spraying. The substrate temperature was maintained at 400 °C. The formation of In_2S_3 resulted from the chemical reaction following the equation:

After the deposition, The weighting method was used to determine the thickness of the films, This method is done by using electrical balance sensitive (Mettler A.K -160) four digits 10^{-4}g . The substrates are weighted before and after deposition, from the variation in weight and the area of substrate, we can measure the thin film thickness (t), according to the following equation.

$$t = \frac{\Delta m}{\rho_0 A_s} \quad (1)$$

Where Δm : is the variation in the weight of substrate in (g), A_s : area of the thin film (cm^2), ρ_0 : the density of the thin film material .

The film crystalline structure was analyzed by X-ray diffraction (XRD) using X-ray device (Shimadzu- XRD 6000, Shimadzu Company /Japan). The source of X-ray radiation has been Cu-K_α radiation with 0.15406 nm wavelength. The device has been operated at 40 kV and 30 mA emission current. The sample is scanned from 20° to 60° . The surface morphology was investigated by means of scanning electronmicroscopy (SEM) and atomic force microscopy (AFM). The SEM study has been carried out by Jeol JSM-6335F scanning electron microscope with magnification power 250000. AFM micrographs were taken with a digital instrument, Inc. Nanoscope III and Dimension 3100. The transmittance spectra was measured using a (CARY 100 CONC plus UV-Vis-NIR, Split-beam Optics, Dual detectors) spectrophotometer equipped with a xenon lamp. The wavelength range (300-900)nm.

3. RESULTS AND DISCUSSION

Figure (1) shows the XRD diffraction patterns of synthesized In_2S_3 thin films deposited on glass substrate at a temperature (400 °C) for four different molarity (0.05, 0.1, 0.15 and 0.2)M.

Fig. 1: XRD pattern of In_2S_3 thin films with different molarity

The XRD patterns of In_2S_3 contain four main plains (311), (400), (422), and (440) planes. This result agrees well with that presented in reference [15]. All the diffraction peaks are indexed to the

cubic structure and there is no trace of other face, which were well matched with standard peaks (JCPDS NO. 32-0456).

Table 1: Summary of XRD characterization for In_2S_3 thin films with different molarity.

Molarity (M)	2 θ (deg)	hkl Plane	d observed ($\text{\AA}$)	FWHM (deg)	D (nm)	$\delta \times 10^{14}$ lines.m ⁻²
0.05	27.57	(311)	3.22	1.10	7.32	186
	33.33	(400)	2.66	0.85	9.36	114
	43.77	(422)	2.11	0.69	11.17	80
	48.04	(440)	1.89	0.67	11.23	79
0.1	27.52	(311)	3.23	0.72	11.06	81
	33.47	(400)	2.65	0.57	13.79	52
	43.92	(422)	2.05	0.61	12.52	63
	48.09	(440)	1.88	0.55	13.72	53
0.15	27.67	(311)	3.22	0.95	8.44	140
	33.53	(400)	2.68	0.82	9.62	107
	43.88	(422)	2.06	0.67	11.40	76
	48.04	(440)	1.89	0.67	11.29	78
0.2	27.58	(311)	3.22	0.96	8.32	144
	33.53	(400)	2.67	1.24	6.36	247
	43.88	(422)	2.05	0.68	11.20	79
	48.07	(440)	1.87	0.67	11.29	78

Figure 2 exhibits the scanning electron micrographs of different samples. The increase in grain size could be clearly observed, which supported the results obtained from the XRD analysis. It was also seen that the samples were free of pinholes and cracks.

Fig. 2 : Shows the SEM images of as-deposited and annealed thin film at different molarity.

The surface morphology of the layers was also studied by AFM technique. The AFM micrographs shown in fig. 3 revealed the continuous growth of the layers. These images showed that the surface morphologies of the films were dependent on molarity concentration.

Fig. 3: 3D AFM image and Granularity accumulation distribution chart of In_2S_3 thin films with different molarity.

it is shown in Table 2 that the root mean square RMS roughness value decreases with increasing molarity. The RMS roughness were estimated to be (6.91–5.25) nm.

Table 2 : The roughness average, RMS and average diameter of In_2S_3 thin films with different molarity.

Molarity (M)	Roughness avg. (nm)	RMS (nm)	Avg. Diameter (nm)
0.1	6.04	6.91	63.15
0.2	4.52	5.25	88.28

In Figure 4, it shows the transmission spectra of as-deposited thin films, These measurements show that the transmission (T) decreases with the molarity.

Fig. 4 : Optical transmission of In_2S_3 thin films varies with different molarity.

The films have transparent in the NIR and Vis. regions. The increased molarity causes generate localized levels within the energy gap, leading to an increase in absorbency and reflectivity of the prepared films and then decrease in the transmittance of the films, where we note that the greatest transmittance of the films when its as 0.05 M. This result agrees well with that presented in reference [18]. Also, we can see from figure 5 energy gap of prepared films for different molarity.

Fig. 5: $(\alpha h\nu)^2$ versus photon energy of In_2S_3 thin films varies with different molarity and the inset is the photon energy as a function of the molarity.

The band gap is found to vary in the range (3.5 to 3.3) eV for direct transitions. The decrease of the obtained band gap energy with increasing molarity, is due to increase by the dangling bonds as a result of increases in molarity.

4. Conclusion

The In_2S_3 films have been prepared by the CSP method at different molarity concentration (0.05, 0.1, 0.15 and 0.2) M. The film thickness is about $0.4\mu\text{m}$. The film at all molarity concentration reveals a cubic crystal structure with a preferential orientation (311). In_2S_3 films exhibit transparency over (75–80)% at 0.05 M in the visible and infrared regions. This is related to the film thickness as well as the crystallinity degree. The band gap is around 3.5 eV to 3.3 eV for direct transitions. The In_2S_3 films prepared are a promising candidate for optoelectronic and photovoltaic devices.

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