

## Structural and Optoelectronic Properties of $In_2S_3$ Thin Films Prepared by CSP Technique for Solar Cell Application

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### ABSTRACT

Indium Sulfide  $In_2S_3$  window layer have been prepared by Chemical Spray Pyrolysis (CSP) at substrate temperature Equal (573 K) from Indium chloride and Thiourea were In/S ratio equal 1.2/8 in the spray solution, the samples prepared with different thicknesses (1.6, 1.7, 2.0  $\mu\text{m}$ ), the structural, optical and electrical of these films was investigated at different annealing temperature ( $T_a$ ). X-ray diffraction studied shows the Structural properties of this layer are polycrystalline with preferred orientation 221, and have good improvement in the crystal structure at the annealing temperature (573K for 1h). The grain size increase with increasing annealing temperature and the optical band gap was found in the range (2.4-2.55 eV) as a function of the film thicknesses and the annealing temperature. Electrical studied of the sprayed and annealed sample shows n-type electrical conductivity, the mobility improved at the annealing temperature equal (573 K) but the resistivity decreased with this temperature.

**Keywords:**  $In_2S_3$  Window Layer; Chemical Spray Pyrolysis; Structural; Optical; Electrical.

الخصائص التركيبية البصريه والكهربائيه لاغشية كبريتيد الانديوم  $In_2S_3$  الرقيقه المحضرة بطريقة الرش الكيميائي الحراري المستخدمه في تطبيقات الخلايا الشمسيه

الخلاصة:

تم تحضير طبقة نفوذ من مادة كبريتيد الانديوم بطريقة الرش الكيميائي الحراري على ارضيات زجاجيه عند درجة حرارة قدرها 573 كلفن من مادة كلورايد الانديوم والثايوريا بنسبة انديوم/

كبريت يساوي 8/1.2 في محلول الرش . حضرت النماذج باسماء مختلفة (1.6 , 1.7 , 2) مايكرومتر . تم دراسته الخصائص التركيبية , البصرية والكهربائية لهذه الاغشية عند درجات حرارة تليدين مختلفه . اظهرت نتائج حيود الاشعة السينيه ان هذه الطبقة هي ذات تركيب بلوري متعدد التبلور عند الاتجاه السائد 221 لمعاملات ميلر, وكذلك تحسن جيد في البنية البلورية عند درجة حرارة التليدين ( 573 كلفن ولمدة ساعة واحده ) . كما وان الحجم الحبيبي ازداد بزيادة درجة حرارة التليدين . بينت الفحوصات البصريه ان فجوة الطاقة البصرية تغيرت بالمدى ( 2.4 – 2.55 الكترون فولت) كدالة لدرجة حرارة التليدين والتحضير . اظهرت نتائج الدراسة الكهربائية للنماذج عند درجة حرارة التحضير والمعدنه بدرجات حراريه مختلفة . انها من نوع حاملات الشحنة ذات التوصيلية السالبة , كما وان قيم التحركية تحسنت ولكن قيم المقاومة قلت عند درجة حرارة التليدين 573 كلفن .

## INTRODUCTION

Recently there has been increasing interest in research on III-VI materials because these material have found great use in the electronic industry , Indium sulfide ( $In_2S_3$ ) is a promising compound which is used in optoelectronic or photovoltaic application [1-3] ,The  $In_2S_3$  compound has a potential application in photovoltaic devices these structures used as window layer [4,5] , due to the wide energy gap [6], and photosensitivity [7].which could be prepared using different methods such as thermal evaporation method [8] ,radio-frequency (rf) sputtering [9],atomic layer epitaxy[10],Chemical bath deposition [11] Spray Pyrolysis (SP) is one of the low cost techniques widely employed to deposit indium sulfide thin films [12,13], this technique has the advantage of being cheap and simple.  $In_2S_3$  thin films appear to be a promising candidate for photovoltaic applications. It can be used as an affective nontoxic cadmium sulfide (CdS) in CIS based Solar cells.

The motivation behind this is not only to eliminate toxic cadmium but also to improve light transmission in the blue wavelength region by using a material having band gap wider than of CdS . $CuInS_2/In_2S_3$  based solar cell with  $In_2S_3$  as the buffer layer could reach efficiencies (12.4%) [14] The primary function of a window layer in hetrojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer, no photocurrent generation occurs in the window layer For high optical throughput with minimal resistive loss the band gap of the window layer should be as high as possible and as thin as possible to maintain low series resistance.

## EXPERIMENTAL

Indium sulfide  $In_2S_3$  as n-type layer can be used as an optical window in photovoltaic cells and it can constitute a good alternative to CdS layers[15].This layer have been prepared by CSP technique, which is simple and low coast technique, using Indium chloride ( $InCl_3$ ) and Thiourea ( $CS(NH_2)_2$ ) in the spray solution with constant molar concentration (0.1 M) sprayed on glass substrate in the dimension (25mm×25mm).Total volume of solution sprayed for depositing was 50 ml with In/S ratio 1.2/8 in the films. In the normal condition, using nitrogen ( $N_2$ ) as carrier gas the distance between the nozzle and the substrate is 30 cm and 1 par is the pressure of the carrier gas. The preparation temperature was 573 K and using different annealing temperature ( $T_a$ )

(523,573,623 K) for one hour (1 h). In the present work, spray solution of indium chloride and Thiourea shows here that possible to prepare  $In_2S_3$  thin films using CSP Technique, these films have obtained shows homogeneous and adherent. Thin films of  $In_2S_3$  were prepared having different thicknesses in ( $\mu m$ ) dimension. Structural of  $In_2S_3$  thin films as prepared and annealed samples were determined using X-ray diffraction type Shimadzu (XRD6000) diffractometer have  $CuK\alpha$  radiation with  $\lambda = 1.5406 \text{ \AA}$ . Optical properties were studied using optical absorbance and transmittance spectrum (UV VIS NIR) spectrophotometer Shimadzu (UV/1650PC), and electrical properties have measured used (ECOPIA HMS-3000) Hall Effect measurement System.

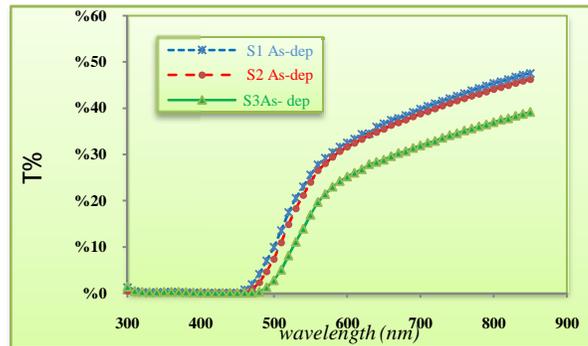
**RESULT AND DISCUSSION**

**Optical analysis**

Figure (1) shows the transmission spectrum T% of the as- deposited (sprayed)  $In_2S_3$  films at (573 K), Figure (2) shows the films annealed at (523, 573, 623 K) at different thickness (1.6, 1.7, 2  $\mu m$ ) with sample name (S1, S2, S3) respectively from this Figures (1, 2) it can be seen that T% is slightly increased with decreasing thickness. Transmission spectra recorded in the wave length rang (300- 900) nm. In order to determine the optical band gap,  $(\alpha hv)^2$  versus  $hv$  graph was plotted, which is found in the range (2.46- 2.54) eV depending on film thickness. For these samples it's clearly energy gap shift towards lower values as thickness increased. Thickness dependence of band gap could arise due to one or combined effect of the following cause along density of dislocations quantum size effect and the change in barrier height due to change in grain size in polycrystalline films. Band gap variation of all the sample in as- sprayed and different annealed temperature is given in Figures. (3), (4) respectively.

$$\alpha(hv) = A(hv - E_g)^{1/2} \tag{16}$$

Where A is a constant and  $E_g$  is the corresponding semiconductor band gap  $\alpha$  is absorption coefficient. This result having significance in solar cells applications as buffer or window layer. Wider band gap materials improve the light transmission in blue region resulting in increase of the short circuit current and open circuit voltage in solar cells.



**Figure (1) Shows transmission spectrum of  $In_2S_3$  As-sprayed.**

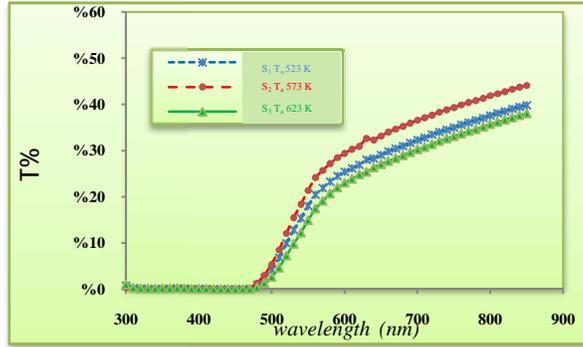


Figure (2) Shows transmission spectrum of  $In_2S_3$  at different  $T_a$ .

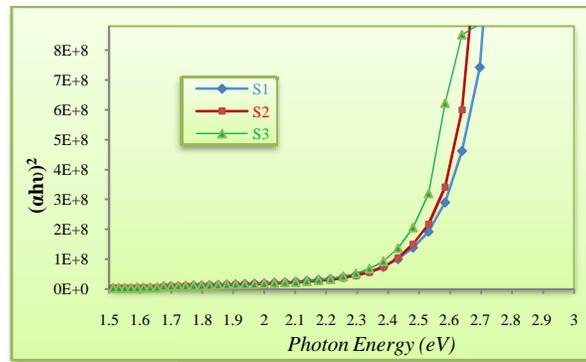


Figure (3)  $(\alpha h\nu)^2$  versus the photon energy ( $h\nu$ ) of  $In_2S_3$  layer as-sprayed at different thicknesses.

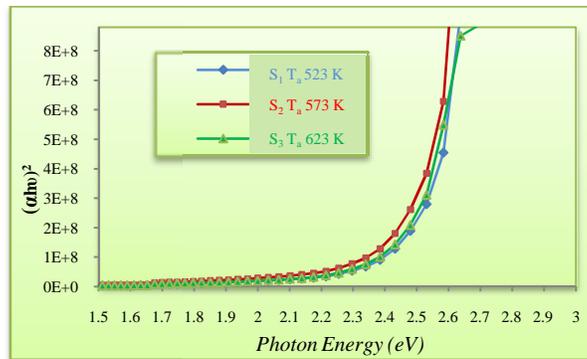


Figure (4)  $(\alpha h\nu)^2$  versus the photon energy ( $h\nu$ ) of  $In_2S_3$  layer with different ( $T_a$ ).

**Structural Analysis**

The structural analysis of indium sulfide thin films was carried out using X-ray diffractometer XRD with varying diffraction angle ( $2\theta$ ) from  $20^\circ - 60^\circ$ .

Figure (5) shows the XRD pattern of indium sulfide thin film at fixed ratio  $[In]/[S]$  equal  $1.2 / 8$  with different annealing temperature ( $T_a$ ) ( 523, 573, and 623 K). These films showed polycrystalline structure according to the standard card (JCPDS 25-0390) with tetragonal structure, the strongest peak of the film have preferred orientation along (221) and (100), these highest intensity peak describes good crystallinity material prepared by this technique. the other low intensity peaks correspond to the (138), (401) plane. The crystallographic parameter of the film was collected and computed with different annealing temperature  $T_a$  and presented in Table (1).

The crystallite size of  $In_2S_3$  thin film was calculated using the Scherer's formula. Lattice parameter computed and  $d$ -value computed and incurred from XRD data observed and compared with (JCPDS 25-0390) and found good agreement with standard card.. Moreover the variation in grain size with different  $T_a$ , as shown in Figure (6). from this figure, it is clear that, the grain size increased with increasing annealing temperature.

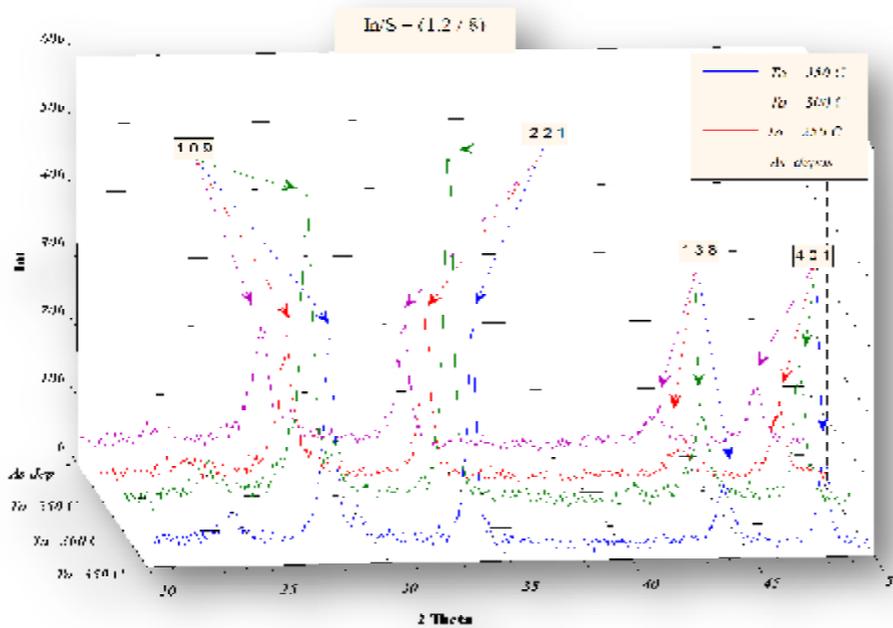


Figure (5). XRD pattern for  $In_2S_3$  layer at different  $T_a$ .

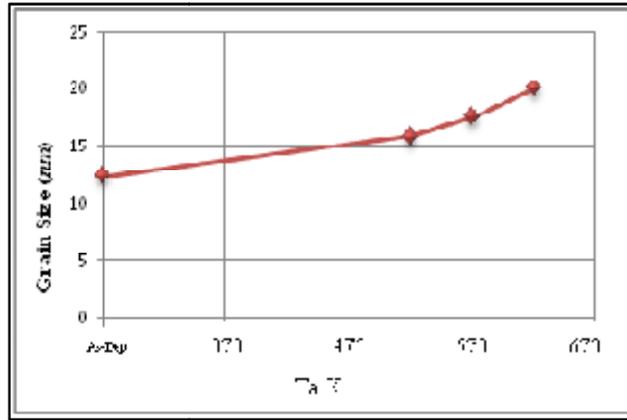


Figure (6). Variation in grain size of  $In_2S_3$  at different  $T_a$ .

Table (1) Shows lattice parameter and  $d$ -value observed compared with standard card of the  $In_2S_3$  layer.

Temp K	2θ	hkl	I/I <sub>0</sub>	FWHM	a observed	a standard	c observed	c standard	d observed	d standard	Error (d) %
As-dep	33.483	2 2 1	100	0.6698	7.5893	7.619	32.3392	32.329	2.6742	2.6844	0.38
	27.604	1 0 9	97	0.815					3.2288	3.2327	0.12
	47.995	4 0 1	54	0.6517					1.894	1.9015	0.39
523	33.474	2 2 1	100	0.5228	7.5913	7.619	32.3252	32.329	2.6749	2.6844	0.36
	27.609	1 0 9	88	0.6678					3.2283	3.2327	0.14
	47.981	4 0 1	47	0.6045					1.8946	1.9015	0.36
573	33.415	2 2 1	100	0.4729	7.6034	7.619	32.4269	32.329	2.6795	2.6844	0.19
	27.537	1 0 9	80	0.6164					3.2366	3.2327	0.12
	47.901	4 0 1	36	0.5505					1.8975	1.9015	0.21
623	33.421	2 2 1	100	0.4138	7.6009	7.619	32.3966	32.329	2.679	2.6844	0.2
	27.557	1 0 9	90	0.5205					3.2343	3.2327	0.05
	47.920	4 0 1	40	0.4925					1.8968	1.9015	0.24

### $In_2S_3$ Layer (n-Type) Electrical Properties

Electrical resistivity, mobility, carrier concentration and also that conductivity were done using Hall Effect system at (R.T) for In/S ratio equal 1.2/8 in the solution. Indicated from that the film was n- type and that due to “S-rich” in the films comparable with “In-poor” that lead to n-type formation, We can see that the result of carrier concentration is  $5.731E+11$ , the mobility is  $1.161E+3$ , the resistivity is  $9.385E+3$ , and the conductivity is  $1.065E-4$  this result match well with the result of Ratheesh et.al .[85] from Figure (7) we can see, that the I-V curve for n-type layer collected from hall effect system.

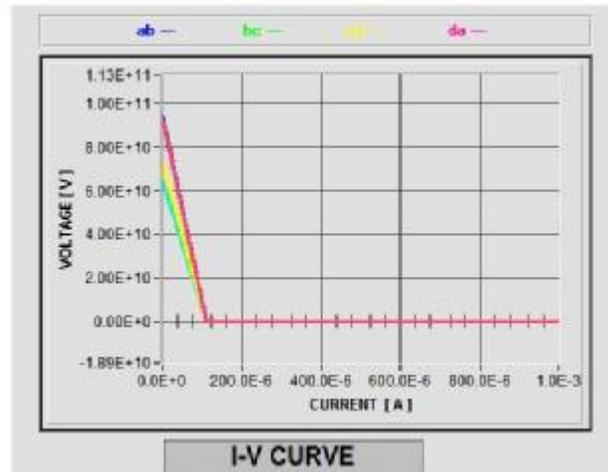


Figure (7) Shows the I-V curve for  $In_2S_3$  (n-type) layer.

## CONCLUSIONS

We reported on the deposition of  $In_2S_3$  by the spray pyrolysis technique using indium chloride and thiourea in the ratio  $[In/S]$  equal to  $[1.2/8]$ , XRD studies showed that the deposited materials are stoichiometric material and have good crystal structure at annealing temperature  $T_a$  573 K with preferred orientation along (109) and (221). optical studied showed this film have a direct band gap in the range (2.46,2.55)eV according to the different annealing temperatures, electrical studied showed n-type layer

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