Study of the Structural, Optical and Electrical Properties of In₂S₃ Thin Films Prepared by Thermal Evaporation Method

Authors Names	ABSTRACT			
Zahraa Azhar Abd Al aziz a [*]	In_2S_3 thin films were prepared on glass substrates by the use of the vacuum			
Saleem Azara Hussain a,b*	thermal evaporation technique, and then thermally annealed in free air			
Publication data: 18 /12 /2023	atmosphere at 350 °C for 2h. The structural, optical and the electrical properties			
<i>Keywords:</i> Annealing temperature, Indium sulfide (In ₂ S ₃), Thermal evaporation, Thin films.	of the films were studied as a function of the annealing temperature and the film thickness. X-ray diffraction analysis shows amorphous nature of thin film and the powder was polycrystalline structure. The films show good homogeneity which was obtained from (UV-Vis) spectrophotometer .The study objective: is Preparing thin films of Indium Sulfide by vacuum thermal evaporation method, studying their Structural, Optical and Electrical properties, and demonstrating the possibility of using them in electronic applications. Conclusion: The structural, optical and electrical tests of the prepared thin film showed agreement with the literature's, with a clear distinction of the effect of annealing on the obtained results represented by an increase in the crystallinity of the prepared films, in addition to the effect of the optical properties because the annealing temperature leads to the loss of part of the sulfur present in the thin films.			

1. Introduction

Semiconducting Indium Sulfide (In_2S_3) has lately received a lot of interest, as a buffer material in the field of thin film photovoltaic, in contrast to this expanding interest, thorough characterizations of the crystal structure of this substance are very sparse and contentious. Wide gap semiconductor (In_2S_3) has good superconductive and photo luminescent characteristics, making it an attractive candidate for optoelectronic applications. Most significantly, its prospective use as a buffer layer in chalcopyrite solar cells has prompted a rise in study into its fundamental material features (such as crystal structure, optical characteristics, electrical band structure, etc.), as well as in deposition technique. It is a flexible substitute to the widely used CdS buffer layer due to its compatibility with diverse thin film deposition techniques[1]. Due to its stable chemical composition, photoconductivity, and luminous properties under ambient circumstances, Indium (III) Sulfide (In₂S₃), an indium chalcogenide, is a (III-VI) semiconductor compound useful for optoelectronic, photoelectric, and photovoltaic (PV) applications. There is still debate about whether it has a direct or indirect bandgap even though it operates as an ntype semiconductor with an optical bandgap of (2.1–2.3) eV. In₂S₃ crystallizes into three different allotrope forms in a range of temperatures: β - In₂S₃ (tetragonal structure below 420 °C), α - In₂S₃ (cubic structure between 420 and 754 °C), and γ - In₂S₃ (trigonal structure above 754 °C) [2]. Additionally, indium sulfide can be used as a binary base material in the formation of semiconductor materials like In_2S_3 and as an absorber material in the hetero-junction of structures for solar cell devices [3]. In_2S_3 is used in a variety of processes, including the creation of red and green phosphors, dry cells, and image tubes for color television. Its stability, intriguing structural features, and optical qualities make it an attractive contender for a variety of technological applications. In general, the deposition method, deposition parameters, and film thickness have a significant impact on the physical characteristics of the grown films [4]. Different methods were used to create β -In₂S₃ thin films, including reactive evaporation in a sulfur atmosphere, spray pyrolysis on glass slides kept at 623K, calcification of the indium electroplated layers in a hydrogen sulfide gas atmosphere at temperatures between 623K and

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673K, and the slurry coating method of the corresponding semiconductor powder followed by annealing in nitrogen and hydrogen. At normal temperature, the chemical transfer reaction-grown β -In₂S₃ crystals were formed. It turns out that it behaves much like an n-type semiconductor. Also visible in the thin films was n-type conduction[5]. In this study, the structural, optical, and electrical characteristics of In₂S₃ thin films were examined, and the effects of annealing on the substance were studied.

2. Experimental work

Thin films of (In_2S_3) were prepared by using a homemade thermal evaporation system with high quality specifications. Where this system requires two steps to complete the vacuum process and reach the required pressure, the first step is to evacuate the air from the vacuum chamber using a rotating mechanical pump, where the pressure reaches (10^{-2} m bar) , then begin the diffusion pump, which completes the vacuum process and reaches (10^{-5} mbar) , and the pressure is measured using a Pirani / Penning gauges (EDWARDS, Burgess Hill, UK, RH159TW, Made in GB). Then, the material that is placed in the crucible is deposited, 9 cm away from the glass substrates. The thickness of the material was (150, 200 and 300 nm), it was measured by the gravimetric method, the deposition was done under pressure $(4 \times 10^{-5} \text{ mbar})$, The substrates were cleaned according to standard methods using water, alcohol and detergents in addition to ultrasound, the prepared films were annealed at a temperature of $(350 \degree \text{C})$ for two hours, The crystal structure of the powder and the prepared thin films of (In_2S_3) was ascertained using the X-ray diffractometer (XRD-6000 Shimatzu), $Cu_{k\alpha} = 1.5405 \text{ nm}$, The optical characteristics were investigated over a range of (300 to 700 nm) using Dual-beam Maga 2100 UV-Vis spectrophotometer (produced in sinco Koria). The DC electrical properties of the films after annealing were investigated, and the Hall effect was investigated (the manufacture company IRASOL).

3. Results and Discussion

(Fig.1) shows the X-ray diffraction for the powder and a preferred crystalline growth towards the plane (109) at the diffraction $(2\Theta=27.83^{\circ})$, it is observed that other peaks appear towards the two plans (0012) and (2212) with accompanying 2Θ (33.504° and 48.48°) respectively, when matching the pattern of the x-ray diffraction with the standard card numbered (JCPDS-25-0390). The results conferred that the powder was polycrystalline structure in tetragonal phase. As mentioned in the search [1].



Fig.1-The pattern of X-ray diffraction for the powder.

(Fig.2) shows the X-ray diffraction for (In_2S_3) thin film with thickness (200 nm) that was deposited on glass substrates under a high vacuum. The results confirmed that the thin film was amorphous structure is consistent with the literature report [6]. And a preferred crystalline growth towards the plane (204) at the diffraction (2 Θ =25.028°) in agreement with several works in the literature[5], it is observed that other peaks appear towards the plans (211), (215) and (2113) with accompanying 2 Θ (26.796°, 29.344° and 44.37°) respectively, when matching the pattern of the x-ray diffraction with the standard card numbered (JCPDS-25-0390), a great match was found in the diffraction pattern and the interplant spacing of different plans, so the prepared film was in the phase of tetragonal which agrees with the researcher[4],[5].



Fig.2- The pattern of X-ray diffraction for (In₂S₃) thin film with thickness 200nm.

(Fig.3) displays the optical transmission spectra for thin films of In_2S_3 with thickness 300nm formed on glass substrates and obtained from (UV-Vis) spectrum before and after annealing at a temperature of (350°C) for 2h . We draw attention to the interference patterns that result from the numerous reflections phenomenon that causes relatively homogeneous films to appear. As a sign of good crystallinity, the spectrum exhibits interference patterns with a steep decline in transmittance at the band edge. Notice how the transmittance values were low at short wavelengths, increased quickly, and reached their highest values for the two films in the visible and infrared ranges. In accordance with the literature [7], it can be seen that all films transmittance exhibits an oscillatory (wavy) characteristic as a result of interactions between electromagnetic waves that are incident on surfaces and waves that are reflected from those surfaces in three different mediums (air, thin-film, and glass). It can be noticed that the absorption edge shifts towards short wavelengths, blue shift, it can be observed for thickness of (300nm before and after annealed). In fact, observe a decrease in the In_2S_3 annealed film transmission values at 350 °C. The decrease in the values transmittance may have been caused by the evaporation of sulfur and the existence of secondary phases in the volume, this result is consistent with the result and interpretation of the literature [7].



Fig.3-The transmittance for thickness (300nm) before and after annealing.

(Fig4) shows that absorption spectra obtained from (UV-Vsi) spectrophotometer was characterize by a wavy (oscillatory) this due to interference between incident and reflected waves at the interfaces between the media air, thin-film, and glass. As for the absorbance of (In_2S_3) thin films, Note that the absorbance values increase after the annealing process.



Fig.4- shows the absorbance of $({\rm In}_2 S_3)$ thin films with thickness 300nm before and after annealing at 350°C for 2h.

(Fig.5) displays the optical transmission spectra for thin films of In_2S_3 with thicknesses 200 nm and 300 nm formed on glass substrates which was annealed at temperature (350°C) for 2h. As a sign of good crystallinity, the spectrum exhibits interference patterns with a steep decline in transmittance at the band edge. Notice how the transmittance values were low at short wavelengths, increased quickly, and reached their highest values for the two films in the visible and infrared ranges it can be seen that all films transmittance exhibits an oscillatory (wavy) characteristic as a result of interactions between

electromagnetic waves that are incident on surfaces and waves that are reflected from those surfaces in three different mediums air, thin-film, and glass. It is clear from the figure that the transmittance values for the annealed films and for the two thicknesses ranged between increase and decrease for them, and this can be attributed to the reason related to the possibility of evaporation of sulfur, whose quantity inevitably increases in films of greater thickness. Therefore, the result shown in (Fig5) may show an increase in Transmittance increases with thickness.



Fig .5-shows the transmittance of (In_2S_3) thin films with thickness (200nm) and (300nm) at 350 °C for 2h.

(A fig6) show that absorption spectra obtained from (UV-Vsi) spectrophotometer was characterized by a wavy (oscillatory). It is clear from the figure that the absorbance values for the annealed films and for the two thicknesses ranged between increase and decrease for them.



Fig.6- shows the absorbance of (In₂S₃) thin films with thickness (200nm) and (300nm) at 350 °C for 2h.

The resistivity of thin films In_2S_3 was calculated according to the Equation ($\rho=R.t.\ell/L$) where ρ (the

resistivity), R(film resistance), t (the films' thickness (cm)), ℓ (the width of the electrode (cm)),and L(the distance between the electrodes(cm)).(Figs 7,8) show the values of the resistivity for thin films with a thickness of (150 and 300nm), it is clear that the resistivity decreases as the absolute temperature rises, this is a general characteristic of semiconductors [8].



Fig.7- shows the values of the resistivity for thin film with a thickness (150nm).



(Figure.8) shows the values of the resistivity for thin film with a thickness of (300nm).

As for the conductivity it was calculated using the relationship ($\sigma = 1/\rho$) and it was found that the values of the conductivity increase with increasing temperature and this is due to the increase in the number of the carriers and the increase in their mobility, figures (9, 10) show the values of the conductivity for thin films with a thickness of (150 and 300) nm.



Fig.9- shows the values of the conductivity for thin film with a thickness of (150nm).



Fig.10 shows the values of the conductivity for thin film with a thickness of (300nm).

Hall tests for thin films (In_2S_3) deposited on glass surfaces using the thermal evaporation technique were performed at room temperature and revealed the mobility, carrier concentration, and Hall coefficient values.

Sample	Mobility (cm ² V ⁻¹ s ⁻¹)	Concentration of carriers (cm) ⁻³	Hall coefficient $R_{\rm H} (cm^{-3}C^{-1})$	Туре
(In_2S_3)	1.31×10^{2}	-5.41×10^{17}	-1.15×10^{1}	Ν

Table.1- displays Hall characteristics.

4. Conclusion

According to the results, it was observed that we could produce Indium Sulfide films using thermal evaporation technique .The structural, optical and electrical tests of the prepared thin film showed agreement with the literature's , with a clear distinction of the effect of annealing on the obtained results represented by an increase in the crystallinity of the prepared films, in addition to the effect of the optical properties because the annealing temperature leads to the loss of part of the sulfur present in the thin films.

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References

- [1] P. Pistor *et al.*, "Structure reinvestigation of α -, β and γ -In2S3," *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, vol. 72, no. 3, pp. 410–415, 2016, doi: 10.1107/S2052520616007058.
- [2] M. A. Mughal, R. Engelken, and R. Sharma, "Progress in indium (III) sulfide (In2S3) buffer layer deposition techniques for CIS, CIGS, and CdTe-based thin film solar cells," *Sol. Energy*, vol. 120, pp. 131–146, 2015, doi: 10.1016/j.solener.2015.07.028.
- [3] T. Yukawa, K. Kuwabara, and K. Koumoto, "Electrodeposition of CuInS2 from aqueous solution (II) electrodeposition of CuInS2 film," *Thin Solid Films*, vol. 286, no. 1–2, pp. 151–153, 1996.
- [4] N. Revathi, P. Prathap, and K. T. R. Reddy, "Thickness dependent physical properties of close space evaporated In2S3 films," *Solid State Sci.*, vol. 11, no. 7, pp. 1288–1296, 2009, doi: 10.1016/j.solidstatesciences.2009.04.019.
- [5] H. S. M. and M. A. M. S. A A El Shazlyy, D Abd Elhadyyz, "Electrical properties of -In2S3 thin films," J. Phys. D. Appl. Phys., vol. 41, no. 23, 1998, doi: 10.1088/0022-3727/41/21/215303.
- [6] B. R. A. Timoumi, H. Bouzouita*, M. Kanzari, "Fabrication and characterization of In2S3 thin films deposited by thermal evaporation technique," *Natl. Sch. Eng. Tunis BP 37 Belve de re 1002 Tunis*, vol. 184, no. 3, pp. 177–184, 2005, doi: 10.1051/epjap.
- [7] A. Timoumi, H. Bouzouita, R. Brini, M. Kanzari, and B. Rezig, "Optimization of annealing conditions of In 2 S 3 thin films deposited by vacuum thermal evaporation," *Appl. Surf. Sci.*, vol. 253, no. 1 SPEC. ISS., pp. 306–310, 2006, doi: 10.1016/j.apsusc.2006.06.003.
- [8] M. Cardona and Y. Y. Peter, Fundamentals of semiconductors, vol. 619. Springer, 2005.