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Structural and Optical Properties of SnS Film Prepared by Chemical Spray Pyrolysis Technique

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Abstract :

In this work, Tin Sulphide (SnS) thin film has been deposited on a glass substrate by Chemical Spray Pyrolysis. XRD pattern of SnS showed that the film has a single crystalline structure, the crystallite size of film estimated by Scherrer's eq and equal (46.9 nm). Results of AFM showed that the SnS film has grain size, roughness, and RMS of the film equal 66.7, 2.8, and 3.7 respectively. The optical properties were studied in the range of 300 to 900nm, and the transmittance increased as the wavelength increased about 300 to 750 nm, it was found that with the lesser transmittance (94%), the energy bandgap has a value of 3.85 eV. The extinction coefficient decreased at the lesser wavelength (300-350) nm and next the extinction coefficient stayed constant.

Keywords: SnS, Thin Films, Structural Properties, AFM .

الخصائص التركيبية والبصرية لاغشية كبريتيد القصدير (SnS)الرقيقة المحضرة بطريقة التحلل الكيميائي الحراري

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مستخلص:

في هذا البحث ، تم ترسيب طبقة رقيقة من كبريتيد القصدير (SnS) على قاعدة زجاجية بتقنية التحلل الحراري بالرش الكيميائي.إذ أظهر فحص XRD أن الغشاء احادي التبلور، وقد تم تقدير الحجم البلوري للغشاء بمعادلة شيرر ويساوي (46.9 نانومتر)، وبينت نتائج مجهر القوى الذرية AFM أن حجم حبيبات غشاء SnS وخشونته وRMS يساوي 66.7، 2.8 و3.7 على التوالي. تمت دراسة الخصائص البصرية في المدى من 300 إلى 900 نانومتر، إذ تزداد النفاذية مع زيادة الطول الموجي حوالي 300 إلى 750 نانومتر، وقد وجد أنه كلما كانت النفاذية أقل (94٪)، فإن فجوة الطاقة تبلغ قيمتها 3.85 فولت. انخفض معامل الخمود عند الطول الموجي الأقل (350-300) نانومتر وبعد ذلك يبقى معامل الخمود ثابتا.

الكلمات المفتاحية: كبريتيد القصدير، اغشية رقيقة، خصائص تركيبية، مجهر القوى الذرية .

1. Introduction

Tin sulfide (SnS) is an IV-VI binary semiconductor compound whose basic elements Tin (Sn) and Sulphur (S) are abundant in nature. SnS in its orthorhombic crystalline structure has indirect and direct bandgap values between 1.3–1.5 eV and 1.0 – 1.1 eV, respectively, and has p-type conductivity. It has a greater absorption coefficient (~105 cm^{-1}) compared with materials like CdTe and GaAs. These properties make it an enhanced alternative absorber material for photovoltaic applications [1]. Research on SnS displays that it has the potential used as a holographic or optical data storage medium [1, 2]. Also, due to its high absorption coefficient have been used as a photovoltaic device [2, 3]. SnS exist in various crystallized states like orthorhombic [4], tetrahedral [2], or a highly distorted rock salt (NaCl) structure [2, 3]. Due to the nature of the tin and Sulphur bonding, it forms a two-dimensional sheet [2]. For a material to be a potential candidate as an active layer in a solar cell, it should not only have an optimum bandgap and high absorption coefficient in the visible range for maximum quantum yield, but it should also allow for the easy flow of charge carriers without recombination across the neutral length of the active layer (i.e. a large diffusion length). While most of the works focus on band-gap and the absorption coefficient, there are very few reports in the literature that compare materials based on their diffusion length in the active layer [1, 3], SnS is rapidly emerging as a popular inorganics thin film candidate for alternative solar cell material [5]. The study aims to produce SnS film using the Chemical Spray Pyrolysis technique and study the film's structural, morphological, and optical properties.

2. Experimental Part

The chemical bouquet pyrolysis method is service to arranged SnS covering all over second-hand mighty forbearance facts (99%), The solutions were prepared by dissolving 0.02M from Tin Chlorides ($SnCl_4.5H_2O$) with molecular weight 350.58g/mol and purity of 99% in 50 ml of distilled water by using a magnetic stirrer for 10 minutes. 0.16 M from thiourea was also dissolved in 50 ml of distilled water by using a magnetic stirrer for 10 min to obtain homogeneous solutions without impurities, after that, an equal volumetric ratio (1:1) was taken from both solutions and mixed, and dissolved by magnetic stirrer for 10 min until a homogeneous solution is obtained. The solutions were sprayed on a glass substrate at a distance of 30±1cm, 60 sec spraying rate, and 10 sec spraying times and temperature of substrates at 350 °C and obtained the film of SnS according to the chemical equations:

$$2NH_2SCNH_2+4H_2O \rightarrow 2H_2S+\uparrow 2Co_2+4NH_3$$
$$2SnCl_2+2S+\uparrow 4HCl \rightarrow 2SnCl_4+2H_2O$$
$$2SnCl_2+2S \rightarrow 2SnS+\uparrow 2Cl_2$$

3. Results

Fig 1 shows the X-ray diffraction results of SnS film, The XRD pattern of SnS shows one peak at 2θ ~ 31.6°, which corresponds to (111) plane, which is in agreement with ICDD card No. (00-039-0354). The position of the peak and the presence of one diffraction peak lead to the conclusion that the film is single crystalline, which is in agreement with another report [6]. The average crystallite size (D) was estimated by using Scherrer's eq[7-11].

$$D_{ave} = \frac{k.\lambda}{\beta.cos\theta} \qquad (1)$$

Where K 0.9, λ the wavelength of x-ray 1.5406 Å, β the full width of half maximum of a peak, and θ the Bragg angle. It is valued that the average crystallite size is about (46. 9 nm) as shown in Table (1). The quality of the materials greatly affects the size of the crystals and possibly the nucleation rate of the SnS molecules. The dislocation density of film (δ) is valued by [8- 10].

$$\delta = \frac{1}{D_{av}^2} \qquad (2)$$

There is an opposite relation between the dislocation density and average crystallite size. It is clear that the dislocation density has a value of 4.5 (line. cm^{-2}), the lower value of the dislocations indicates a decrease in crystal defects, as shown in Table (1) so it is essential to decrease the dislocation density and improve uniformity for the SnS film surface [1]. The number of the crystallite (N_o) estimated by [8, 11]:

$$No = \frac{(t)}{D_{av}^3} \qquad (3)$$

Where t is the thickness of the sample (350) nm. It absorbed that the number of the crystallite of thin film has value (33 cm $^{-2}$), as shown in table (1)

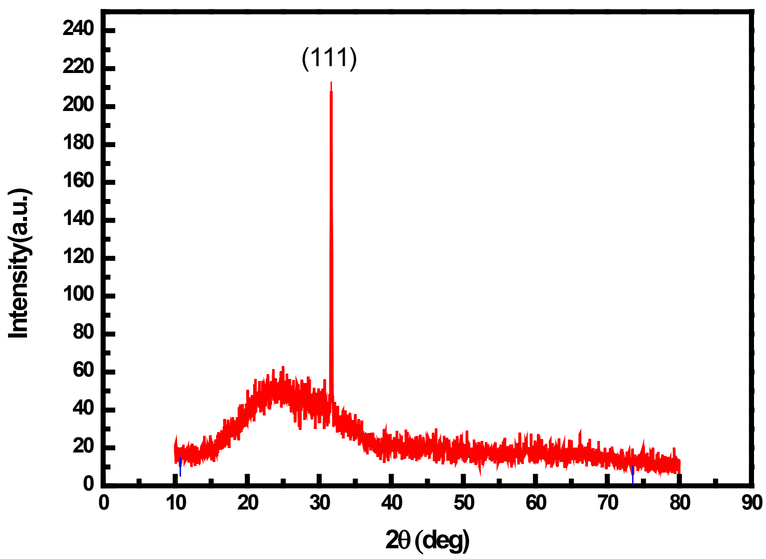

Fig 1. X-ray diffraction pattern of SnS thin film.

Table 1. XRD results of SnS film

Film	β (rad)	2θ(deg)	Hkl	D_{av} (nm)	δ(line. cm^{-2}) *10^{+18}	N_o (cm^{-2}) *10^{+18}
SnS	0.1759	31.6	(111)	46.9	4.5	33

3.2 AFM Result

The morphological investigation of single crystalline SnS thin was accomplished by using AFM. The size of the scanned area was (2x2 μm^2.) as shown in Fig 2. The grain size, roughness, and root mean square (RMS) roughness for film, valued from the AFM, is given in Table 2. The increase in the grain size possibly will be produced by columnar grain growth in the structure.

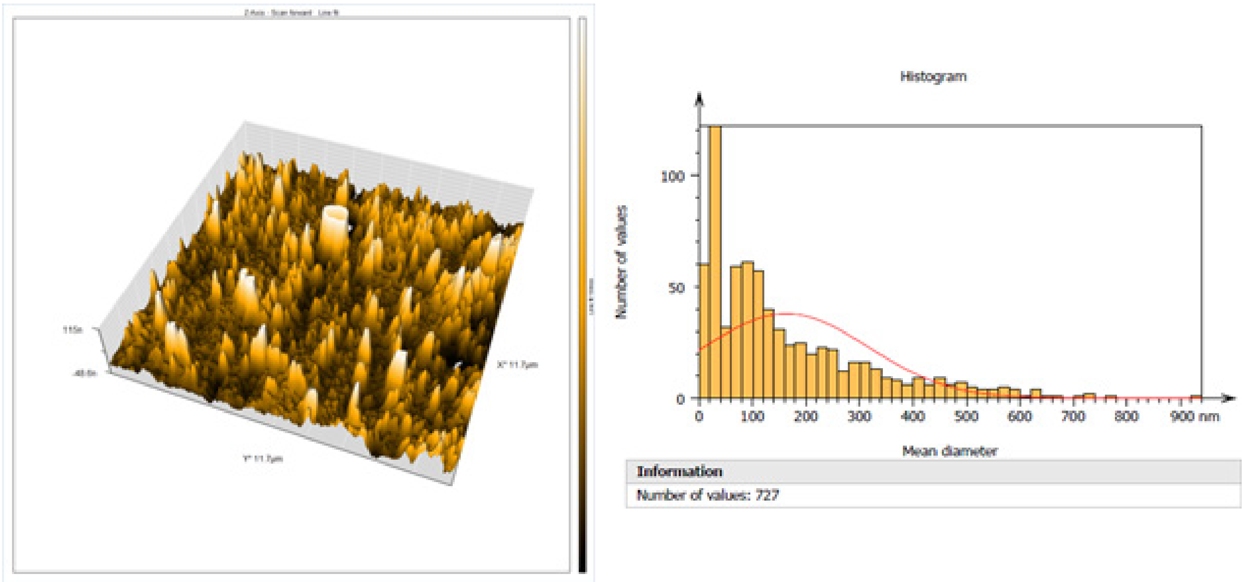

Fig 2. 3D AFM image of SnS thin film

Table 2. Surface roughness, root mean square (RMS), and grain size of SnS films

Sample	Surface roughness (nm)	RMS (nm)	Grain size (nm)
SnS	2.8	3.7	66.7

3.3 Result of The Optical Properties

The optical properties of SnS film have been estimated by studying the transmittance and absorbance of a film within the wavelength 300 to 900 nm. Fig. 3. shows the transmittance against the wavelength of film absorbed that the transmittance increased when the wavelength increased 300-750 nm, It was found that the higher transmittance (94%) for film as shown in Fig 3a, The increase in transmittance results in the formation of new localized states at the bottom of the conduction band. These levels accept electrons and create tails that help reduce the energy gap. Unlike the transmittance in general, the absorbance behavior can be seen that the absorbance decreases when the wavelength increases by about 300-500 nm as shown in Fig 3b.

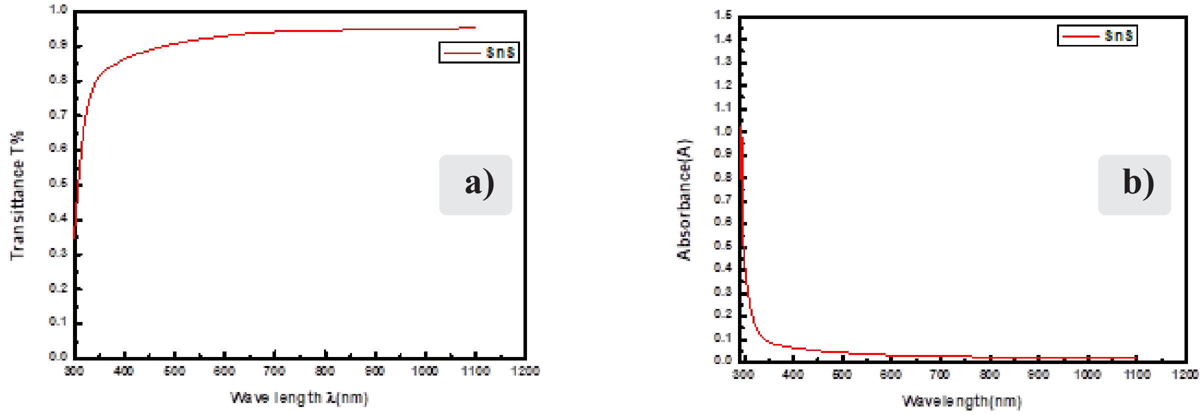

Fig. 3 a) Transmittance and b) Absorbance as a function wavelength of SnS film

The absorption coefficient α of SnS film is estimated by [10, 14].

$$\alpha = 2.303\ \frac{A}{t} \qquad (4)$$

Where t is the thickness of the film. Fig 4 a. showed the difference of the absorption coefficient beside the photon energy of the film and observed that the absorption coefficient increased when the photon energy increased, the results indicate that the colloidal prepared at this ratio provides a higher absorption compared to another [4].

The energy gap of films estimated by used [3, 11]:

$$\alpha h\nu = B(h\nu - E_g)^r \qquad (5)$$

Where: hν is the energy, B: constant. r is equal to 0.5 for direct transition. The energy bandgap value was given by a line straight to the $(\alpha h\nu)^2=0$, as shown in Fig 4b. It can be seen that the energy bandgap value is equal to 3.85 eV and the average crystallite size is responsible for the energy band gap value [16].

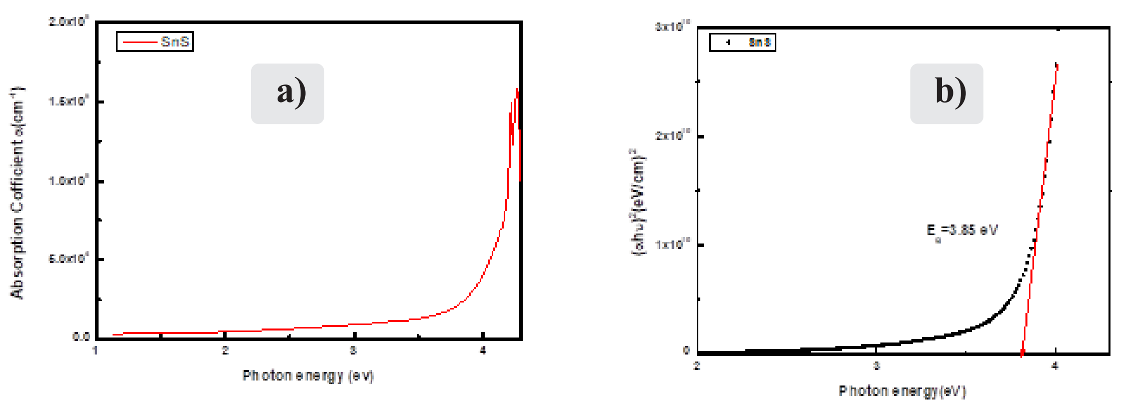

Fig 4. a) Absorption coefficient and b) energy band gap for SnS film.

The extinction coefficient () is valued by [8, 11]:

$$K_o = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

Where λ is the wavelength, the relation between the extinction coefficient and wavelength for SnS film is shown in Fig 5. It can be seen that the extinction coefficient decreased at a lesser wavelength (300-350) nm and next the extinction coefficient stayed constant.

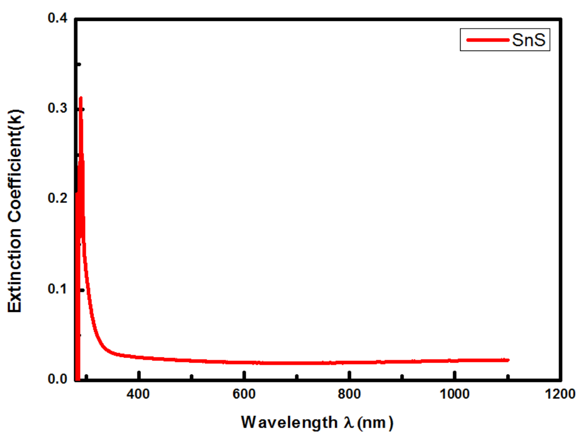

Fig 5. Extinction coefficient against to the wavelength

4. Conclusion

In this study, a Tin Sulphide (SnS) film was deposited onto a glass substrate using Chemical Spray Pyrolysis to a thickness of 350 nm. The X-ray diffraction (XRD) pattern of the SnS showed that the film has a single crystalline structure, with a crystallite size estimated to be 46.9 nm using Scherrer's equation. The Atomic Force Microscopy (AFM) results indicated that the SnS film has grain size, roughness, and root mean square (RMS) values of 66.7, 2.8, and 3.7, respectively. Additionally, the energy bandgap of the film was found to be 3.85 eV.

5. References

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