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Effect of Substrate Temperature on the Structural and Optical Properties of Chemically Sprayed SnS Thin Films

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Abstract - In this work, tin Sulphide (SnS) thin films were deposited on glass substrate by chemical spray pyrolysis technique (CSP). Stannous chloride and thiourea were mixed in a 1:1 ratio to make the precursor solution. The effect of substrate temperature was studied at temperature varied (250, 350, and 450) ºC. Structural and optical properties of the films were determined using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Atomic Force Microscopy (AFM), and UV–VIS-NIR spectrophotometer were used to assess these films. The crystalline nature of the SnS compound with orthorhombic structure along the (111) plane was shown by X-ray diffraction study. The Full-Width Half Maximum (FWHM) quantities of the Bragg peak at the optimal substrate temperature were used to determine the size of the tin sulfide crystallites with nano-dimension. Surface morphology on the surface of these films was examined using SEM and AFM equipment. At the substrate temperature of (450) ºC, a single-phase, p-type SnS thin film with a direct permitted band gap of 1.5 to 1.7 eV was determined.

Keywords - Chemical spray pyrolysis technique, Optical Characteristics, Structural Characteristics, Tin Sulfide.

INTRODUCTION

Thin film technology is one of the most important technologies for dealing with systems with very thin thicknesses ranging from tens of nanometers to a few micrometers, which has contributed to the advancement of semiconductor research by providing a clear understanding of many of the physical properties and crystalline structure of the fabricated membrane material, as well as knowledge of the nature of electronic transitions and their efficiency in the field of application. Scientific and practical, resulting in the creation of a process for making thin films with high specifications at a reasonable cost [1][2]. The study of the properties of semiconductors played a prominent role in determining their uses for example When studying the optical properties of a material in terms of transmittance, absorption, and reflectivity, if it is found that for a specific wavelength, but if (window) the prepared material has a high transmittance, it can be used as a window. And if the (solar cell) or (gas sensor) has a high absorbency, it can be used in the manufacture of solar cells (mirror) had high reflectivity so it could be used as a mirror. Thin film materials are critical components of ongoing technical advancements in optoelectronic, photonic, and magnetic devices.

Many new fields of research in solid-state physics and chemistry have been advanced as a result of thin-film investigations, which are based on phenomena that are unique to the thickness, geometry, and structure of the thin film. [3][4].

Thin films always need a base to be prepared, regardless of the methods adopted for their manufacture. The membrane or the thin layer, even if. Sometimes we can separate the layer from the base, and accordingly, Therefore, it will be imperative to take into account this main concept, which is that this rule has a strong influence on The physical properties of the sedimentary layer. For example, if we take two thin layers made of the same material we put one of them on a crystal base like glass, and the other on a monocrystalline substrate for silicon, their physical properties differ greatly [5]. Thin semiconductor films are used instead of conductors and insulators due to their many advantages [6] [7]. that can be easily changed according to what is required, for example, we can easily change certain electrical properties or optical by changing the preparation conditions such as changing the temperature of the base or the type of substance to be deposited or the rate of Sedimentation, which provides great flexibility in handling these materials.

Therefore, studies related to this technology have increased.

EXPERIMENTAL

In this study, Putting (22g) of stannous chloride (SnCl2-2H_2O) [It's a white powder with a molecular weight of (225.63g/mol)] and adding (100 ml)of distilled water in the beaker to reach(80 $\pm$ 3 C$^{\circ}$). Then HCl (5 ml) was added to improve the solubility of SnCl2-2H2O, HCl (5 ml), and is filtered To obtain a pure substance from tin (Sn). And Putting (7.6g) of thiourea (CS(NH2)2) [It's a white

powder with a molecular weight of (76.11 g/mol)] and adding (100 ml)of distilled water in the beaker to reach (80 ± 3 C°). Then HCl (5 ml) was added to improve the solution and is filtered to obtain a pure sulfur (S).In a beaker, sulfur is mixed with tin and placed in a magnetic stirrer, after which the solution is filtered and left for 24 hours to guarantee that no residues are left and that the resulting solution, which is tin sulfide, is homogeneous (SnS)[8][9].

Using the following equation, the dissolving weight (Wt.) of the above materials was obtained. [10]:

$$M = \frac{W_t}{M_{wt}} \times \frac{1000}{V} \quad (1)$$

Where:

M: is the molar concentration{0.1M materials [$SnCl2\text{-}2H_2O$ and $(CS(NH2)2)$] }

M_{wt} : molecular weight .

V: *volume* of distilled water.

$W_{t.}$: weight of powder material was measured by using electrical balance.

The CSP apparatus has depicted is shown in Fig(1)

FIGURE 1

CHEMICAL SPRAY PYROLYSIS SYSTEM[11]

STRUCTURAL PROPERTIES

X-RAY DIFFRACTION ANALYSIS (XRD)

XRD patterns of the SnS films deposited on glass substrate at different temperatures (250,350 and 450) °C are shown in Figure (2). The XRD peaks have been discovered at 2=31.7° and 2=38.5°.

According to card number 26-0575 from the International Center of Diffraction Data (ICDD). The strongest peak is at 2=31.7°, which is known as the preferred plane (301). We can be noticed that all the patterns exhibit diffraction peaks around (2θ=31°, 16.2°, 21.4 °, 26.7 and 44.7 °) referred to (111), (301), (311), (411) and (602) favorite directions respectively as shown in Table (I) The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the films are polycrystalline with an Orthorhombic crystalline structure and it is consistent with previous research [12][13]. When the temperature of the substrate rises, the mobility of the atoms on the surface rises, allowing them to rearrange their locations to occupy more stable places.

For all films, the crystallite size was calculated from (FWHM) (β) of the preferred orientation diffraction peak by using the Debye-Sherrers equation (1)[14]

$$D = \frac{0.94\,\lambda}{\beta \cos\theta}, \quad (2)$$

Where: λ: is the X-ray wavelength (Å), β: FWHM, θ: Bragg diffraction angle of the XRD peak, and (D) is a mean crystallite size or average grain size,

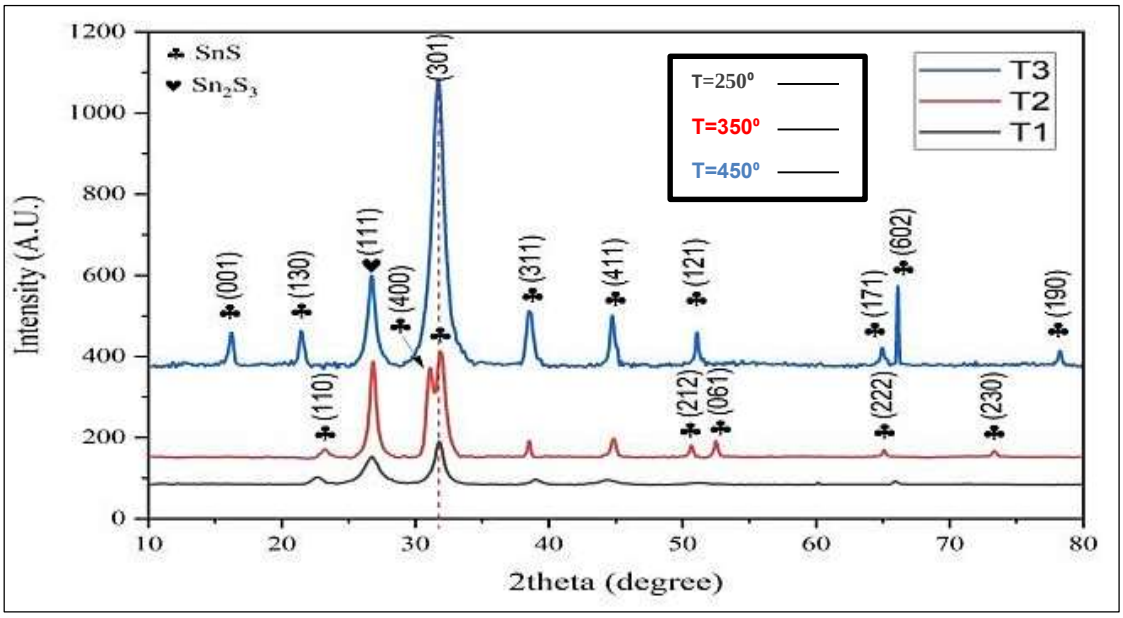


FIGURE 2

X-RAY DIFFRACTION (XRD) PATTERN OF SNS THIN FILM AT DIFFERENT ANNEALING TEMPERATURES.

TABLE I

EXPERIMENTAL AND STANDER XRD DATA FOR SNS FILMS AT DIFFERENT TEMPERATURES

Substrate Temperature TS (°C)	**(hkl)**	**2Θ (Deg.) Std**	**2Θ (Deg.) Exp**	**d_{hkl} Exp (nm)**	**d_{hkl} Std . (nm)**	**FWHM (rad)**	**D (nm)**	**Average D (nm)**
250	(110)	22.667	22.731	3.9197	3.90887	0.933	8.8	15.675
	(111)	26.732	26.587	3.33215	3.35	1.331	6.2	
	(301)	31.781	31.666	2.81338	2.82335	0.816	10.2	
	(311)	39.019	39.096	2.30656	2.3022	0.856	9.9	
	(411)	44.409	44.792	2.03829	2.02175	1.603	5.4	
	(212)	51.166	50.719	1.78385	1.79853	2.15	4.1	
	(170)	60.164	60.623	1.53678	1.52626	0.169	57	
	(222)	65.957	65.919	1.41515	1.41588	0.406	23.8	
350	(110)	22.909	22.731	3.87879	3.90887	0.871	9.4	23.88
	(111)	26.827	26.587	3.32054	3.35	0.577	14.4	
	(400)	31.066	31.666	2.8765	2.82335	0.548	15.3	
	(301)	31.903	31.987	2.80284	2.79575	0.827	10.1	
	(311)	38.527	39.096	2.33484	2.3022	0.23	37.9	
	(411)	44.845	44.792	2.0195	2.02175	0.393	22.3	
	(212)	50.676	50.719	1.79995	1.79853	0.274	33	
	(061)	52.508	52.591	1.74137	1.73882	0.326	27.9	
	(222)	65.094	65.504	1.43181	1.42384	0.249	39.1	
	(230)	73.363	73.335	1.28949	1.28991	0.345	29.4	
450	(001)	22.909	22.731	3.87879	3.90887	0.3424	24	27.35
	(130)	26.827	26.587	3.32054	3.35	0.3625	22.8	
	(111)	31.066	31.666	2.8765	2.82335	0.6244	13.3	

	(301)	16.2288	16.239	5.45731	5.454	1.0754	7.7	
	(311)	21.4677	21.499	4.13591	4.13	0.5237	16.3	
	(411)	26.7295	26.587	3.33247	3.35	0.4028	21.7	
	(121)	31.7086	31.666	2.81962	2.82335	0.2618	34.7	
	(171)	38.5899	39.096	2.33119	2.3022	0.3424	28.2	
	(602)	44.7496	44.792	2.02357	2.02175	0.1424	70.7	
	(190)	51.085	51.177	1.78649	1.7835	0.3084	34.1	

1. Scanning Electron Microscopy Analysis (SEM)

The topology of a surface in which SnS films grow at different temperatures is analyzed with SEM and the samples are shown in figure (3). The morphology has the same shapes of grains with grain boundaries. With increasing the temperature there is a change in the grain boundaries as well as the grain size. When the films are deposited at setting up substrate temperature of (250) ºC it can be seen that the particles are elongated and the surface appears rougher. From the SEM images, the average size of the grains is found to be in the range of (25-122) nm. At (450ºc) the crystallites are packed densely and grown with various sizes in different directions and it is seen that it has pinhole-free, smoother, and more homogeneous film surface than films sprayed at lower temperatures. The granular surface structure vanished at higher temperatures (350ºC and 450ºC), and the films became thicker and more compact.

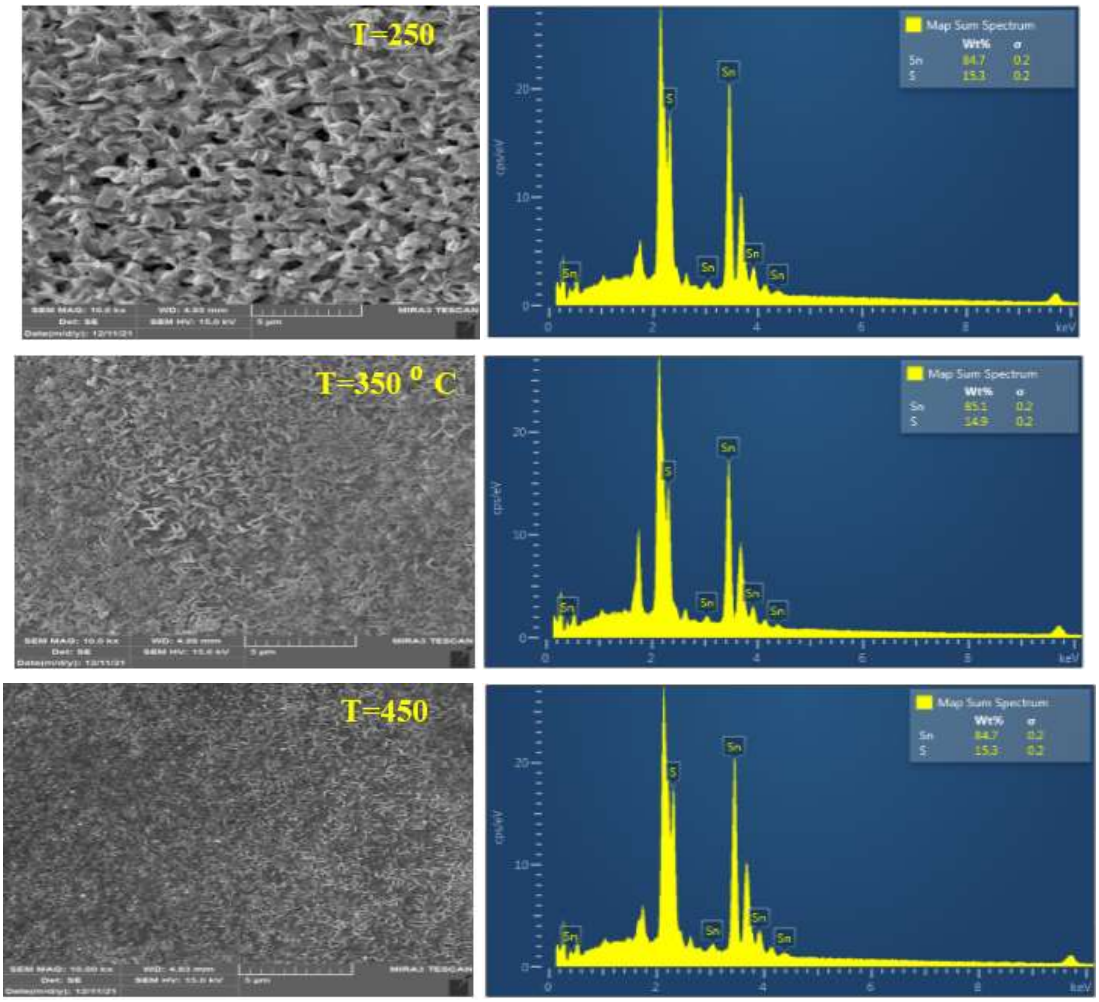


FIGURE 3

SEM IMAGES OF THE PURE SNS THIN FILMS AT (250, 350 AND 450)ºC.

2. Energy-Dispersive Spectroscopy Measurements (EDS)

3. *Energy-dispersive x-ray spectroscopy is a strong technique to analyze the chemical composition of the sample, being based on x-rays emitted by the atoms in the sample. Table (II) shows that all films contain just sulfur and tin-based on the molar ratios. When the temperature is increased from 250°C to 350°C, all ratios It turns out an excess of tin, but when the substrate temperature reaches 450 °C, then a reduction in the amount of tin is observed. In the EDS pattern shown in Fig. (4) the presence of the elements Sn and S in the layers is indicated app which confirms that they are made of SnS. As appears red in color and sulfur green color.*

TABLE II

SNS THIN FILMS OBTAINED BY EDS AT DIFFERENT TEMPERATURES

Temperature	Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
250º	S	K series	2.02	0.02157	14.91	0.20	39.33.	FeS2	Yes
	Sn	L series	9.15	0.10299	85.09	0.20	60.67	Sn	Yes
	Total:				100.00		100.00		
350º	S	K series	2.47	0.01742	15.25	0.22	39.98	FeS2	Yes
	Sn	L series	10.88	0.09148	84.75	0.22	60.02	Sn	Yes
	Total:				100.00		100.00		
450º	S	K series	2.50	0.02132	16.09	0.20	41.52	FeS2	Yes
	Sn	L series	10.30	0.10883	83.91	0.20	58.48	Sn	Yes
	Total:				100.00		100.00		

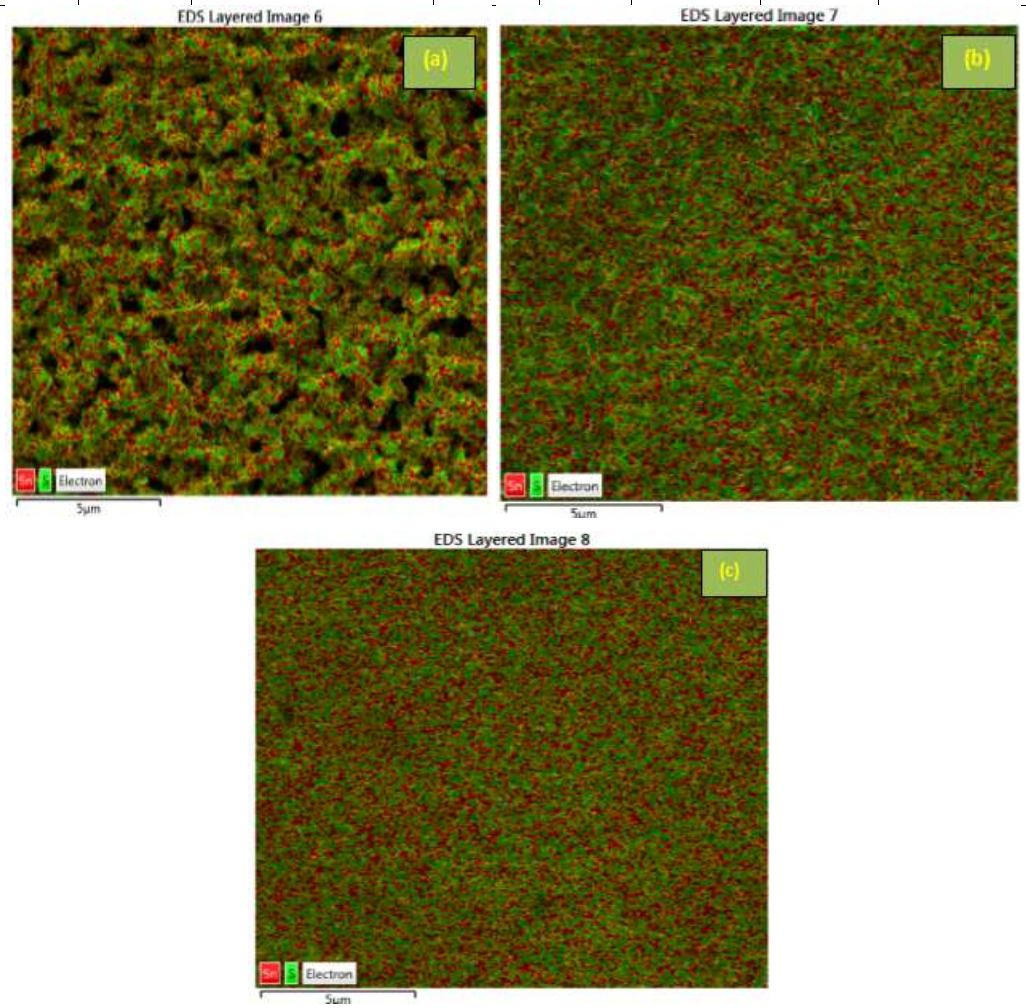


FIGURE 4

EDS PATTERN PRESENCE OF THE ELEMENTS SN AND S AT (A) 250 °C (B) 350 °C (C) 450 °C

4. Atomic Force Microscopy Measurement (AFM)

AFM images analysis is used to measure the morphology in the property of SnS thin films prepared on a glass substrate. This analysis aims to obtain accurate information about the surface and give the statistical values with high accurateness about the pore average diameter, roughness average, and root means square (RMS). Through microscopic analysis (AFM), We can study the distribution and arrangement of atoms on film surfaces and learn about the differences in inhomogeneity features or attributes linked to each atom individually, as well as an illustration of the crystalline size distribution rate onto surfaces [15]. AFM and 2-D image scanning were used to analyze the surface topography of SnS films produced at various substrate temperatures. Roughness and grain size for all samples are shown in Table (III). The effect of the base temperature on the surface of the prepared films, where the value of the square root (RMS) of the average roughness decreases from (38.1) nm to (28) nm. The homogeneity of the surface grains rises with the reduction in the value of the roughness rate with an increase in temperature. According to the findings from XRD and AFM tests, increasing the substrate temperature leads to the creation of more crystallites with smaller diameters.

This effect is thought to be caused by the formation of a larger density of nucleation sites as the temperature rises.

TABLE III

AFM PARAMETERS OF SNS THIN FILMS

Temperature substrate T (°C)	**Roughness (nm)**	**RMS (nm)**	**Average diameter (nm)**
250	38.1	47.5	15.6
350	28.6	37.6	23.88
450	28	35.3	27.35

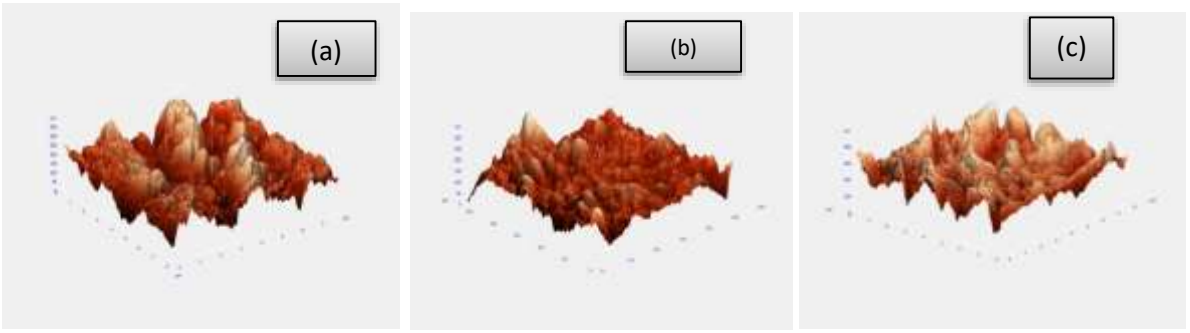
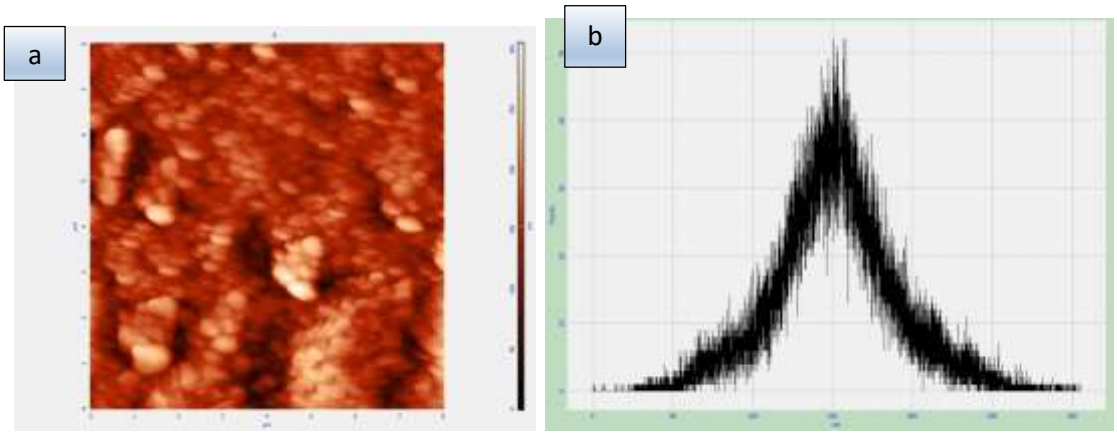


FIGURE 5

SURFACE MORPHOLOGY OBTAINED BY ATOMIC FORCE MICROSCOPE FOR SNS DEPOSITED FILMS AT (A) 250 °C (B) 350 °C (C) 450 °.



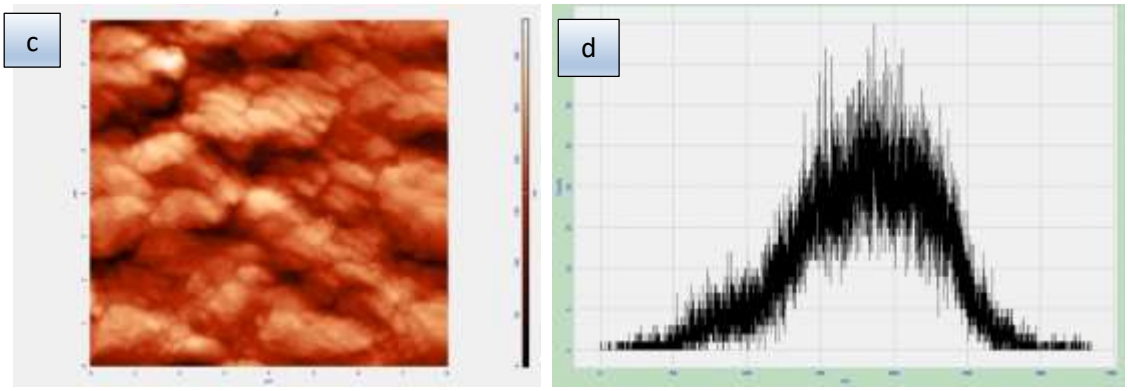


FIGURE (6): GRANULARITY DISTRIBUTION AND 2-D IMAGES OF SNS DEPOSITED FILMS: (A, B) 250 °C (C, D) 350 °C (E, F) 450°C

OPTICAL ANALYSIS

1. Absorptance Spectrum

Figure (7) shows the increase in the absorbance values in terms of wavelengths For all the prepared films, where it is clear from the figure that the absorbance increases with increasing temperature, especially in the infrared region (400-1000) nm and close to it. The lowest value of the absorbance spectrum for the films prepared at a temperature (250ºC), while the highest value for the prepared films was at temperature (450º)c the absorbance of thin films decreases as the wavelength increases. Because the falling photon energy is less than the energy value of the semiconductor, the falling photon could not vaporize the electron and shift it from the valence pack to the conduction beam. As a result, raising the wavelength reduces the absorbance. It's also worth noting that when the temperature of the substrate rises, the permeability of the surface decreases due to increased particle size and roughness. As a result, at substrate temperature (450) °C, thin films are formed. In agreement with other data, this study shows the highest absorption value [16] [17].

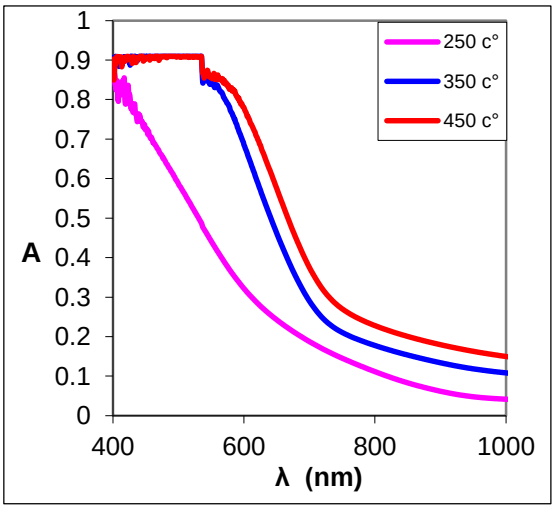


FIGURE 7

ABSORBANCE SPECTRUM FOR (SNS) THIN FILMS AT A DIFFERENT SUBSTRATE TEMPERATURE

2. Transmittance Spectrum

Figure (8) shows the optical transmittance of SnS thin films produced by CSP onto ordinary glass in the (400–1000) nm range. We observed a poor transmittance at 250ºC and a rise in transmittance from 350ºC to 450ºC as the substrate temperature was raised from 250ºC to 450ºC. We also observed, mainly that films prepared at a substrate temperature in the range of 350ºC to 450ºC had the same transmittance variation.

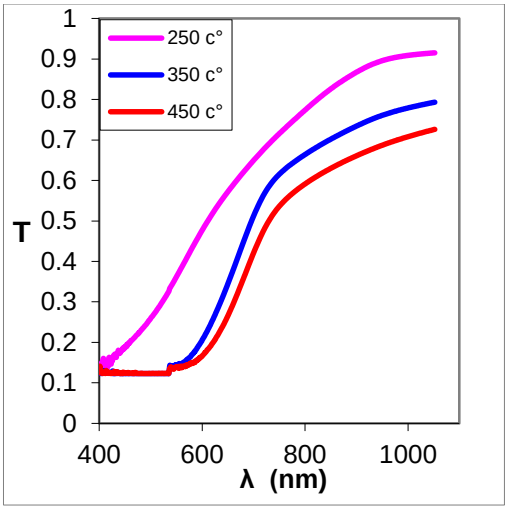


FIGURE 8

TRANSMITTANCE SPECTRUM FOR (SNS) THIN FILMS AT A DIFFERENT SUBSTRATE TEMPERATURE

3. Optical Energy Gap for Direct Allowed Transitions

Optical energy difference Eg was calculated for all thin-film preparations from the plot of (αhv) 2 versus (hv) photon energy (figure 9) by drawing an extended straight line of the curve and intersecting it with the x-axis, which yielded the value of the energy gap for prepared thin films. Figure (9) shows the direct optical energy gap values of SnS thin films at substrate temperature (250, 350, and 450) °C. The optical band gaps are found equal to (1.75, 1.56, and 1.5)eV, respectively. It is discovered that the value of the bandgap for the direct electronic transitions diminishes as the substrate temperature increments, as shown in Table (IV).This agreement with other reports[18][19]. Where the optical permitted energy gap of permitted is equal to (1.5) eV at 450 °C. This result supports the improvement of the crystal structure concluded from the XRD analysis. Suggesting that the deposited films are good candidates as absorber layers in solar cells.

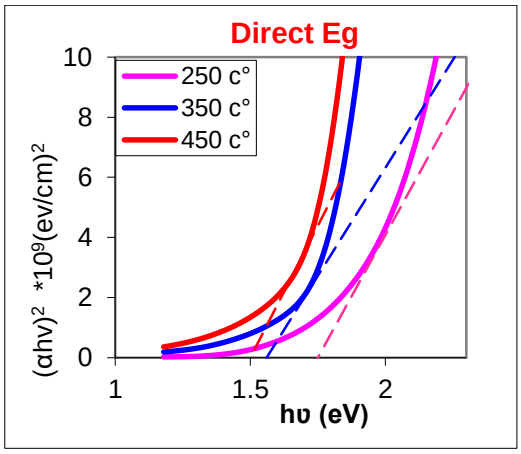


FIGURE 7

ABSORBANCE SPECTRUM FOR (SNS) THIN FILMS AT A DIFFERENT SUBSTRATE TEMPERATURE

TABLE IV

VALUES OF OPTICAL ENERGY GAP FOR SNS THIN FILMS

Substrate Temperature °C	E_g (eV)
250	1.75
350	1.56
450	1.5

CONCLUSION

Thin films multi-crystal of SnS are prepared in a thermal chemical spraying method and at different substrate temperatures (250, 350 and 450) ºC on glass.

Structural properties showed that the SnS films were the installation of orthorhombic polymorphism, as well as the presence of several levels and preferential levels (301). The practical results have shown that the granular size (grain size) Its crystalline development increases with the temperature of the base, as demonstrated by x-ray, AFM measurements and through the average root mean square of SnS films, which shows that films are highly absorbent, as confirmed by the study of the optical properties of these films (absorption) and Note that the rate of roughness decreases by increasing the temperature. The results of optical measurements through absorption and permeability value readings showed that increased temperature resulted in increased film absorption and a decrease in their permeability**.** The possession of films prepared at different temperatures showed direct electronic transmissions and bandgap between (1.5-1.7)eV.

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