The influence of solution temperature of SnS thin films grown by successive ionic layer adsorption and reaction (SILAR) method

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Abstract. Tin sulfide is a promising optoelectronic material, which has a particular interest due to its absorption coefficient, direct (indirect) bandgap and its non-toxic components. SnS thin films were deposited on glass substrates by SILAR (Successive Ionic Layer Adsorption and Reaction) method at different solutions temperature and it is rarely developed by this parameter. The cationic (SnCl2.2H2O) and anionic (Na2S.9H2O) solutions were used as precursors materials. The structure, films composition, morphology, and optical properties were investigated by using X-ray diffraction, Raman spectroscopy, energy dispersive X-ray analysis, Scanning electron microscopy (SEM) and spectrophotometer. X-ray diffraction (XRD) patterns indicated that the deposited SnS thin films have an orthorhombic crystal structure. Raman spectroscopy confirmed the presence of the SnS phase. Uniform deposition of the material over the entire glass substrate was showed by Scanning electron microscopy (SEM). The optical band gap energy was found between 1.6 and 1.85 eV.

Keywords: Tin sulfide, solution temperature, SILAR, Thin films.

1. Introduction
The recent importance of photovoltaic thin films, which is mainly involved in the improvement of cell manufacturing costs and efficiency of the conversion. In this context, efforts were made to find new non-toxic materials at a reduced cost-effectiveness.
To obtain solar cells cost-effective thin-film for the wide-scale production of solar energy, the semiconductor material used in the device has to meet many requirements. First, the components of solar cells must be inexpensive and nontoxic. Second, to achieve high-energy conversion efficiency, the material must have appropriate optical properties. In this side, tin monosulfide meets some of these criteria and thus is a promising candidate as an absorber material in photovoltaic applications [1]. Its components (Tin and Sulphur) are inexpensive, abundant in
nature and respectful of the environment. In addition, the binary compound SnS presents the cubic [2] and orthorhombic structure [3]. Thus, SnS has appropriate optical properties for PV applications; it has indirect and direct optical band gaps, the first one from 1 to 1.1 eV, the second from 1.3 to 1.5 eV; and a high absorption coefficient (>10^3 cm^-1) above the absorption edge [4]. The SnS thin films can be made by physical and chemical methods. Such as thermal evaporation [5], RF sputtering [6], (CBD) Chemical bath deposition [7], spray pyrolysis [8], electrodeposition [9] and SILAR method [10]. In this work, we were interested by the last technic, which is simple, less expensive and useful for depositing on large surfaces. The growth can be easily controlled by various parameters, including solution concentration, temperature, number of cycles and immersion time, etc.

2. Materials and Methods

2.1. Elaboration of SnS
Before the deposition, the glass substrates (26 × 76 × 1 mm3) have been carefully cleaned and degreased. The cationic and anionic precursor solutions, 0.2 M SnCl2 + 2H2O and 0.1 M Na2S+9H2O respectively were dissolved in 100 ml of distilled water. Each cycle of SILAR method contains immersion of the substrate in a cationic precursor solution (SnCl2, 2H2O) for 20 s, tin ions were adsorbed on the surface. Then, the substrate is rinsed in distilled water for 10 s. Next, the substrate is immersed in the anionic solution (Na2S, 9H2O) for 20 s, Sulfide ions react with those of tin adsorbed on the active center of the substrate. Again, the substrate is rinsed in distilled water for 10 s to remove the ions weakly related to the substrate [11]. So, the first cycle of growth by SILAR method is finished. We have repeated this cycle for 40 times. The experiment was performed at different solution temperatures 27°C, 40°C and 60°C with stirring solution, which are according to samples S1, S2 and S3 respectively. In the process, the preparatory important parameters are concentrations, temperature, immersion period and pH of solutions.

2.2. Reaction mechanism
The SILAR deposition for SnS thin films follows the below chemical reaction:

\[ \text{SnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{SnS} + 2\text{NaCl} \] (1)

2.3. Characterization
The analysis by X-ray diffraction (XRD) was performed using an XPERT-3 diffractometer with a radiation (Cu-Kα, λ =1,5406 Å) in the range 2θ=10°-60°. The surface morphology and films composition were studied, using scanning electron microscopy (EDX-SEM). The optical vibratory modes of films were determined by Raman spectroscopy. The band gap energy was investigated using the Perkin Elmer Instrument Lambda 900 UV / Vis / NIR spectrophotometer.

3. Results and discussions

3.1. Structural and compositional studies
Figure 1 shows the XRD patterns of the SnS films deposited on glass substrates at various solution temperatures, 27°C, 40°C and 60°C, respectively. The comparison of interreticular distance values “d” in observed XRD patterns with those of standard (JCPDS card # 1-984) confirms the formation of SnS phase having orthorhombic Pmcn (62) crystal structure without a secondary phase. The peaks observed in XRD spectrum corresponding to SnS phase were (012); (110); (013); (104). The highest intensity observed for the (013) diffraction peak at 31.78° is the preferential crystallographic direction for S1
sample and for S2 and S3 samples the (012) peak dominates. The clarity of the major peaks indicates a good crystallinity.

The relation between the lattice plane index (hkl), the interplanar distance dhkl and the lattice parameters for the orthorhombic crystal is [12]:

\[
\frac{1}{d_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

(2)

The lattice parameters values “a”, “b” and “c” for orthorhombic structure calculated for the deposited films are found to be (a = 4.07Å; b = 4.13Å; c= 11.45 Å), these values are in good agreement with the reported values [13]. An approximation of the crystallite size, the dislocation density (δ) and microstrain (ε) of samples were calculated from XRD using the following formulas [14]:

- **Crystallite size:**
  \[ D = \frac{0.9\beta}{\lambda \cos \theta} \]

- **Dislocation density:**
  \[ \delta = \frac{1}{d^2} \]

- **Micro strain**
  \[ \varepsilon = \frac{\beta \cos \theta}{4} \]

Where D is the grain size, λ is the wavelength of the Cu-Kα radiation used (λ=1.5405 Å), β is experimentally observed diffraction peak width at half-maximum intensity (FWHM), θ is the Bragg angle.

Table 1 indicates the (hkl) plane, crystallite size (D), Full width at half maximum FWHM value, dislocation density (δ) and micro strain (ε) for all SnS thin films. As the temperature increase, the microstrain and dislocation density of the film also increase. The lower microstrain values and the dislocation density of the deposited film at temperature 27°C indicate a densely packed structure with minimal defects and good crystallinity of the deposited film at 27°C Compared to the others.

| (hkl) | D (nm) | FWHM | δ (10^2 nm)^2 | ε         |
|-------|--------|------|--------------|------------|
|       | S1     | S2   | S3           | S1         | S2   | S3   | S1  | S2  | S3  |
| 012   | 31.929 | 19.655 | 13.049        | 0.295      | 0.472 | 0.708 | 9.8 | 25.8 | 58.7 | 0.5243 | 0.8592 | 1.2666 |
| 110   | 32.216 | 19.846 | 26.670        | 0.295      | 0.472 | 0.354 | 9.6 | 25.3 | 14.05 | 0.4515 | 0.7313 | 0.5396 |
| 013   | 32.290 | 19.890 | 26.736        | 0.295      | 0.472 | 0.354 | 9.5 | 25.2 | 13.98 | 0.4374 | 0.7092 | 0.5206 |
| 104   | 13.469 | -     | -             | 0.354      | -     | -    | 55.12 | -   | -   | 0.4233 | -   | -   |

Table 1. (hkl) plane, grain size (D), FWHM value, dislocation density (δ) and micro strain (ε) values of SnS thin film.
Figure 1. XRD spectra of films deposited at different solution temperatures, 27°, 40° and 60°

3.2. Morphological Studies

The morphological features of SnS samples for different solution temperatures are investigated by SEM image at ×16,000 magnification. The Figure 2 shows the three samples of SnS thin films deposited on glass substrates using SILAR method. The substrates are covered with the tin sulfide film. With increasing the temperature of the solutions we see the average grain size decreases. However, for each sample, we have a nearly equal distribution of average grain size. The sample S1 has the rough distribution and shows aggregates of small particles as agglomerates of grains that occur on the surface [15]. The increase in the solution temperatures has reduced the compactness of grains as shown in S2 and S3, which is due to the problem of adhesion caused by a small thickness of layers.

To evaluate the elementary composition, the deposited SnS thin films were characterized by EDX-SEM. Fig.3 shows the EDX spectra of as-deposited thin films. Elemental analysis shows the presence of tin (Sn) and sulfur (S) with other elements such as silicon (Si), chlorine (Cl), sodium (Na) and oxygen (O) are due to the glass substrate. The corresponding Sn:S ratio of S1, S2 and S3 was found to be: 0.88; 0.92;
0.89 respectively. The as-deposited SnS thin films have almost a stoichiometric composition with ratios are nearly equal ~1. Thus, the as-deposited films are slightly richer with the sulfur component.

![Figure 3](image)

Figure 3. EDX spectra of as-deposited SnS thin film samples S1, S2 and S3.

### 3.3. Raman Studies

![Figure 4](image)

Figure 4. Raman spectra of SnS films deposited by SILAR method at different temperatures
The room temperature Raman spectra of SnS thin films have been shown in figure 4. The Raman modes for SnS thin films are observed at 111 cm\(^{-1}\), 174 cm\(^{-1}\), 201 cm\(^{-1}\), 223 cm\(^{-1}\) and 284 cm\(^{-1}\). The modes located at 111 cm\(^{-1}\), 201 cm\(^{-1}\) and 223 cm\(^{-1}\) are associated to Ag mode, 174 cm\(^{-1}\) and 284 cm\(^{-1}\) are associated to B2g mode. All modes detected are corresponding to the SnS monocrystalline modes [16] without secondary phase, which are in good agreement with the XRD spectra.

3.4. Optical Studies

Fig. 5(a) shows the optical absorbance variation in the wavelength range 400 to 1000 nm of SnS thin films deposited at different temperatures. The high absorbance in the visible region has clearly shown that the SnS thin films are absorber layers. As can be seen in this figure, while increasing the temperature of the solutions, the absorbance of SnS thin films decreased. The decrease of the absorbance is attributed to the adhesion, which is due to the low thickness.

The optical band gap of SnS films, based on the UV-Vis-NIR spectrophotometer, depending on growth method, deposition temperature and kind of substrate [17]. The optical absorption theory gives the relation between the photon energy \((h\nu)\) and the absorption coefficient \((\alpha)\) as follow [18]:

\[
(ahv)^n = A(h\nu - E_g)
\]

Where \(A\) is constant, \(n\) is the number that depends on the electronic transition [19]. The value of \(n\) is 2 and 1/2 for direct and indirect transition respectively.

![Figure 5](image)

Figure 5. (a) Optical absorption spectra and (b) Plot of \((ahv)^2\) versus the photon energy \((h\nu)\) of SnS thin films prepared at different substrate temperatures.

4. Conclusions

SILAR method was used to deposit SnS thin films on glass substrates, the quality of films depends on the preparative parameters. The XRD studies showed that our SnS thin film had an orthorhombic structure. Raman spectroscopy confirmed the XRD results with modes associated to the SnS orthorhombic structure without any secondary phase for all samples. SEM image revealed nearly equal size distribution of grains. EDX indicated nearly stoichiometry between elements with Sn: S ratio \(\approx\) 1. In addition, the optical band gap was obtained as 1.68, 1.7 and 1.85 eV by using the UV-Vis-NIR spectrophotometer.
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