

# Morphological Changes of SnS Thin Films Deposited on Stainless-Steel Substrates at Low Temperatures

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**Abstract**—Orthorhombic tin sulfide (SnS) thin films have been deposited on stainless steel (SS) substrates by Chemical Bath Deposition (CBD) at 25, 35 and 70 °C with a deposit time of 8 hours each one. XRD analysis showed that samples obtained at 25 °C and 70 °C present very small diffraction peaks. This can be attributed in the case of the sample obtained at 25 degrees, that the crystallization process is not completed because the temperature is so low and in case of the sample deposited at 75 degrees, a redissolution of the material is carried out. However, sample obtained at 35 °C was polycrystalline with orthorhombic structure and preference plane (111). All samples showed the Raman vibrational modes TO and LO of the SnS and confirms that the samples do not have by-products. It was observed from SEM micrographs that the films consisted of spheres for the sample deposited at 25 °C and small flakes for the other samples. From diffuse reflectance measurements the optical band gap calculated was between 1.45 eV to 1.59 eV.

**Index Terms**—Tin Sulfide; Chemical Bath; Stainless Steel; Low Temperature.

## I. INTRODUCTION

Some years ago, tin sulfide (SnS) has been considered as potential material for photodetectors, heat mirrors, photocatalysis, photovoltaic devices because of their high optical absorption coefficient in the visible range ( $\approx 10^4 \text{cm}^{-1}$ ). One of the advantages of using SnS is due to the abundance in nature; it is not toxic and is readily available [1]. SnS is found in Zinc blend [2],[3], orthorhombic [4],[5] and herzenbergite phases [6]. Some methods of preparation of SnS are: electrochemical deposition [7],[8], spray pyrolysis [9]–[11], Chemical Bath Deposition (CBD) [2],[12]–[15], etc. On the other hands, solar cells that use glass substrates have certain disadvantages for some applications such as cell phones, identification cards, etc. [16] For this reason, recently several researchers have been working on the replacement of glass by plastic or metal substrates, such is the case of stainless steel [16],[17].

In this work, the effect of temperature on the crystalline, morphological and optical properties of the SnS thin films deposited on SS substrates by CBD was analyzed.

## II. MATERIAL AND METHODS

SnS thin films were deposited on SS 304 substrates with thickness of 0.455 mm and 2.5 cm x 7 cm. The SS substrates were cleaned with detergent (Extran), rinsed with deionized water (DW) and dried with air. The bath solution was prepared as follow: 1 g of 0.1 M tin chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) is dissolved into 5 ml of acetone ( $\text{C}_3\text{H}_6\text{O}$ ), once dissolved; 12 ml of 3.7 M triethanolamine (TEA:  $\text{C}_6\text{H}_{15}\text{NO}_3$ ) were added, then, 50 ml of deionized water (DW), 8 ml of 1M thioacetamide (TA:  $\text{CH}_3\text{CSNH}_2$ ) and 5 ml of 4 M ammonia ( $\text{NH}_4\text{OH}$ ) to control the pH (10.5) are added to the solution. Finally, 20 ml of DW was included for completing a total volume of 100 ml. All the chemical reagents were from J.T. Baker, excepting TA (99.0%) which was purchased from Sigma-Aldrich. To make SnS thin films deposition SS substrates were immersed vertically into the precursor solution and the chemical process was carried out for 8 h at 25, 35 and 70 °C.

The films were characterized by grazing incidence angle into a diffractometer (Bruker D8 Advanced) by using the  $\text{CuK}_\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ) radiation. The diffraction patterns were obtained at 1° as grazing incidence angle in the range from 20° to 70°, step of 0.02°, 2 s/step, 40 kW and 40 mA as measurement conditions. Diffuse reflectance was carried out with Cary Agilent 5000 UV-vis-NIR spectrophotometer into the 200 nm to 2500 nm range and scanning speed of 600 nm/min. Microscopy images were also obtained with a scanning electron microscope (SEM) Vega Tescan, TS5136SB with 5 kV. Raman spectra were recorded on a Micro-Raman spectrometer (Horiba-Jobin Won, Model LabRam-HR) by using a 632.8 nm Laser Source (He-Ne 150mW), 10 cycles and 6.28mW/cm<sup>2</sup>.

## III. RESULTS AND DISCUSSION

Fig. 1 presents XRD patterns of SnS thin films obtained at several temperatures. We observe that the samples obtained at 25 °C and 70 °C present very small diffraction peak at  $2\theta = 31.4^\circ$ . This can be attributed in the case of the sample obtained at 25 °C, that the crystallization process is not completed because the temperature is so low and we do not have enough thermal energy to form crystalline SnS. In case of the sample deposited at 70 degrees, a redissolution of the material is carried out. The absence of diffraction

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peaks has been reported by D. Xia et. al. [18] and attributed it to the presence of SnS amorphous. In diffractogram of sample deposited at 35° several diffraction peaks are present, at  $2\theta = 21.9^\circ, 25.9^\circ, 30.4^\circ, 31.4^\circ, 39^\circ$ , corresponding to diffraction planes (110), (120), (101), (111) and (131) respectively, which are in good agreement with orthorhombic phase of SnS (PDF No. 01-075-1803). As a reference, an XRD spectrum of SS is shown in Fig. 1, in it we can see three diffraction peaks at  $2\theta = 43.6^\circ, 44.4^\circ$  and  $50.7^\circ$  which corresponds to (111), (110) and (200) planes of SS (PDF 00-033-0397, 00-034-0396). However, in the samples with SnS film, only the peak corresponding to the (110) plane is observed. The decrease in the intensity of this peak we can be attributed to the thickness of the SnS film, which shields the signal from the substrate. We can mention that they are not observed diffraction peaks corresponding with byproducts. We can mention that they are not observed diffraction peaks corresponding with byproducts. Crystallite size was calculated using Debye-Scherrer's equation  $D = K\lambda/\beta \cos \theta$ . The estimated crystallite size for sample obtained at 35 °C was 8.34 nm and 7.57 nm to 70 °C.

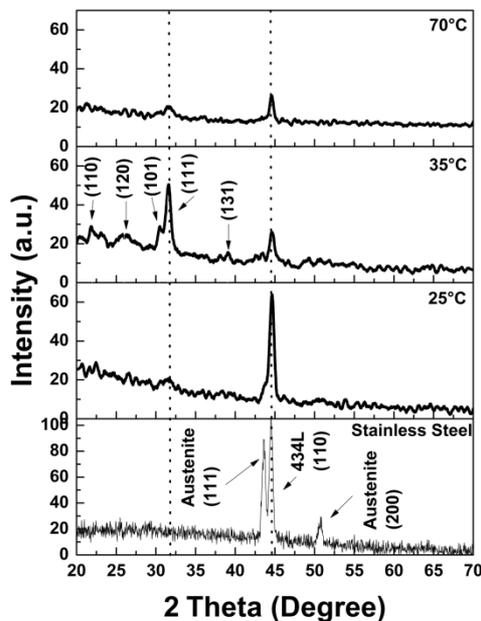


Fig. 1. SnS thin films deposited on SS substrates with 8 hours of deposit time at 25, 35 and 70 °C

Raman analysis was carried out in the range of 80 to 500  $\text{cm}^{-1}$ . Fig. 2 shows Raman spectra of our samples, we can see five peaks located at 94, 163, 189, 226 and 287  $\text{cm}^{-1}$ , which are related with TO ( $A_g$ ), LO ( $B_{3g}$ ), LO ( $A_g$ ), LO ( $A_g$ ) and LO ( $B_{2g}$ ) of SnS respectively [19],[20]. These results confirm that the obtained samples are formed of pure SnS and that by-products derived from the chemical reaction do not exist. It is observed in this figure that the sample obtained at 25 °C presents a signal with low intensity, this is attributed to the poor crystalline quality that this sample presents.

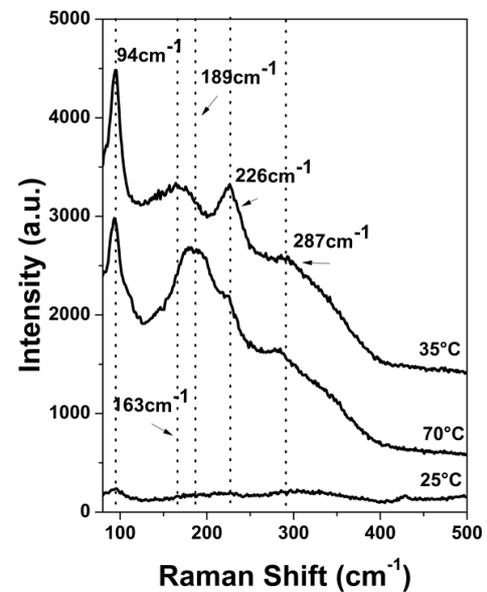


Fig. 2. Raman spectra of SnS thin films deposited at different temperature.

Because the stainless-steel substrates are opaque, diffuse reflectance was measured in the range of 400 to 800 nm and is shown in Fig. 3. Plot of  $(F(R)h\nu)^{1/2}$  vs. photon energy ( $h\nu$ ) is shown in the inset of Fig. 3, the energy gap was estimated by extrapolating linear part of  $(F(R)h\nu)^{1/2}$ . The energy gap of SnS thin films was found to be 1.48 eV, 1.45 eV and 1.59 eV which corresponds to samples deposited at 25, 35 and 70 °C respectively and are associated to indirect transition.

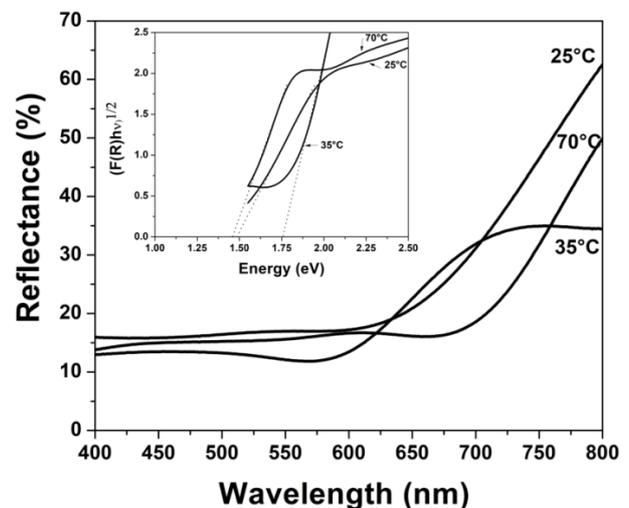


Fig. 3. Diffuse reflectance of SnS thin films deposited at several temperatures, the inset shows curves of  $(F(R)h\nu)^{1/2}$  vs.  $h\nu$ .

The evolution of the surface morphology of films was carried out by SEM. Fig. 4-a corresponds to the sample obtained at 25 °C, in which two structures are observed mainly, spheres and some small flakes. Sample deposited at 35 °C (Fig. 4-b). We can observe a high density of well-defined SnS flakes. Finally, sample obtained at 70 °C (Fig. 4-c). It is observed that the flakes have a large area with respect to other samples. The flake morphology is characteristic of SnS posited by CBD on glass substrate as reported by D. Xia et. al.[18].

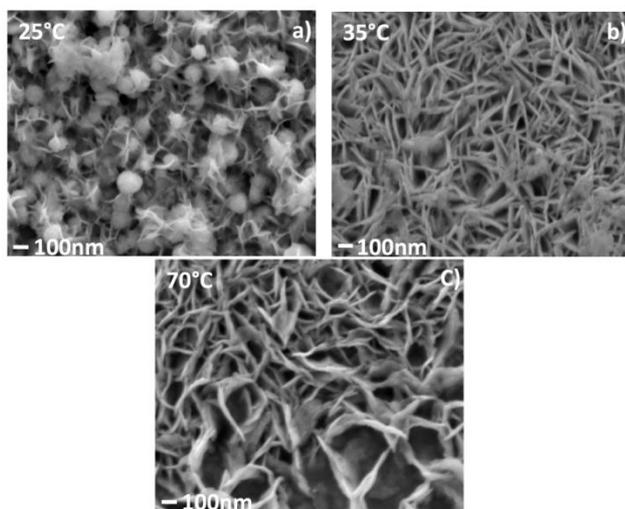


Fig. 4. Micrographs SEM of SnS thin films at different temperature of deposit.

Variation of Sn/S atomic ratio of the SnS samples with respect of the bath temperature has been studied from EDS. Fig. 5-a shows typical elements of SS substrate, like C, Cr, Fe, Mn and Ni. We can observe that film obtained at 25 °C has a Sn/S ratio of 0.90 while the one deposited at 35 °C has a ratio of 0.98, which indicates that both samples have an excess of sulfur. The sample obtained at 70 °C has a ratio of 1.40, which indicates that has a deficiency of sulfur. From the above we can say that the sample with the best stoichiometry is the one obtained at 35 °C.

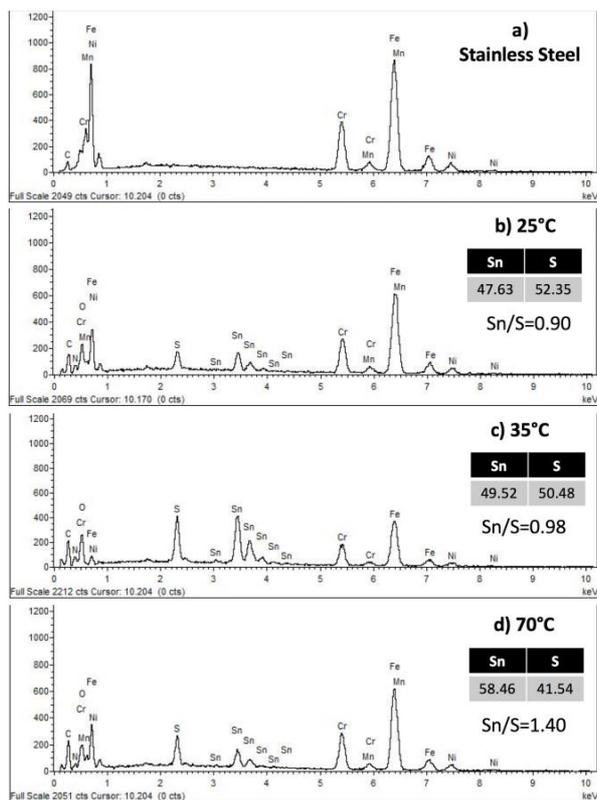


Fig. 5. EDS spectra of a) stainless-steel substrate and SnS thin films deposited at: b) 25 °C, c) 35 °C and d) 70 °C.

#### IV. CONCLUSION

In this work, orthorhombic phase SnS thin films were deposited successfully on SS substrates by chemical bath

deposition. X-ray diffraction studies show that the sample deposited at 25 °C does not have enough energy to obtain crystalline SnS. However, the samples obtained at 35 and 70 °C are polycrystalline films, although the 70 °C sample shows redissolution effects. The formation of SnS was confirmed by Raman spectroscopy, in which only the vibrational modes corresponding to SnS are observed. Morphologically, it was observed a combination of spheres and flakes at 25 °C, while at 35 and 70 °C it is obtained only flakes. Indirect band gap of samples was between 1.45 and 1.59 eV, which are in agreement with bulk gap value. The sample that presents a better stoichiometry is the one obtained at 35 °C, while the one obtained at 25 °C has a tin deficit and the one obtained at 70 °C has a deficit of sulfur. From the above results it can be concluded that the adequate temperature to deposit SnS on stainless steel substrates is 25 °C.

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