PHYSICAL PROPERTIES OF In$_2$S$_3$ THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION AT DIFFERENT TEMPERATURES


$^a$Facultad de Química, Materiales, Universidad Autónoma de Querétaro, Querétaro, 76010, México.
$^d$Escuela Superior de Física y Matemáticas del IPN, México D.F. 07738, México.

Indium sulphide thin films were deposited on SnO$_2$:F/soda-lime glass substrates at different temperatures by chemical bath deposition. InCl$_3$ and C$_2$H$_5$NS were employed as indium and sulfur sources, respectively. The In$_2$S$_3$ films were deposited at temperatures of: 60 °C, 70 °C and 80 °C. The as-grown films were annealed at 300 °C in nitrogen atmosphere. The physical properties were analyzed as a function of the bath temperature, before and after the thermal treatment. The X-ray diffraction and Raman characterizations indicate that In$_2$S$_3$ films with tetragonal phase were obtained. Atomic force microscopy showed that after the annealing features of grain coalescence on surface are present. The UV-Vis analysis indicated that after thermal treatment In$_2$S$_3$ films have high transmission in the visible range and a bandgap above 2.50 eV.

(Received July 10, 2016; Accepted August 30, 2016)

Keywords: In$_2$S$_3$ films; Chemical bath deposition; Room temperature photoluminescence; Optical properties; Solar cells applications

1. Introduction

The development of low-cost processing techniques for the fabrication of photovoltaic materials and electronic devices is critical for cost-competitive photovoltaic electricity production in comparison with conventional sources of energy. Thin-film solar cells based on CdTe, CIGS and CZTS employ a CdS binary compound as window thin film layer. The replacement of CdS with other sulfides such as In$_2$S$_3$ has given good results. The indium sulphide (In$_2$S$_3$), a III-VI semiconductor compound, appears as a promising candidate for this application due to its stability, bandgap in the range 2.0-2.9 eV depending on its composition, and transparency [1]. Besides, In$_2$S$_3$ films have been used as substitute for CdS in thin film solar cells to avoid toxic cadmium and obtain more environment friendly photovoltaic technology [2]. Using a In$_2$S$_3$ layer replaces the toxic cadmium, besides the optical properties of the buffer layer are improved because this material has a bandgap wider than the one of CdS. In$_2$S$_3$ films have been grown by co-evaporation of In and S [3], electrochemical deposition [4], spray pyrolysis [5] and chemical bath deposition (CBD) [6]. The CBD technique is very attractive due to its feasibility to produce at low cost large-area thin films [7]. In this work, we report the influence of the growth temperature on physical properties of In$_2$S$_3$ films grown by CBD.

* Corresponding author: fcomoure@hotmail.com
2. Experimental details

2.1 Growth of In$_2$S$_3$ films

In$_2$S$_3$ films were deposited on commercial SnO$_2$:F/soda lime-glass (10 Ω/□ and 0.5 µm) substrates by CBD at different temperatures: 60 °C, 70 °C and 80 °C for 1 h. The reaction solution was prepared mixing 20 ml of 0.025 M InCl$_3$, 0.075 M C$_2$H$_5$NS (thioacetamide) and acetic acid. Deionized water (DI water-18 MΩ) was used for the preparation of solutions. The InCl$_3$ and C$_2$H$_5$NS were employed as indium and sulfur sources, respectively. The acetic acid formed complexes in the reaction process and maintained a pH of 3. The temperature was controlled with a hot plate equipped with magnetic stirrer. After deposition, films were rinsed in distilled water in ultrasonic bath for 5 min. Then, as-grown In$_2$S$_3$ films were heated at 300 °C in nitrogen atmosphere for 1 h. In$_2$S$_3$ thin films were labeled according to the bath temperature, see Table 1.

The decomposition of thioacetamide in an aqueous medium is as follows [1,8]:

\[
\text{CH}_3\text{CSNH}_2 \leftrightarrow \text{CH}_3\text{C(SH)NH}
\]

The protonation from acetic acid forms: \( \text{CH}_3\text{C(SH)NH} + \text{H}^+ \leftrightarrow \text{CH}_3\text{C(H}_2\text{S}^+)\text{NH} \), which dissociates to give H$_2$S:

\[
\text{CH}_3\text{C(H}_2\text{S}^+)\text{NH} \rightarrow \text{CH}_3\text{CNH}^+ + \text{H}_2\text{S}
\]

In aqueous medium, H$_2$S dissociates to produce:

\[
\text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{H}_3\text{O}^+
\]

\[
\text{HS}^- + \text{H}_2\text{O} \rightarrow \text{S}^{2-} + \text{H}_3\text{O}^+
\]

Then, ion-by-ion deposition mechanism between indium and sulfur ions takes place:

\[
2\text{In}^{3+} + 3\text{S}^{2-} \rightarrow \text{In}_2\text{S}_3
\]

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained with a Rigaku Smartlab diffractometer, using the Cu-K$_\alpha$ line (1.5406 Å). XRD patterns were collected at a grazing-incidence of 1.5°, with a step size of 0.02° and a step time of 1 s. Raman spectroscopy measurements were carried out in a Labram Dilor micro-Raman system, employing a HeNe laser (632.8 nm) as excitation source. The morphology studies were performed by Atomic Force Microscopy (AFM), using a ThermoMicroscope Autoprobe CP Research AP-2001 in contact mode. Atomic concentration measurements of films were determined by Energy Dispersive Spectrometry (EDS) with a Bruker 5010 X-Flash detector installed in a JEOL JSM-6300 scanning electron microscope. Film thicknesses were measured in a KLA Tencor P15 profilometer. A Perkin-Elmer Lambda 25 UV-Vis spectrophotometer was used to obtain optical transmittance. Photoluminescence (PL) spectra were obtained at room temperature using an Omnichrome-Series 56 He-Cd laser emitting at 325 nm. The radiative emission from the samples was focused to the entrance slit of a HRD-100 Jobin-Yvon double monochromator with a resolution better than 0.05 nm and detected with an Ag-Cs-O Hamamatsu photomultiplier.

3. Results and discussion

3.1 Structural characterization

Fig. 1 shows XRD patterns of In$_2$S$_3$ films grown at different temperatures (60 °C, 70 °C and 80 °C) by CBD, before and after the annealing. Fig. 1a) shows the XRD diffractograms of as-grown In$_2$S$_3$ films. The sample deposited at 60 °C has three diffraction peaks at 27.70°, 33.45° and 48.00°, which correspond to In$_2$S$_3$ cubic or tetragonal phase. The diffraction planes are (311)/C(109)T, (400)/C(0012)T and (440)/C(2212)T, respectively. The diffraction peaks were
indexed using the power diffraction files (PDF) 32-0456 and 25-0390. From XRD patterns in Fig. 1a), note that the intensity of diffraction peaks decreases as the temperature of the bath increases, indicating a reduction in the crystalline quality of In$_2$S$_3$ films; in fact the film grown at 80 °C is practically amorphous. Fig. 1b) shows diffractograms of In$_2$S$_3$ films after the heat treatment. The In$_2$S$_3$-60°C film, after the annealing, has three additional diffraction peaks at 36.38°, 38.08° and 51.78°, which correspond to In$_2$S$_3$ cubic or tetragonal phase and diffraction planes are: (311)C/(303)T, (421)C/(1013)T and (610)C/(415)T, respectively. After the annealing, the diffractogram of the In$_2$S$_3$-80°C film has three additional diffraction peaks at 27.70°, 33.45° and 43.82°, the peak at 43.82° may correspond to In$_2$S$_3$ cubic or tetragonal, and the diffraction plane is (511)C/(1015)T, other peaks were discussed above. The annealing produces the presence of additional diffraction peaks, this may be due to a crystallization of amorphous material during the annealing. The crystallite size was calculated using the Scherrer formula: $D = \frac{0.9\lambda}{B\cos\theta_b}$, where $D$ is the crystallite size, $\lambda$ is the XRD wavelength (1.5406 Å), $B$ is the full width at half maximum (FWHM) of diffraction peak and $\theta_b$ is the Bragg angle. The crystallite size of each film, before and after the thermal treatment, is shown in Table 1. The crystallite size of In$_2$S$_3$-60°C film has a value of 22.05 nm, for a growth temperature of 70 °C the crystallite size was 25.59 nm and the In$_2$S$_3$-80°C as-grown sample has an average crystallite size of 17.65 nm. Note that after the annealing in nitrogen, the crystallite size decreases for all samples (see Table 1). The film thicknesses, before and after of the thermal treatment, are displayed in Table 1. The thickness of as-grown films are in the range of 149-188 nm. After the annealing in nitrogen the thickness of In$_2$S$_3$ films have a reduction of approximately 8%. The thickness for the In$_2$S$_3$ films in this work is in the range used in the processing of solar cells [9].

![Fig.1. XRD patterns of In$_2$S$_3$ thin films grown by CBD for 60 min and different temperatures: 60 °C, 70 °C and 80 °C.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bath temperature (°C)</th>
<th>As-grown</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$S$_3$-60°C</td>
<td>60</td>
<td>22.05</td>
<td>13.86</td>
</tr>
<tr>
<td>In$_2$S$_3$-70°C</td>
<td>70</td>
<td>25.59</td>
<td>14.76</td>
</tr>
<tr>
<td>In$_2$S$_3$-80°C</td>
<td>80</td>
<td>17.65</td>
<td>18.23</td>
</tr>
</tbody>
</table>

Table 1. Growth parameters, crystallite size and thickness of In$_2$S$_3$ films.
Raman spectra of In$_2$S$_3$ thin films grown at different temperatures are shown in Fig. 2. In$_2$S$_3$ films have three Raman peaks at 115 cm$^{-1}$, 135 cm$^{-1}$ and 180 cm$^{-1}$, the signals correspond to tetragonal phase of the In$_2$S$_3$ (β-In$_2$S$_3$) [10,11]. The In$_2$S$_3$-60°C has an additional shoulder of lower intensity at 379 cm$^{-1}$, corresponding to In$_2$O$_3$ [12]. The In$_2$S$_3$-80°C sample has an additional peak at 305 cm$^{-1}$, assigned to β-In$_2$S$_3$ phase [10]. After heating the samples have a better definition in the β-In$_2$S$_3$ peaks located at 115 cm$^{-1}$, 135 cm$^{-1}$ and 180 cm$^{-1}$ can be observed in all the samples, note also the In$_2$O$_3$ peak detected in the In$_2$S$_3$-60°C film has disappeared. It is important to mention that the Raman analysis did not detect any peaks due to cubic phase (α-In$_2$S$_3$). Therefore, this analysis shows that In$_2$S$_3$ films grown by CBD have a tetragonal phase (β-In$_2$S$_3$).

![Raman Spectra](image)

**Fig. 2.** Raman spectra of In$_2$S$_3$ films grown at different temperatures; 60 °C, 70 °C and 80 °C.

### 3.2 Atomic force microscopy characterization

Fig. 3 shows AFM (4 µm$^2$) images of In$_2$S$_3$-60°C and In$_2$S$_3$-80°C films, before and after the annealing in nitrogen at 300 °C. Note that the annealing produces a coalescence of grains in both samples. Figs. 3a-b) show the topography of the In$_2$S$_3$-60°C sample before and after the annealing, respectively. The root mean square (rms) roughness of In$_2$S$_3$-60°C as-grown and In$_2$S$_3$-60°C annealed films was 4.04 nm and 3.26 nm, respectively. The rms roughness of the In$_2$S$_3$-80°C film, before and after the heat treatment (Figs. 3c-d), was 4.03 nm and 3.75 nm, respectively. Thus, in general the annealing in nitrogen produces a coalescence of grains and reduces the rms roughness of In$_2$S$_3$ films grown by CBD. The conversion efficiency of solar cells is a parameter that strongly depends on the low roughness of buffer films used to manufacture such devices, remarking that the smallest rms roughness is obtained by this technology [13].
3.3 Compositional characterization
In order to determine the composition of In$_2$S$_3$ thin films grown by CBD, EDS measurements were performed. In Table 2 the In and S atomic concentrations as well as the S:In ratio are listed. The In$_2$S$_3$-60°C as-grown film has a S:In ratio of 1.51, which is approximately the stoichiometry of the In$_2$S$_3$ compound. After heat treatment the S:In ratio of the In$_2$S$_3$-60°C has a value of 1.31, which is due to a lower vapor pressure of S respect to In. This analysis indicates that for a growth temperature of 60 °C In$_2$S$_3$ films with good stoichiometry were obtained, in agreement with those results of XRD and Raman.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-grown</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_g$ (eV)</td>
<td>In (%)</td>
</tr>
<tr>
<td>In$_2$S$_3$-60°C</td>
<td>2.27</td>
<td>39.81</td>
</tr>
<tr>
<td>In$_2$S$_3$-70°C</td>
<td>2.71</td>
<td>41.96</td>
</tr>
<tr>
<td>In$_2$S$_3$-80°C</td>
<td>2.32</td>
<td>32.17</td>
</tr>
</tbody>
</table>

3.4 Optical characterization
The optical transmittance spectra of In$_2$S$_3$ films grown by CBD at different temperatures, before and after heat treatment, are shown in Fig. 4. The transmittance of In$_2$S$_3$ as-grown films are shown in Fig. 4a), the In$_2$S$_3$-70°C as-grown film has the higher transmittance; between 60% and 75% in the visible region (400-700 nm), which is suitable for solar cells applications. The transmittance of In$_2$S$_3$ films after heat treatment increases in 10%, which is due to the reduction of film thicknesses during the heat treatment. The absorption coefficient ($\alpha$) was calculated by the relation: $T=(1-R)^2\exp(-ad)$, where $T$ is the transmittance, $R$ the reflectance and $d$ the film thickness. The absorption coefficient was used to determine the bandgap ($E_g$) for each film using the direct bandgap semiconductor relation $\alpha h\nu=(h\nu-E_g)^{1/2}$, where $h\nu$ is the photon energy. Fig 5 shows the graphic of $(\alpha h\nu)^2$ vs $h\nu$, $E_g$ was calculated by fitting the lineal part of the curve. Bandgap values, before and after of the heat treatment, are displayed in Table 2. The In$_2$S$_3$-60°C as-grown sample
has a bandgap value of 2.27 eV. The In$_2$S$_3$-70°C and In$_2$S$_3$-80°C as-grown samples have an $E_g$ of 2.71 eV and 2.32 eV, respectively. The $E_g$ value of In$_2$S$_3$ annealed films increases about 8%, this increase in the $E_g$ may be due to change in the crystallite size [14].

Fig. 4 Transmittance spectra of In$_2$S$_3$ films deposited by CBD at different temperatures; 60 °C, 70 °C and 80 °C.

![Transmittance spectra](image)

Fig. 5. Bandgap calculations for In$_2$S$_3$ films grown by CBD at different temperatures.

![Bandgap calculations](image)

Fig. 6 shows the PL at room temperature of In$_2$S$_3$ films grown by CBD at different temperatures. In$_2$S$_3$ as-grown films have two emissions at 2.38 eV (high intensity) and 2.90 eV (low intensity), see Fig. 6. The green luminescence at 2.38 eV may be an emission from the indium interstitial sites, whereas the signal at 2.90 eV can be attributed to the presence of several deep trap states or defects in the In$_2$S$_3$ structure [12]. The PL of In$_2$S$_3$ films with annealing are shown in Fig. 6b). Observe that the signal at 2.90 eV attributed to defects disappears. After the annealing the PL spectra present two peaks at 1.74 eV (red emission) and the green emission...
centered in 2.35 eV. The red emission is attributed to Donor-Acceptor Pair (DAP) recombination [15].

![Photoluminescence spectra at room temperature of In$_2$S$_3$ thin films grown at different temperatures: 60 °C, 70 °C and 80 °C.]

Fig. 6. Photoluminescence spectra at room temperature of In$_2$S$_3$ thin films grown at different temperatures: 60 °C, 70 °C and 80 °C.

4. Conclusions

In$_2$S$_3$ thin films by chemical bath deposition at different temperatures were obtained. The structural and optical properties were analyzed as a function of growth temperature. The structural characterization (XRD and Raman) showed that In$_2$S$_3$ films have tetragonal phase ($\beta$-In$_2$S$_3$). The XRD showed that for a growth temperature of 60 °C the best polycrystalline quality was obtained, when the growth temperature increases the crystalline quality degrades. In$_2$S$_3$ films has high transmittance; between 60% and 75% which is suitable for photovoltaic applications. The structural and morphology analysis showed that the annealing in nitrogen produces a crystalline coalescence of grains which reduces the rms roughness of In$_2$S$_3$ thin films. The optical bandgap increases after the annealing, which is due to change of crystallite size produced during the thermal treatment. The PL signal attributed to defects disappears after the thermal treatment, which indicates an improvement in the crystalline quality of In$_2$S$_3$ thin films grown by chemical bath deposition.

Acknowledgments

We acknowledge the technical support of Marcela Guerrero, A. Garcia-Sotelo, Rogelio Fragoso, Zacarias Rivera (from the Physics Department, CINVESTAV-IPN), Benito Ortega and the partial support by SEP-PRODEP DSA/103.5/15/6976.

The authors acknowledge financial support for this work from FONDO SECTORIAL CONACYT-SENER-SUSTENTABILIDAD ENERGÉTICA through CeMIE-sol, within of the strategic project number 37; “Development of new photovoltaic devices and semi-superconductor materials”.
References