STRUCTURAL AND OPTICAL PROPERTIES OF In$_2$S$_3$ THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION ON PET FLEXIBLE SUBSTRATES

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Indium sulfide thin films were grown onto flexible PET-substrates by chemical bath deposition. Indium trichloride and thioacetamide were used as precursor solutions of indium and sulfur, respectively. Growth temperatures were 60°C, 70°C, 80°C and 90°C. The optical measurements showed films had a maximum transmittance of 85% in the visible region. Energy band gap varied in the range 2.32–2.83 eV. Structural properties were analyzed by Transmission Electron Microscopy and Raman Spectroscopy, which indicates that In$_2$S$_3$ thin films grown on flexible PET-substrates have tetragonal phase.

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1. Introduction

Over the last years, flexible substrates have demonstrated a great potential to be used in flexible solar cells, flexible displays and flexible organic light-emitting diodes fabrication [1,2]. Particularly, polyethylene terephthalate (PET) substrate has been used for photovoltaic devices because it provides higher electrical conductivity, transmittance in the visible range, low cost and good flexibility with light weight [2,3].

Indium sulfide (In$_2$S$_3$) is a semiconductor compound which has photovoltaic applications due to its transparency, transmittance, structure and band gap of 2.3 eV – 2.7 eV [4-7]. In$_2$S$_3$ has three sort of crystallographic phases: cubic phase ($\alpha$), tetragonal phase ($\beta$) and hexagonal phase ($\gamma$). $\beta$-In$_2$S$_3$ phase is the stable structure at room temperature [4, 8,9]. As it is more environmentally friendly and the wide band gap, In$_2$S$_3$ can be used as substitute in thin film solar cells of cadmium sulfide having a bandgap of 2.4 eV [10-14]. In$_2$S$_3$ thin films can be prepared trough different methods, however chemical bath deposition (CBD) is interesting as it requires simple and cheap technology, further it is an easily scalable technique [4,9,12,15].

In this work, In$_2$S$_3$ thin films were grown on PET substrates by chemical bath deposition to prepared non-toxic photovoltaic devices, physical properties of In$_2$S$_3$ films were examined as function of temperature.

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2. Experimental details

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

Indium sulfide films were grown on PET/ITO substrates with a size of 2.0 x 2.5 cm$^2$ by CBD at different temperatures. Indium trichloride (InCl$_3$) 0.025 M and thiocetamide (CH$_3$CSNH$_2$) 0.075 M were used as indium and sulfur precursors, respectively. Acetic acid was used as the complexing agent, which controls pH values between 2 and 3.

The substrates were vertically immersed in the aqueous solution bath mounted on a heating magnetic agitator which controls temperature and homogeneity of the solution. In$_2$S$_3$ thin films were grown at bath temperatures of: 60°C, 70 °C, 80 °C and 90°C and at a constant deposition time of 120 minutes. After deposition, thin films were washed with deionizer water in ultrasonic bath for 5 minutes.

2.2 Characterization of films

The structural characterization was obtained with High Resolution Transmission Electron Microscopy (HR-TEM) using a JEOL JEM2010 microscope with a lanthanum hexaboride filament at an acceleration voltage of 200 kV. Raman spectroscopy was carried out in a Labram Dilor micro-Raman system, employing a HeNe laser (632.8 nm) as excitation source. An UV-Vis Perkin Elmer Lambda 25 spectrophotometer was used to obtain the optical transmittance spectra. Finally, film thickness was measured with a KLA Tencor D-100 profilometer.

3. Results and discussion

3.1 HR-TEM analysis

HR-TEM micrographs of In$_2$S$_3$ films grown at different temperatures by CBD are shown in Fig. 1. The fringes appearing in the micrographs allow the identification of the interplanar distance, which corresponding to four crystallographic planes of In$_2$S$_3$ crystals with tetragonal phase and the orientations observed are (2113), (204), (0012), (217) and (2212). This suggested that In$_2$S$_3$ thin films grown by CBD on PET substrates have the In$_2$S$_3$ tetragonal phase ($\beta$-In$_2$S$_3$).

![HR-TEM images of In$_2$S$_3$ films deposited by CBD for 120 minutes, using acid acetic as complexing agent: (a) 60°C, (b) 70°C, (c) 80°C and (d) 90°C.](image)

3.2 Raman spectroscopy

The Raman spectra of In$_2$S$_3$ films grown by CBD at different temperatures are in Fig. 2. In$_2$S$_3$ films have four Raman peaks at 113 cm$^{-1}$, 137 cm$^{-1}$, 180 cm$^{-1}$ and 199 cm$^{-1}$, these signals correspond to tetragonal phase of the In$_2$S$_3$ ($\beta$-In$_2$S$_3$) [16,17] in agreement with the HR-TEM results; In$_2$S$_3$ films grown by CBD on PET substrates have tetragonal phase ($\beta$-In$_2$S$_3$). Raman peaks at 137 cm$^{-1}$, 180 cm$^{-1}$ and 199 cm$^{-1}$ are well defined with the peak localized at 137 cm$^{-1}$ having the strongest intensity. In order to evaluate the crystalline quality of In$_2$S$_3$ films, the Full Width at Half Maximum (FWHM) of Raman peak at 137 cm$^{-1}$ was analyzed. The FWHM of In$_2$S$_3$ films grown at different temperatures are displayed in Table 1. Observe the tendency of FWHM
values suggesting the increase in the growth temperature improves the crystalline quality of In$_2$S$_3$ films.

![Raman spectra](image)

**Fig. 2.** Raman spectra of In$_2$S$_3$ thin films grown by CBD at 60°C, 70°C, 80°C and 90°C.

### 3.3 Optical properties

The optical transmittance of indium sulfide films grown at different temperatures by CBD is shown in Fig. 3. In$_2$S$_3$ films have high transmittance in the visible range of electromagnetic spectrum (400-700 nm). The In$_2$S$_3$-90°C and In$_2$S$_3$-70°C have a transmittance between 60% and 85%, which is suitable for solar cells. The film thicknesses are compiled in Table 1. In$_2$S$_3$ films grown at 70 °C and 90 °C; have 253 nm and 246 nm in thickness, respectively. This suggests that In$_2$S$_3$ films grown at 90 °C have better crystalline quality [18], it is important to mention they have a high transmittance in spite of the thickness.

![Optical transmission spectra](image)

**Fig. 3.** Optical transmission spectra of In$_2$S$_3$ thin films deposited on PET by CBD at different temperatures.

The optical absorption coefficient ($\alpha$) was calculated from transmittance spectrum with the formula: \( T = \exp(-\alpha d) \), where \( d \) is the film thickness and \( T \) is the optical transmittance. The energy bandgap (\( E_g \)) was determined using the relation: \( (\alpha h\nu)^2 = A(h\nu-E_g) \), where \( A \) is a constant depending on the transition probability and \( h\nu \) is the photon energy. Fig. 4 shows the graphic of \((\alpha h\nu)^2\) vs \( h\nu \), the band gap (\( E_g \)) value was calculated by fitting the lineal part of the curve with the abscises axis. The direct band gap varies from 2.32 to 2.83 eV. The \( E_g \) values are shown in Table 1. The bandgap of the In$_2$S$_3$-60°C sample has a value of 2.32 eV, the \( E_g \) increases to 2.74 eV for a growth temperature of 70 °C whereas for a growth temperature of 80 °C the \( E_g \) decreases to 2.53 eV and finally the In$_2$S$_3$- 90°C sample has a band gap of 2.83 eV. It is important to mention that when using a buffer layer with a wide band gap can improve the conversion efficiency of a solar cell.
Fig. 4. Bandgap calculations for In$_2$S$_3$ thin films deposited on PET by CBD at different temperatures.

The PL at room temperature of In$_2$S$_3$ films and PET/ITO substrate are shown in the Fig. 5. In$_2$S$_3$ films present two emissions signals one centered between 2.38-2.52 eV and the other at 3.0 eV. The green luminescence (2.38-2.52 eV) may be an emission from the indium interstitial sites [19]. The PET/ITO substrate has a blue emission at 3.0 eV. The signal at ~3.0 eV in the In$_2$S$_3$ samples is red-shifted with respect to the emission from the substrate; the In$_2$S$_3$-60°C sample has the emission at 2.99 eV, for the In$_2$S$_3$-70°C the signal centered at 2.97 eV and, for the In$_2$S$_3$-80°C and In$_2$S$_3$-90°C samples at 2.94 and 2.92 eV, respectively. The blue emission can be attributed to the presence of several deep trap states or defects in the In$_2$S$_3$ structure [19].

Fig. 5. PL spectra of In$_2$S$_3$ thin films grown by CBD on flexible PET-substrates. Note the strong green and blue signals.

Table 1. Growth parameters, FWHM of the Raman peak at 137 cm$^{-1}$, thickness and band gap ($E_g$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth temperature (°C)</th>
<th>FWHM$_{137}$ (cm$^{-1}$)</th>
<th>Thickness (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$S$_3$-60°C</td>
<td>60</td>
<td>3.23</td>
<td>139 nm</td>
<td>2.32</td>
</tr>
<tr>
<td>In$_2$S$_3$-70°C</td>
<td>70</td>
<td>3.00</td>
<td>253 nm</td>
<td>2.74</td>
</tr>
<tr>
<td>In$_2$S$_3$-80°C</td>
<td>80</td>
<td>3.00</td>
<td>228 nm</td>
<td>2.53</td>
</tr>
<tr>
<td>In$_2$S$_3$-90°C</td>
<td>90</td>
<td>3.09</td>
<td>246 nm</td>
<td>2.83</td>
</tr>
</tbody>
</table>

4. Conclusions

In$_2$S$_3$ thin films were deposited on PET substrates by chemical bath deposition at different temperatures; 60 °C, 70 °C, 80 °C and 90 °C. TEM analysis and Raman spectra indicates that In$_2$S$_3$ films have tetragonal phase ($\beta$-In$_2$S$_3$). The In$_2$S$_3$ films grown at 70 °C and 90 °C have the highest transmittance in the visible region; between 65% and 85%. The maximum band gap corresponds
to the sample grown at 90 °C and was 2.83 eV. This make In$_2$S$_3$ films grown by chemical bath deposition at 90 °C potentially reliable for flexible photovoltaic applications.

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