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Indium sulfide thin films as window layer in chemically deposited solar cells

S. Lugo-Loredo [a,1], Y. Peña-Méndez [a,*,1], M. Calixto-Rodriguez [b], S. Messina-Fernández [c], A. Alvarez-Gallegos [d], A. Vázquez-Dimas [a,1], T. Hernández-García [a,1]

[a] Universidad Autónoma de Nuevo León, UANL, Fac. de Ciencias Químicas, Av. Universidad S/N Ciudad Universitaria San Nicolás de Los Garza Nuevo León, C.P. 66451, Mexico
[b] Universidad Tecnológica Emiliano Zapata del Estado de Morelos, Av. Universidad Tecnológica No. 1, C.P. 62760 Emiliano Zapata, Morelos, Mexico
[c] Universidad Autónoma de Nayarit, Ciudad de la Cultura "Amado Nervo" S/N, C.P. 63190 Tepic, Nayarit, Mexico
[d] Universidad Autónoma del Estado de Morelos, Centro de Investigación en Ingeniería y Ciencias Aplicadas, Av. Universidad 1001, C.P. 62209, Cuernavaca Morelos, Mexico

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ABSTRACT

Indium sulfide (In_2S_3) thin films have been synthesized by chemical bath deposition technique onto glass substrates using $In(NO_3)_3$ as indium precursor and thioacetamide as sulfur source. X-ray diffraction studies have shown that the crystalline state of the as-prepared and the annealed films is β-In_2S_3. Optical band gap values between 2.27 and 2.41 eV were obtained for these films. The In_2S_3 thin films are photosensitive with an electrical conductivity value in the range of 10^{-3}–10^{-7} $(\Omega\ cm)^{-1}$, depending on the film preparation conditions. We have demonstrated that the In_2S_3 thin films obtained in this work are suitable candidates to be used as window layer in thin film solar cells. These films were integrated in SnO_2:F/In_2S_3/Sb_2S_3/PbS/C–Ag solar cell structures, which showed an open circuit voltage of 630 mV and a short circuit current density of 0.6 mA/cm^2.

1. Introduction

Many efforts have been done by several research groups in order to replace CdS buffer layer in thin film solar cells by using an alternative semiconductor with a wide band gap, mainly due to environmental reasons. Indium sulfide has been recognized as an alternative material due to their stability, transparency, photoconductive nature and because of the energy band gap that can be varied between 2 and 2.75 eV depending on its composition [1–6]. Several crystalline phases have been reported for the In_2S_3 thin films (α, β and γ) and it has been found that the most stable phase at room temperature is the β-tetragonal [6]. Polycrystalline In_2S_3 thin films have been used as window layer in In_2S_3/$CuInX_2$ (X = S or Se) solar cell structures [4].

Among the chemical methods used for the preparation of In_2S_3 thin films are metal–organic chemical vapor deposition [7], atomic layer deposition [8], thermal evaporation technique [9], modulated flux deposition [10], spray pyrolysis [11], electrodeposition [12], and chemical bath deposition (CBD) [1,13]. CBD has been recognized as the simplest and most economical method to obtain semiconductor thin films. In this work we report the deposition of In_2S_3 thin films using CBD and their application as window layers in thin film solar cells.

* Corresponding author at: Facultad de Ciencias Químicas-UANL, C.P. 66451, Mexico. Tel.: +52 8183294000x6363; fax: +52 8183765375.
E-mail address: yolapm@gmail.com (Y. Peña-Méndez).
[1] Tel.: +81 83294000x6363

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2. Experimental details

2.1. In_2S_3 window layer

The deposition of the indium sulfide thin films was done on Corning glass substrates (2.5 cm x 7.5 cm x 0.1 cm). The substrates were previously washed out with a soapy solution, then rinsed with distilled water and dried in flowing air. For depositing the indium sulfide thin films, an acidic chemical bath solution composed of $In(NO_3)_3$ 0.01 M, CH_3COOH 2×10^{-3} M and CH_3CSNH_2 0.16 M at a pH of 2.60 was used. Normally, the addition of CH_3COOH is used to reduce the pH value of the bath and to promote the hydrolysis of thioacetamide [14]. The substrates were vertically placed into the beaker. The chemical reaction was carried out at 35 °C, and the deposition time was varied from 12 to 39 h.

2.2. Thermal treatments

The indium sulfide thin films were annealed in a Thermolyne 21100 tubular furnace at temperatures of 350 and 400 °C for 1 h under a stream of N_2 flowing through the tube.

2.3. Solar cell structures

The structure of the proposed solar cell is similar to that reported previously in Ref. [15], however, in the present work we have substituted the CdS layer by our In_2S_3 window layer. The Sb_2S_3 thin film

(200 nm) was deposited onto the In_2S_3 thin film previously deposited on 3 mm glass substrates coated with SnO_2:F, a transparent conductive oxide (TEC-15 by Pilkington). The SnO_2:F/In_2S_3/Sb_2S_3 structure was subsequently heated in N_2 flow at 350 °C for 0.5 h. After that a PbS thin film (200 nm) was deposited as p^+ absorber, as suggested in Ref. [16]. Then graphite paint was applied on the PbS film and finally, a silver paint electrode was applied to be used as p-side contact.

3. Characterization of the In_2S_3 thin films

X-ray diffraction (XRD) analysis was performed on a Rigaku D-Max 2000 X-ray diffractometer using Cu-K_α radiation ($\lambda = 1.5406$ Å) in the grazing incidence mode at $\Omega = 1.5°$. The optical transmittance response was measured in a Shimadzu 1800 UV–Vis spectrophotometer in the wavelength range of 250–1100 nm using air as reference. Photocurrent response of the films was obtained using a tungsten–halogen lamp and a Keithley 6487 multimeter. Morphology of the films was studied by atomic force microscopy (AFM) using an AA3000 atomic force microscope from Angstrom Advanced, the measurements were performed in the contact mode. Field emission scanning electron microscopy (FE-SEM) images of the In_2S_3 thin films were obtained using a FE-SEM JEOL JSM 6701F microscope, the operating voltage was 2–3 kV.

4. Results and discussion

It was found that the In_2S_3 thin films chemically deposited for 12 h have a thickness of 85 nm and those deposited for 39 h have a thickness of ~500 nm.

4.1. Structural properties of In_2S_3 thin films

Fig. 1 shows the XRD patterns of the In_2S_3 thin films (500 nm) recorded at a grazing incidence angle of 1.5° for the as-prepared and annealed samples at 350 and 400 °C for 1 h in N_2. The XRD patterns match well with that of the standard pattern of the tetragonal phase β-In_2S_3 (PDF 25-0390). The as-prepared films showed a polycrystalline nature, and after the annealing treatment at 400 °C a little improvement of the films crystallinity was observed. The standard pattern for β-In_2S_3 (PDF 25-0390) is given in Fig. 1 for comparison.

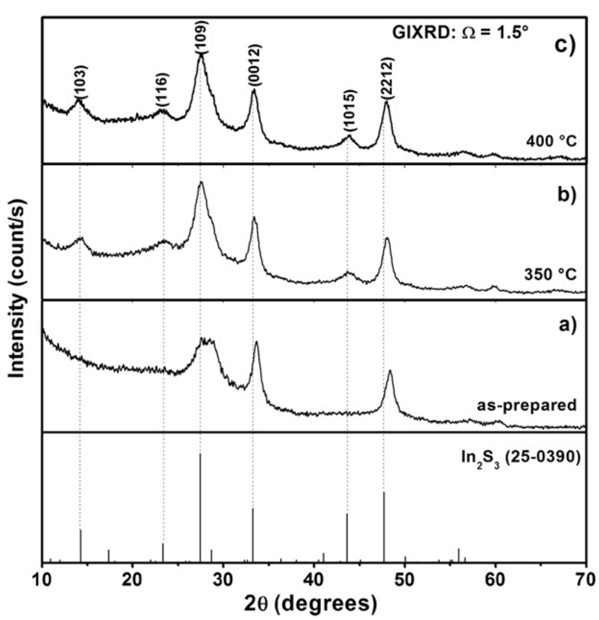

Fig. 1. X-ray diffraction patterns of In_2S_3 thin films with 39 h of deposition, a) as-prepared, b) annealed at 350 °C, and c) annealed at 400 °C in N_2 atmosphere for 1 h.

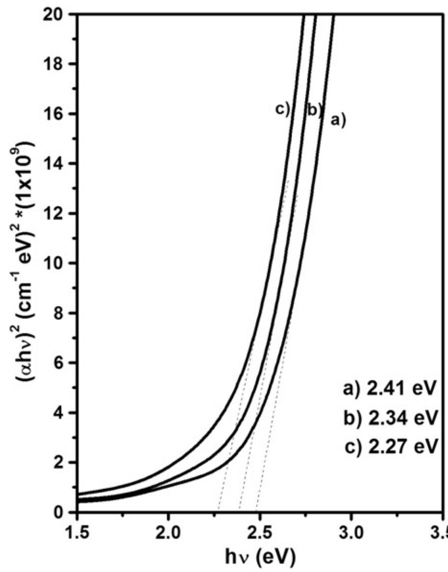

Fig. 2. Energy band gap values for the In_2S_3 thin films with 39 h of deposition, a) as-prepared, b) annealed at 350 °C, and c) annealed at 400 °C in N_2 for 1 h.

4.2. Optical properties of In_2S_3 thin films

The band gap (E_g) values were calculated from the optical transmittance spectra results considering that the absorption coefficient (α) is a function of the photon energy ($h\nu$) using the following equation [17]:

$$\alpha = (1/d)ln(100/\%T)$$

where d is the thickness of the film and T the optical transmittance.

The E_g value was determined by extrapolating the linear part of the plot $(\alpha h\nu)^2$ vs. $(h\nu)$ in the abscissa (axis x), which indicates a direct optical transition. The $(\alpha h\nu)^2$ vs. $(h\nu)$ plots are shown in Fig. 2 for as-prepared and annealed β-In_2S_3 films (500 nm). For these β-In_2S_3 samples the calculated band gap values were 2.41, 2.34 and 2.27 eV for the as-prepared, annealed at 350 °C, and 400 °C, respectively. These values are in agreement with those reported in the literature for this material [1]. We observed a decrease in the E_g value when the annealing temperature increases, which can be attributed to an increase in grain size.

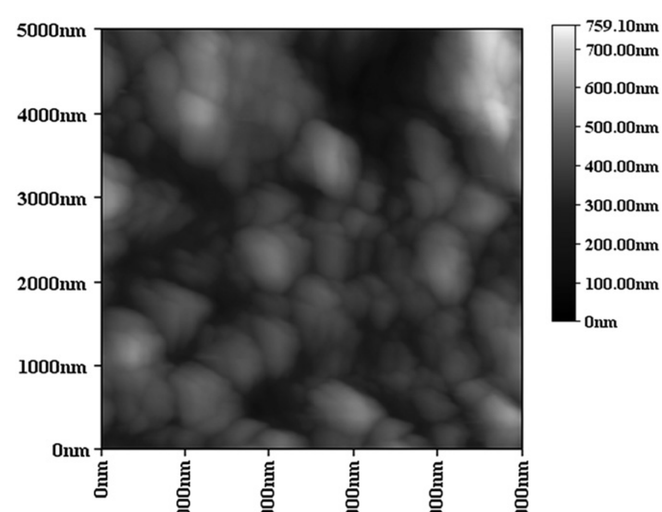

Fig. 3. AFM image of the β-In_2S_3 thin film with 39 h of deposition, after thermal treatment at 400 °C in N_2 atmosphere for 1 h.

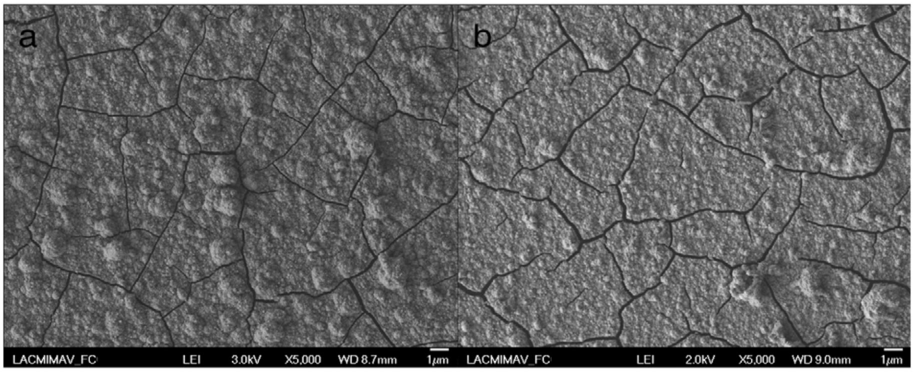

Fig. 4. FE-SEM images of β-In_2S_3 thin films with 39 h of deposition, a) before and b) after thermal treatment at 350 °C in N_2 atmosphere for 1 h.

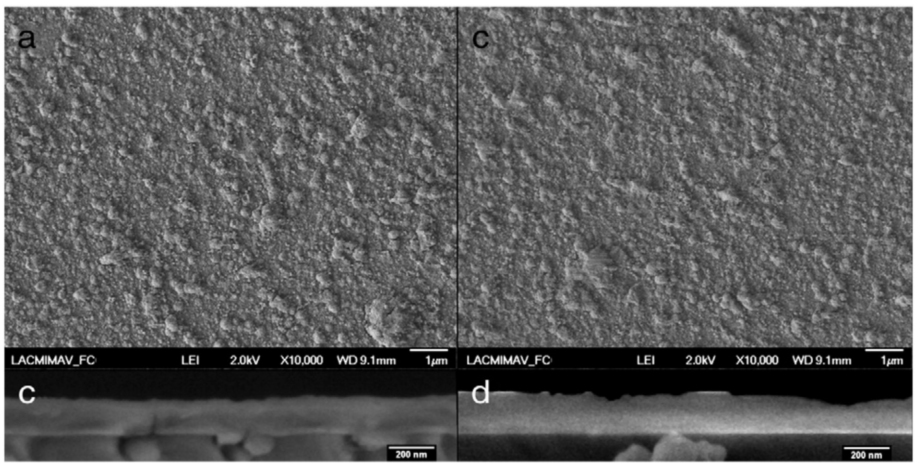

Fig. 5. FE-SEM images for In_2S_3 thin films with 16 h of deposition, a) top and b) cross-section views of the as-prepared films; and c) top and d) cross-section views of the films after thermal treatment at 350 °C in N_2 atmosphere for 1 h.

4.3. Morphological properties of In_2S_3 thin films

Fig. 3 shows a 2D AFM image for the β-In_2S_3 thin film with an average thickness of 500 nm after the annealing treatment at 400 °C in N_2. The morphology of the film surface shows grain sizes from <100 nm up to 800 nm. On the other hand, FE-SEM images of In_2S_3 thin films (500 nm) revealed a cracked surface for the as-prepared and annealed samples at 350 °C (see Fig. 4).

Fig. 5a and b shows a representative FE-SEM image of the top and cross-section views of the as-prepared In_2S_3 films (165 nm). Fig. 5c and d corresponds to the In_2S_3 thin film annealed at 350 °C for 1 h in N_2 atmosphere. According to this figure, after the annealing process a slight difference in thickness (157 nm) is observed in the film, which can be due to shrinking. In this case, the film surface is homogeneous and crack-free. According to these results, the 157 nm In_2S_3 film shows suitable characteristics to be employed as window layer in thin-film solar cells.

4.4. Electrical properties of In_2S_3 thin films

The photocurrent response of as-prepared and annealed at 350 and 400 °C β-In_2S_3 thin films (500 nm) are shown in Fig. 6. Inset in Fig. 6 shows the photocurrent response of In_2S_3 film (150 nm) after the annealing process at 400 °C for 1 h in N_2 atmosphere. The electrical conductivities of the β-In_2S_3 thin films (500 nm) were 4.34×10^{-8} $(\Omega\ cm)^{-1}$ and 2.05×10^{-7} $(\Omega\ cm)^{-1}$ after annealing at 350 °C and 400 °C, respectively. In the case of In_2S_3 thin films with a thickness of 150 nm, an electrical conductivity value of 2.8×10^{-3} $(\Omega\ cm)^{-1}$ was obtained after performing the thermal annealing at 400 °C. This is a very important result since there are no electrical conductivity values reported in the literature for In_2S_3 thin films obtained by CBD.

4.5. J–V characteristics of the SnO_2:F/In_2S_3/Sb_2S_3/PbS/C–Ag photovoltaic structure

The current density (J) vs. voltage (V) characteristics of three solar cell structures are given in Fig. 7. The fabricated solar cells have the SnO_2:F/In_2S_3/Sb_2S_3(200 nm)/PbS(200 nm)/C–Ag structure, formed using an as-prepared In_2S_3 (Fig. 7a and b) and a thermally treated In_2S_3 thin-film at 350 °C in N_2 flow for 1 h (Fig. 7c). In the solar cell

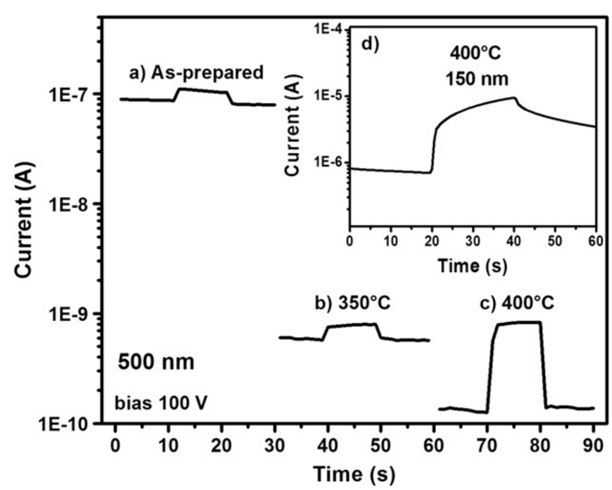

Fig. 6. Photoresponse of the β-In_2S_3 thin films with 39 h of deposition, a) as-prepared, b) annealed at 350 °C in N_2, and c) annealed at 400 °C in N_2. Inset d): photoresponse of the β-In_2S_3 thin film with 16 h of deposition after annealing at 400 °C.

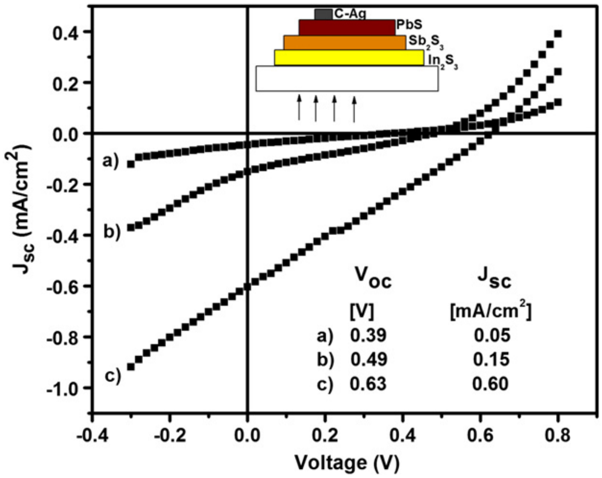

Fig. 7. J–V characteristics of the SnO_2:F/In_2S_3/Sb_2S_3/PbS/C–Ag photovoltaic structures using a) an as-prepared In_2S_3 layer with a thickness of 200 nm; b) an as-prepared In_2S_3 layer with a thickness of 165 nm; and c) an In_2S_3 layer with a thickness of 157 nm after thermal treatment at 350 °C in N_2.

structures of Fig. 7a and b we used two as-prepared In_2S_3 layers with thicknesses of 200 and 165 nm, respectively. While in the solar cell structure of Fig. 7c, we used an annealed In_2S_3 thin film with a thickness of 157 nm. The photovoltaic parameters obtained for these structures were: $V_{oc} = 390$ mV and $J_{sc} = 0.05$ mA/cm^2, $V_{oc} = 490$ mV and $J_{sc} = 0.15$ mA/cm^2, and $V_{oc} = 630$ mV and $J_{sc} = 0.60$ mA/cm^2 for Fig. 7a, b and c, respectively. According to these results, a thinner In_2S_3 layer produces better cell characteristics probably due to a wider band gap value.

The results showed in this work have demonstrated the feasibility of using In_2S_3 films as window layers in cadmium free thin film solar cells. However, the deposition conditions could be further optimized in order to improve the optoelectronic properties of In_2S_3 films, so that the J–V characteristics of the solar cells can also be improved.

5. Conclusions

It was shown that In_2S_3 thin films can be obtained by using CBD technique. XRD analysis confirmed that the films have a polycrystalline nature showing the β-In_2S_3 phase in both cases, the as-prepared and thermally treated films. The calculated band gap values for the In_2S_3 films are in the range of 2.27 to 2.41 eV, these values are in agreement with those reported in the literature for this material. The films are photosensitive with electrical conductivity values of ~10^{-3}–10^{-7} $(\Omega\ \mathrm{cm})^{-1}$, depending on the film preparation conditions. In this work, it has been shown that the In_2S_3 thin films obtained by CBD have optoelectronic properties suitable to be used as window layers in thin film solar cells. The best J–V results obtained for the SnO_2:F/β-In_2S_3/Sb_2S_3/PbS/C–Ag structure were $V_{oc} = 630$ mV and $J_{sc} = 0.6$ mA/cm^2, which corresponds to the 157 nm In_2S_3 thin film thermally treated at 350 °C. The results obtained in this work, for the Cd free solar cell structures are promising, however further work must be done in order to improve the optoelectronic properties of the In_2S_3 layers.

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