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

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Abstract
Indium sulfide (In2S3) thin films have been synthesized by chemical bath deposition technique onto glass substrates using In(NO3)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-In2S3. Optical band gap values between 2.27 and 2.41 eV were obtained for these films. The In2S3 thin films are photosensitive with an electrical conductivity value in the range of 10−2−10−7 (Ω cm)−1, depending on the film preparation conditions. We have demonstrated that the In2S3 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 SnO2:F/In2S3/Sb2S3/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/cm².

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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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS [1]. 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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS. Many attempts have been made 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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS [1]. 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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS [1]. Many attempts have been made 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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS. Many attempts have been made 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 their low cost. Indium sulfide is a metal-organic semiconductor, it has been used as a window layer in amorphous silicon solar cells, but after the development of a polycrystalline silicon material it was replaced by CdS.
(200 nm) was deposited onto the In$_2$S$_3$ 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$_2$S$_3$/Sb$_2$S$_3$ 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$_2$S$_3$ thin films

X-ray diffraction (XRD) analysis was performed on a Rigaku D-Max 2000 X-ray diffractometer using Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ Å) in the grazing incidence mode at $\omega = 1.5^\circ$. 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. Photo-current 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$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ thin films

Fig. 1 shows the XRD patterns of the In$_2$S$_3$ 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$_2$S$_3$ (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$_2$S$_3$ (PDF 25-0390) is given in Fig. 1 for comparison.

4.2. Optical properties of In$_2$S$_3$ thin films

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

$$\alpha = \left( \frac{1}{d} \ln \left( \frac{100}{T} \right) \right)$$

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

Fig. 2. Energy band gap values for the In$_2$S$_3$ 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.

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$_2$S$_3$ films (500 nm). For these β-In$_2$S$_3$ 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$_2$S$_3$ thin film with 39 h of deposition, after thermal treatment at 400 °C in N$_2$ atmosphere for 1 h.
4.3. Morphological properties of In$_2$S$_3$ thin films

Fig. 3 shows a 2D AFM image for the $\beta$-In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ films (165 nm). Fig. 5c and d corresponds to the In$_2$S$_3$ 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$_2$S$_3$ film shows suitable characteristics to be employed as window layer in thin-film solar cells.

4.4. Electrical properties of In$_2$S$_3$ thin films

The photocurrent response of as-prepared and annealed at 350 and 400 °C $\beta$-In$_2$S$_3$ thin films (500 nm) are shown in Fig. 6. Inset in Fig. 6 shows the photocurrent response of In$_2$S$_3$ film (150 nm) after the annealing process at 400 °C for 1 h in N$_2$ atmosphere. The electrical conductivities of the $\beta$-In$_2$S$_3$ thin films (500 nm) were $4.34 \times 10^{-8}$ (Ω cm)$^{-1}$ and $2.05 \times 10^{-7}$ (Ω cm)$^{-1}$ after annealing at 350 °C and 400 °C, respectively. In the case of In$_2$S$_3$ thin films with a thickness of 150 nm, an electrical conductivity value of $2.8 \times 10^{-3}$ (Ω 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$_2$S$_3$ thin films obtained by CBD.

4.5. J–V characteristics of the SnO$_2$:F/In$_2$S$_3$/Sb$_2$S$_3$/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$_2$S$_3$/Sb$_2$S$_3$(200 nm)/PbS(200 nm)/C–Ag structure, formed using an as-prepared In$_2$S$_3$ (Fig. 7a and b) and a thermally treated In$_2$S$_3$ thin-film at 350 °C in N$_2$ flow for 1 h (Fig. 7c). In the solar cell...
structures of Fig. 7a and b we used two as-prepared In$_2$S$_3$ layers with thicknesses of 200 and 165 nm, respectively. While in the solar cell structure of Fig. 7c, we used an annealed In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ 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 the In$_2$S$_3$ layers.

5. Conclusions

It was shown that In$_2$S$_3$ thin films can be obtained by using CBD technique. XRD analysis confirmed that the films have a polycrystalline nature showing the $\beta$-In$_2$S$_3$ phase in both cases, the as-prepared and thermally treated films. The calculated band gap values for the In$_2$S$_3$ 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 $10^{-3}$–$10^{-7}$ (Ω cm)$^{-1}$, depending on the film preparation conditions. In this work, it has been shown that the In$_2$S$_3$ 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/$\beta$-In$_2$S$_3$/Sb$_2$S$_3$/PbS/C–Ag structure were $V_{oc} = 630$ mV and $J_{sc} = 0.6$ mA/cm$^2$, which corresponds to the 157 nm In$_2$S$_3$ 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$_2$S$_3$ layers.

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