



Characterization of CuInS₂ thin films prepared by chemical bath deposition and their implementation in a solar cell

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ABSTRACT

CuInS₂ thin films were formed by the sequential deposition of In₂S₃–CuS layers on glass substrates, by chemical bath deposition technique, and heating these multilayer 1 h at 350 °C and 400 mPa. The morphology and thickness of the CuInS₂ thin films were analysed by scanning electron microscopy, showing particles with elongated shape and length about 40 nm, and thickness of 267 and 348 nm for samples from 15 and 24 h of deposition time in the chemical bath of In₂S₃, respectively. The energy band gap values of the films were around 1.4 eV, whereas the electrical conductivity showed values from 64.91 to $4.11 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for the samples of 15 and 24 h of In₂S₃ deposition bath, respectively. The obtained CuInS₂ films showed appropriate values for their application as an absorbing layer in photovoltaic structures of the type: glass/SnO₂:F/CdS/Sb₂S₃/CuInS₂/PbS/C/Ag. The whole structure was obtained through chemical bath deposition technique. The solar cell corresponding to 15 h of In₂S₃ deposition duration bath showed energy-conversion efficiency (η) of 0.53% with open circuit voltage (V_{oc}) of 530 mV, short circuit current density (J_{sc}) of 2.43 mA cm^{-2} , and fill factor (FF) of 0.41. In the case of the structure with 24 h of deposition of In₂S₃ bath, $\eta = 0.43\%$ was measured with the following parameters: $V_{oc} = 330 \text{ mV}$, $J_{sc} = 4.78 \text{ mA cm}^{-2}$ and $FF = 0.27$.

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1. Introduction

I–III–VI₂ ternary semiconductor compounds have been of great interest because of their potential application in the field of solar cells, light emitting devices, pigments, etc. [1]. Among the most studied of these semiconductor materials are CuInSe₂ [2], CuInS₂ [3] and AgInS₂ [4,5], because they are promising materials for photovoltaic applications, due to their suitable electrical and optical properties [6]. CuInS₂ films offer great advantages such as energy band gap (E_g) close to 1.5 eV at room temperature (in the optimal response zone for terrestrial photovoltaic conversion), high optical absorption coefficient in the visible region (10^5 cm^{-1}), high thermal and electrical stabilities [7,8], high energy conversion efficiency in photovoltaic structures and low cost in the large area production [9]. This material has been applied in a solar cell prototype by Chen et al. [10]; the thin films of CuInS₂ were prepared by the deposition of Cu–In nanoparticles synthesized by a polyol method and chalcogenisation. The thin films were incorporated in the solar cell structure of the type: Mo/CuInS₂/CdS/(i)-ZnO/SnO₂:In/Ag showing the following values: open circuit voltage (V_{oc}) of 0.37 V, short circuit current density (J_{sc}) of 6 mA cm^{-2} , fill factor (FF) of 0.30 and energy-conversion

efficiency (η) of 0.7%. Similarly, Nguyen et al. [11] used CuInS₂ films as absorber layers, prepared by spray pyrolysis method, incorporated in structures of the type: glass/SnO₂:F/TiO₂/In₂S₃/CuInS₂/C, with: $V_{oc} = 0.50 \text{ V}$, $J_{sc} = 10.36 \text{ mA cm}^{-2}$, $FF = 0.44$ and η of 2.35%. Maier et al. [12] deposited the poly(3-(ethyl-4-butanoate)thiophene)/CuInS₂:Zn nanocomposite on SnO₂:In by spin-coating followed by thermal treatment at 180 °C, with the following results: $V_{oc} = 0.66 \text{ V}$, $J_{sc} = 1.4 \text{ mA cm}^{-2}$, $FF = 0.27$ and η of 0.4%. In the same way, Sandino et al. [13] fabricated a solar cell of the type: glass/Mo/CuInS₂/ZnS/ZnO/Al depositing CuInS₂ films by co-evaporation and ZnS by chemical bath deposition (CBD); this solar cell showed an energy conversion efficiency of 5.4%. Other research groups have reported energy conversion efficiencies up to 12.5% [14], 11.4% [15] and 9.5% [16] with ternary material CuInS₂ as an absorbing layer. Thin films prepared by chemical methods are generally less expensive than those prepared by the capital-intensive physical techniques [17]. The CBD method as technique for the preparation of thin films has many advantages, which includes low cost of the required equipment and operation, simplicity, low energy consumption, and easily scalable to large area applications [18]. Up-to-date, CBD method has been widely used to deposit many different semiconductors thin films [17].

In this paper we reported the formation and characterization of thin films of CuInS₂ through the solid state reaction of In₂S₃–CuS stack films, heated at 350 °C during 1 h and their integration as an absorber layer in thin film solar cells, all prepared by CBD technique.

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2. Materials and methods

2.1. Chemical bath deposition of CuInS_2 thin films

The films were deposited on Corning glass substrates with the dimensions $2.5 \text{ cm} \times 7.5 \text{ cm} \times 0.1 \text{ cm}$.

In a first step an In_2S_3 layer was deposited by mixing the chemical reagents: 1.0 mol/L $\text{C}_2\text{H}_5\text{NS}$ (thioacetamide, 99.8%, Fisher Chemicals), 0.1 mol/L $\text{In}(\text{NO}_3)_3$ (indium(III) nitrate, 99.99%, Alfa Aesar) and 0.1 mol/L CH_3COOH (acetic acid, CTR Scientific, 99.9%). The film deposition occurs after 15 h up to 24 h at 35°C [19].

In a second step, solution grown CuS was deposited on the previously obtained In_2S_3 layer. The chemical bath was composed of CuCl_2 (copper (II) chloride, 99%, Fisher Chemicals), $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, 99.7%, Fermont) and $\text{C}_3\text{H}_8\text{N}_2\text{S}$ (1,3-dimethyl-2-thiourea, 99%, Aldrich), under the conditions reported previously [20].

The thin films obtained by this method are reported to be amorphous. To promote reaction between In_2S_3 and CuS as well as crystallization to a CuInS_2 thin film a thermal treatment was applied in a vacuum oven (T-M Vacuum Products, model V/IG-803-14) at 350°C and 400 mPa for 1 h.

2.2. Fabrication of the thin film solar cells

The cells were prepared in the superstrate configuration. We used transparent $\text{SnO}_2:\text{F}$ (FTO) coated glass as substrate. The FTO substrate was previously washed with soap and rinsed with deionized water, and then further cleaned by sonication in acetone and ethanol for 10 min in each solvent.

Substrates were coated with a CdS layer as an n-type window material and a thin film of Sb_2S_3 as an intrinsic material. CdS deposition was carried out according to the conditions reported previously by Nair et al. [21].

The CBD of Sb_2S_3 was performed according the method reported by Nair et al. [22] at 10°C for 2 h. After deposition, the Sb_2S_3 layer was heat treated in N_2 atmosphere at 300°C for 1 h.

CuInS_2 thin films were prepared through the thermal annealing at 350°C during 1 h of the stack films of 15 and 24 h of In_2S_3 bath and CuS 2.5 h, which were integrated as an absorbing layer in the development of the all chemically deposited solar cell.

Finally, a thin film of PbS , was deposited as a p^+ layer, which was prepared using the method reported by Moreno-García et al. [23]. The chemical bath for the PbS films was maintained at 40°C for 1 h. The final structure of the solar cell was: glass/ $\text{SnO}_2:\text{F}/(\text{n})\text{CdS}/(\text{i})\text{Sb}_2\text{S}_3/(\text{p})\text{CuInS}_2/(\text{p}^+)\text{PbS}$; the structure was completed with graphite and silver paint on the top layer (PbS) as electrodes.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected with a Rigaku diffractometer (model D-max 2000) at glancing incidence, angle of $\theta = 0.5^\circ$ using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ nm}$). Optical properties were measured in a spectrophotometer Shimadzu (model UV-1800).

Electrical conductivity of the samples was determined using a picoammeter/voltage source Keithley (model 6487); pairs of silver paint electrodes with an area of 1 cm^2 each (1 cm separation between them) were printed on the surface of the films for the photocurrent measurements under a tungsten-halogen lamp providing an illumination of 850 W m^{-2} ; a bias voltage of 10 V was applied. With these data, and knowing the thickness of the films, conductivities were evaluated.

The morphology of CuInS_2 films was determined by scanning electron microscopy (SEM) using a field-emission scanning electron microscope JEOL (model JSM 5800LV), operating at 1 kV ($25\,000\times$) and 3 kV ($100\,000\times$ and $200\,000\times$). Atomic force microscopy (AFM) images of the CuInS_2 films were obtained on a scanning probe microscope Angstrom Advance (model AA3000) in the contact mode.

The current–voltage (I – V) characterization was performed using a picoammeter/voltage source Keithley (model 6487) connected to a computer with a RS-232 interface. The applied voltage was varied from -0.3 to 0.8 V (20 mV step) collecting the current for each step, under both, dark and illumination conditions (1000 W m^{-2}) using a solar simulator Oriel (model 96000).

3. Results and discussion

3.1. CuInS_2 thin films

Fig. 1 shows the XRD patterns of the CuInS_2 films corresponding to 15 and 24 h of In_2S_3 bath and 2.5 h of CuS bath, followed by heat treatment at 350°C . These XRD patterns exhibit well solved peaks that correspond to the tetragonal chalcopyrite of CuInS_2 (JCPDS 27-0159), which confirms the complete formation of the CuInS_2 phase at 350°C . The solid state reaction between the In_2S_3 and CuS layers obtained by CBD is shown in the following equation:



The crystallite sizes were calculated to be around 12.8 nm and 61.2 nm corresponding to 15 h and 24 h of In_2S_3 bath, and 2.5 h of CuS bath, followed by heat treatment at 350°C and 400 mPa for 1 h by using the well-known Scherrer equation with the peak corresponding to the (112) plane.

The optical absorption coefficient (α) of the CuInS_2 thin films was calculated from the transmittance (%T) and reflectance (%R) spectra measurements, using Eq. (2) [24]:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2 + \sqrt{(1-R)^4 + (2RT)^2}}{2T} \right] \quad (2)$$

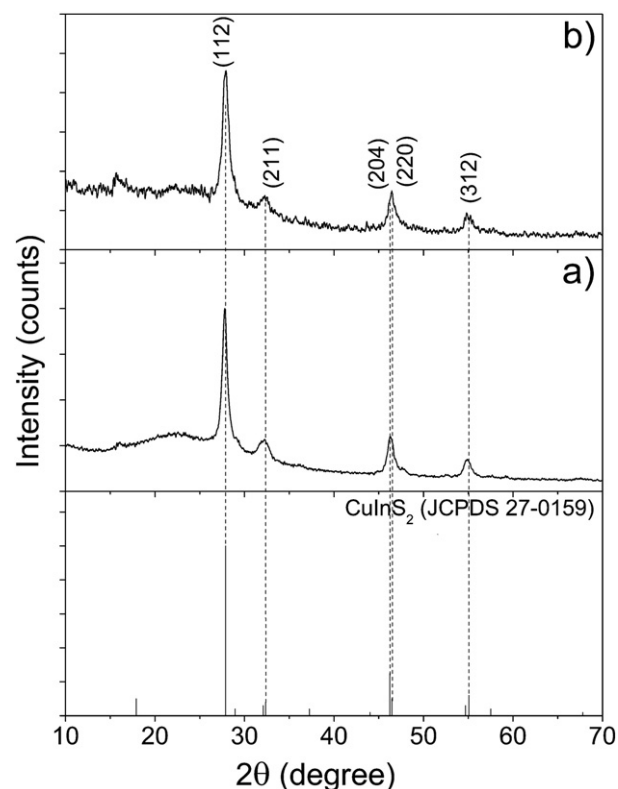


Fig. 1. XRD patterns of the CuInS_2 films corresponding to a) 15 h and b) 24 h of In_2S_3 bath, and 2.5 h of CuS bath, followed by heat treatment at 350°C and 400 mPa for 1 h.

Here, d is the thickness of the film. In semiconductors, α varies with $h\nu$ according to the empirical relation [25]:

$$\alpha = A \left(\frac{(h\nu - E_g)^m}{h\nu} \right) \quad (3)$$

where A is a constant and $m = 2$, for indirect transitions. E_g values were estimated by plotting $(\alpha h\nu)^2$ vs. $(h\nu)$, from the transmittance and reflectance values of CuInS₂ films. The plot of $(\alpha h\nu)^2$ vs $h\nu$ provide the value of E_g for each film, by extrapolating the straightest line to the $h\nu$ axis intercept, as shown in Fig. 2. The estimated E_g values of the CuInS₂ thin films are about 1.46 and 1.40 eV for 15 h and 24 h of In₂S₃ bath, respectively, which are in good agreement with the energy values reported for CuInS₂ thin films [26].

Fig. 3 shows typical AFM images of a) 15 and b) 24 h of In₂S₃ with 2.5 h CuS chemical baths, respectively after annealing at 350 °C and 400 mPa for 1 h; thin films deposited on soda lime glass substrates. It is observed that CuInS₂ thin films show a similar structure with crystallites that are uniformly distributed over the substrate surface. The grain size of CuInS₂ thin film deposited on glass substrates increases when the film thickness increases. The AFM measurements also revealed that thin film surface morphology of as-deposited CuInS₂ films varies with films thickness, which was corroborated by grain size calculations from X-ray diffraction measurements.

SEM images of the CuInS₂ thin films are shown in Fig. 4. In this figure, the morphology is formed by particles with elongated shape and length close to 40 nm. Thicknesses of these films were evaluated as 267 and 348 nm for 15 h and 24 h of In₂S₃ bath, respectively (Fig. 4b and c). From the thicknesses observed by cross-section, we can see that there is a correlation between time and deposit thickness, since the film of 24 h of In₂S₃ shows greater thickness (348 nm) compared to the sample of 15 h (267 nm).

The electrical conductivity of the CuInS₂ thin films was evaluated as 64.91 and $4.11 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ for 15 and 24 h of In₂S₃ bath, respectively. The 15 h thin films show higher conductivity compared to that

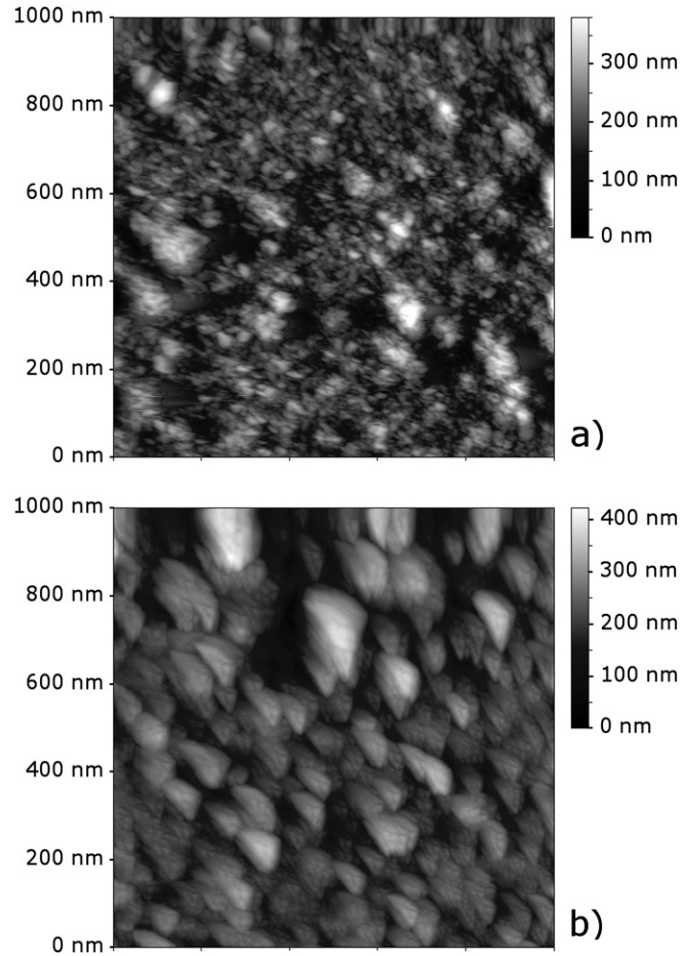


Fig. 3. AFM images of CuInS₂ films corresponding to a) 15 h and b) 24 h of In₂S₃ bath, with 2.5 h of CuS bath, followed by heat treatment in N₂ at 350 °C and 400 mPa for 1 h.

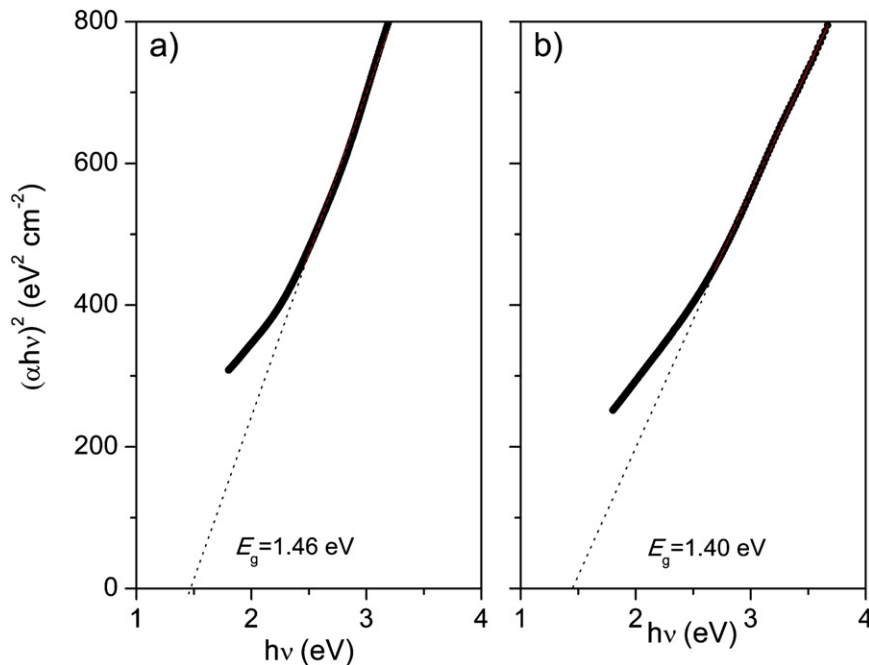


Fig. 2. Tauc's plots of CuInS₂ films corresponding to a) 15 h and b) 24 h of In₂S₃ bath, with 2.5 h of CuS bath, followed by heat treatment in N₂ at 350 °C and 400 mPa for 1 h.

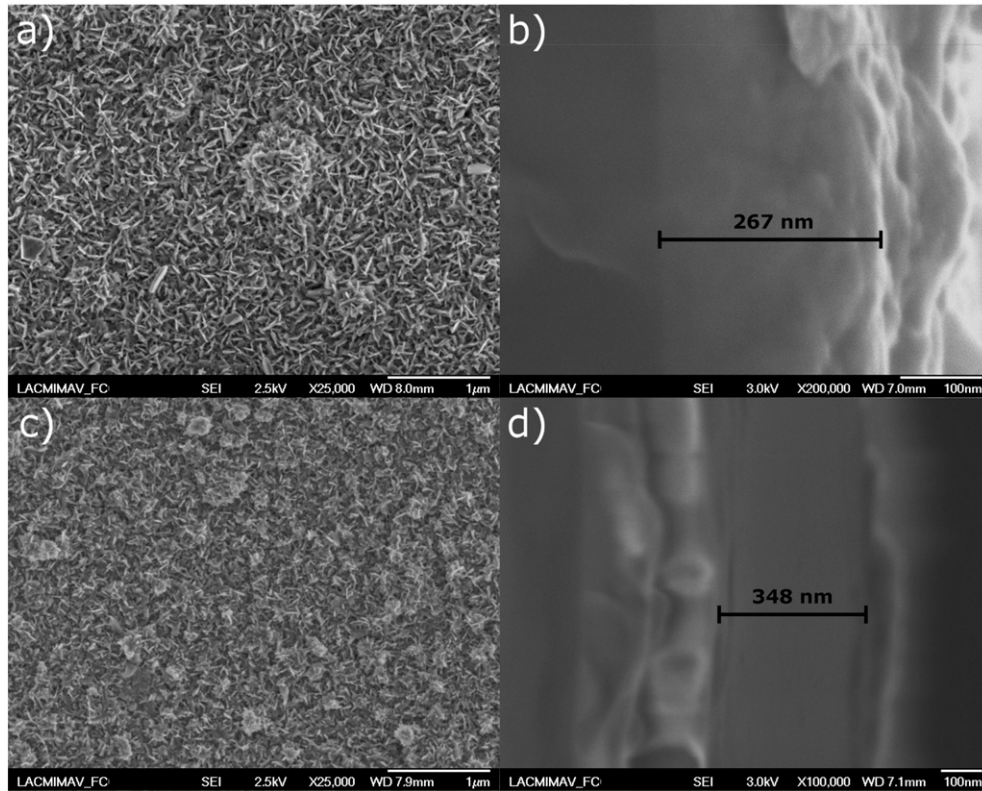


Fig. 4. SEM images of the CuInS_2 nanoparticles deposited for a) 15 h and c) 24 h of In_2S_3 bath, with 2.5 h of CuS bath, followed by heat treatment at 350°C and 400 mPa for 1 h; and the thickness of CuInS_2 films for b) 15 h and d) 24 h of In_2S_3 bath.

corresponding of 24 h; this can be due to the presence of the unreacted In_2S_3 layer material along with ternary layers of CuInS_2 . However by the X-ray diffraction analyses at angle incidence of 0.5° used in this work, peaks corresponding to the binary phase were no detected. The conductivity values indicate that these films are suitable for their application in solar cells, as an absorbing layer.

3.2. Formation of solar cell structures

The obtained thin films of CuInS_2 were incorporated as an absorbing layer in solar cell structures of the type: glass/ SnO_2 :F/ CdS / Sb_2S_3 / CuInS_2 / PbS , with electrodes painted on the top (graphite and silver). All constituent layers were obtained by CBD technique. Fig. 5 shows the I - V characteristics of such solar cell under dark and illumination conditions. For the solar cell with CuInS_2 absorber layer with 15 h of In_2S_3 chemical bath,

the measured parameters were: $V_{oc} = 530$ mV, $J_{sc} = 2.43$ mA cm^{-2} , $FF = 0.41$ and $\eta = 0.53\%$. On the other hand, for the solar cell with a CuInS_2 absorber film obtained from 24 h of In_2S_3 chemical bath, the characterization shows $V_{oc} = 330$ mV, $J_{sc} = 4.78$ mA cm^{-2} , $FF = 0.27$, and η close to 0.43% .

From these results, it is noticeable that the short circuit current density for the samples of 24 h is higher (double) compared to that 15 h. This can be due to the effect of the thickness in the constituent layers resulting in a higher number of absorber photons; however, complications with the parallel and series resistances cause a loss in the V_{oc} values, and therefore, in the conversion efficiency. In the film of 15 h have a slightly higher E_g and better conductivity, which means it has a better open circuit voltage and consequently the efficiency is improved, as it shows. In 1998, Nakada et al. [27] report that the efficiency of CuInS_2 cells, with a CdS buffer layer, is approximately 8%; which is due to interdiffusion at the $\text{CuInS}_2/\text{CdS}$

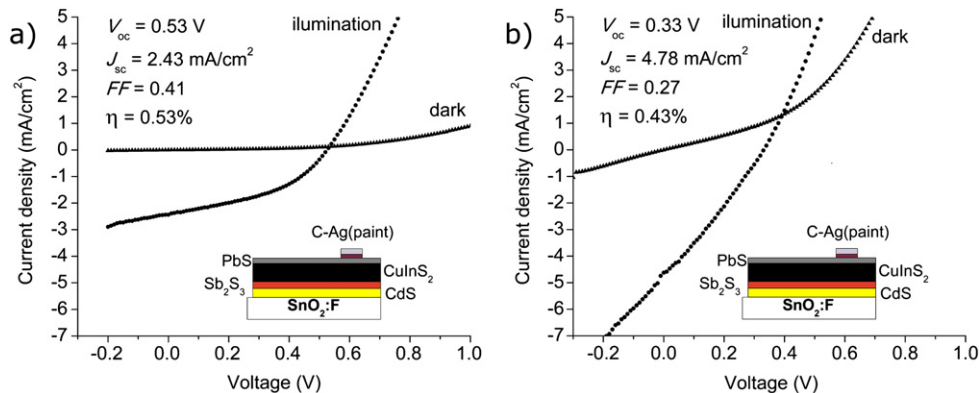


Fig. 5. I - V characteristics of the solar cells with CuInS_2 as absorbing layer corresponding to a) 15 and b) 24 h of In_2S_3 bath, with 2.5 h of CuS bath, followed by heat treatment at 350°C and 400 mPa for 1 h.

interface. In this work, we present the deposition of a Sb_2S_3 layer between the CuInS_2 and CdS , followed of a heat treatment, which avoids the diffusion between the layers and this increases the cell efficiency.

A better contact between layers, and an additional cell, fabricated in the substrate configuration will be tried in future work in order to evaluate interface problems in such structures. We suppose that the low conversion efficiency of the cells presented in this work could be a consequence of the layer intermixing during the annealing process. Further work is necessary to improve the solar cell performance.

4. Conclusions

CuInS_2 thin films were formed from In_2S_3 – CuS stack layers obtained by CBD, followed by heat treatment at 350 °C and 400 mPa for 1 h. We have demonstrated that CuInS_2 thin films can work as an effective absorbing layer in a solar cell structure type: $\text{glass/SnO}_2\text{:F/CdS/Sb}_2\text{S}_3/\text{CuInS}_2\text{/PbS}$. The whole structure presented in this work was obtained by CBD technique. The solar cell integrated with a CuInS_2 absorbing layer obtained by 15 h of In_2S_3 bath showed an energy conversion efficiency of 0.53% showing the following parameters $V_{\text{oc}} = 530$ mV, $J_{\text{sc}} = 2.43$ mA cm^{−2} and FF of 0.41. Further work will be focused in the thickness optimization of each constituent layer and the selection of suitable electrodes with the purpose of improving the cell efficiency.

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