

# Electrosynthesis and Characterization of a $\text{CuInS}_2$ Good Absorber Semiconductor for Thin Film Solar Cells

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## ABSTRACT

Thin films of  $\text{CuInS}_2$  have been prepared by electrodeposition on  $\text{SnO}_2/\text{glass}$  substrate from aqueous solutions of  $\text{InCl}_3$ ,  $\text{CuSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . This semiconductor is one the most promising ternary absorber materials for thin film solar cells. A stoichiometric composition and good crystallinity were obtained by a one step electrodeposition at -1145 mV vs. saturated calomel electrode (SCE). To improve their crystallinity, the samples were annealed under sulfur atmosphere at 450 °C for 30 minutes. Scanning Electronic Microscopy, Energy Dispersive Spectroscopy and X-Ray diffraction were used to characterize the films. Particles Size distribution, film thickness and normalized composition of the semiconductor, under different conditions, have been estimated. Optical studies, using absorption spectroscopy, gave an absorption coefficient of  $10^5 \text{ cm}^{-1}$  and an energy band gap of 1.53 eV, which is in good agreement with the values reported in literature regarding the growth of thin films of this material using other methods.

**Keywords:**  $\text{CuInS}_2$ , Electrodeposition, Thin Films, Semiconductors, Solar Cells.

## 1. INTRODUCTION

Copper indium disulfide ( $\text{CuInS}_2$  denominated CIS) semiconductor has been considered a good candidate as an absorbing material for solar cells since it has an optimal direct band gap ( $E_g = 1.55 \text{ eV}$ ) exhibiting a high absorption coefficient ( $\alpha = 10^5$ ) [1] the maximal within the solar spectrum range. The maximum energy conversion efficiency obtained until now of CIS based solar cells is 11.4% [2]. The simulation work on the  $\text{CuInS}_2$  thin film solar cells reveals a theoretical efficiency of 20.6% by using parameters  $L_h = 1.6 \mu\text{m}$ ,  $L_e = 2.5 \mu\text{m}$ , and  $V_{oc} = 1.01 \text{ V}$ , midgap defect density of  $2 \times 10^{15} \text{ cm}^{-3}$ , carrier lifetime of 50 ns and band gap of 1.5 eV [3] however, it is still well below the 32% single-junction limit determined by the detailed balance between the solar cell and the sun modelled as black bodies, as proposed by Shockley and Queisser [4]. The material can be deposited as a thin film by employing a suitable technique for a reasonable scale production. There are several techniques to grow semiconducting thin films, some of them are costly and others being cost effective. Various methods, namely vacuum deposition [5], sputtering [6], heating evaporation [7], spray pyrolysis [8] and electrodeposition [9] have been used to prepare thin films of  $\text{CuInS}_2$ . Electrodeposition has some advantages compared to other well known physical and chemical deposition techniques: it is easy to manipulate, relatively less expensive and semiconductors could be synthesized with a minimum of waste materials. Since the purification process has been performed by in situ electrodeposition, the use of highly pure starting materials is not required as it is for conventional physical methods.

The deposits have been made either by chalcogenization of electrodeposited Cu-In alloy (by  $\text{H}_2\text{S}$  or S) [10], or through simultaneous

electroreduction of the three elements (codeposition) [9]. Given the wide range of possible ternary material composition, side reaction can lead to co-deposition of undesirable phases if parameters such as deposition potential and concentration in solution are not suitably adjusted. Thickness, morphology and crystalline structure during the growth process are critical factors regarding the requirements for solar conversion efficiency.

In this paper,  $\text{CuInS}_2$  thin films will be grown under potentiostatic conditions from aqueous solutions of the three constituents. The crystalline structure of deposited layers and the influence of annealing treatment will also be discussed using X-ray diffraction patterns.

## 2. EXPERIMENTAL

Thin films of  $\text{CuInS}_2$  were prepared using a one-step electrodeposition method at room temperature, without stirring, in a conventional electrochemical cell. A saturated calomel electrode (SCE) was used as reference, a platinum mesh as the counter electrode, while the working electrode was a  $\text{SnO}_2/\text{glass}$  substrate. The working electrode was ultrasonically cleaned with acetone, rinsed off with ultrapure water and then vacuum dried. The electrolytic bath contained 5.0 mM  $\text{CuSO}_4$ , 5.0 mM  $\text{InCl}_3$ , and 7.5 mM  $\text{Na}_2\text{S}_2\text{O}_3$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$ . The solution was adjusted to pH 2.5 with diluted  $\text{H}_2\text{SO}_4$ . Oxygen was evacuated from the bath under a steam of  $\text{N}_2$  for 15 minutes prior to experiments. A BAS. Epsilon potentiostat was used for electrochemical measurements. The cyclic voltammograms were registered at  $20 \text{ mV s}^{-1}$ . After electrodeposition, precursor thin films were annealed in a vacuum chamber at 450°C during 30 minutes under  $\text{N}_2$  and sulfur atmosphere, respectively. SEM measurements were done with a Hitachi S-2500

microscope, the chemical composition and crystalline properties of the films were determined by Energy Dispersive X-ray Spectroscopy (EDX, Noran from System Six Company), and X-ray Diffraction (XRD, Siemens model D5005), respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1.- Cyclic voltammetry studies of single Cu, In and S constituents

Figure 1, shows the cyclic voltammograms of the three single constituents on SnO<sub>2</sub>/glass electrode in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5. Electrodeposition of Cu begins at -100 mV vs. SCE with a maximum at -180 mV associated to the reduction of Cu<sup>2+</sup> ion to Cu<sup>0</sup> according to equation 1:



Considering the electrochemical Nernst potential (73 mV) and comparing with the observed reduction potential of -180 mV, there is a considerable potential shift that can be attributed to a substrate effect [11] due to the presence of oxides on the electrode surface.

The pH of the solution and the presence of sulphate ions have no influence on the mechanism of copper deposition [12], however, the presence of Na<sup>+</sup> ions has the effect of increasing the copper nucleation overpotential [13]. Beyond -800 mV there is a strong increase in current attributed to hydrogen evolution on the electrodeposited copper. Cyclic voltammetry in 5.0 mM InCl<sub>3</sub> dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5 shows a small increase in the cathodic current from -600 mV, associated to the reduction of In<sup>3+</sup> ions to In<sup>0</sup> according to the reaction:



It is noteworthy that during the course of the experiment, gas bubbles could be observed at the surface of the electrode, suggesting that the charge transfer reaction for metallic indium deposition is occurring parallel to the reduction of the electrolytic medium, [14, 15] which explains the low current values observed. A shift of the In<sup>3+</sup> reduction potential can be explained by an increase in the concentration of sulfate ions that favors formation of complex type In(SO<sub>4</sub>)<sub>2</sub>, [16]. On the other hand, it has been reported [16, 17] that depending on the pH, hydroxycomplexes of type In(OH)<sup>2+</sup> and In(OH)<sup>+</sup> can be formed in solution and it could affect the deposition processes.

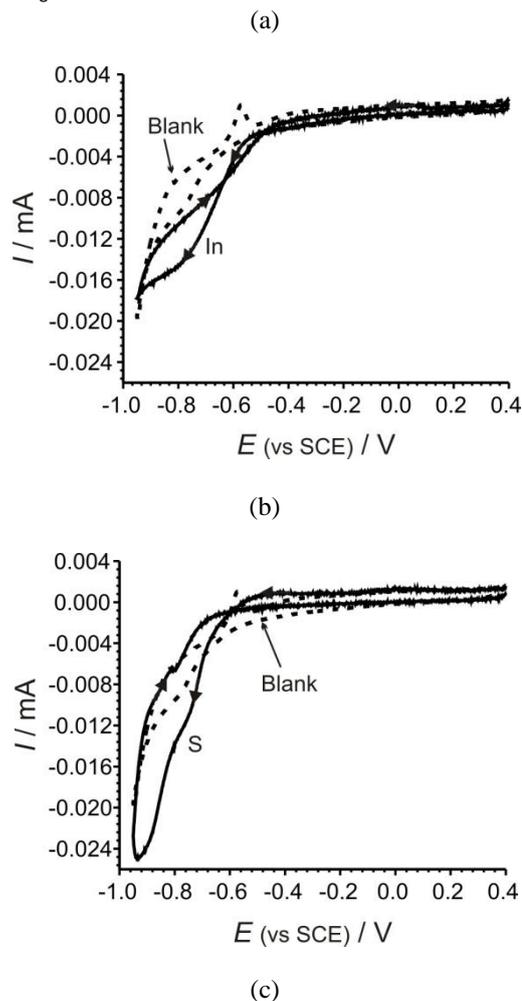
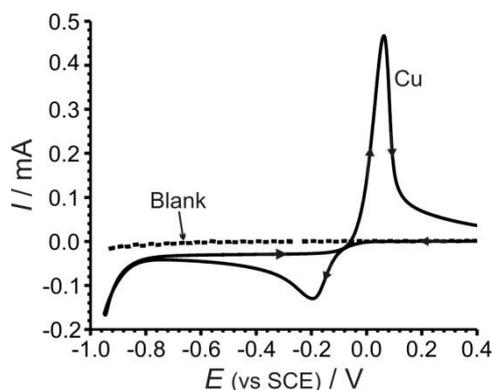


Figure 1. - Cyclic voltammograms in (a) copper (b) indium and (c) thiosulfate ions dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5 at a scan rate of 20 mVs<sup>-1</sup> on SnO<sub>2</sub>/glass substrate

Thiosulfate ions play a double role in the system Cu-In-S: (a) it is a complexing agent for the copper ions, and (b) it is a sulfur source [18]. Once the solution containing S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions was prepared, it gradually became muddy due to the decomposition of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions to form colloidal sulfur whose amount will depend on the acidity of the medium [19] according to reaction 3:



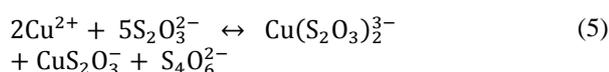
At pH < 3, decomposition of thiosulfate increases in above 9% [20] indicating that a considerable amount of sulfur is decomposed in the electrolytic medium.

#### 3.2.- Cyclic voltammetry studies of binary Cu-S, In-S and Cu-In systems

The complexity of the ternary Cu-In-S system requires a previous view of the voltammetric behavior of the binary Cu-S, In-S and Cu-In systems. The cyclic voltammograms of the separate solutions were used as a control reference. For the Cu-S system, in S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, no precipitate or turbidity was observed because the ions S<sub>2</sub>O<sub>3</sub><sup>2-</sup> are complexed with Cu<sup>2+</sup> ions to form some stable species in solution that inhibit the production of

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elemental sulfur. Although there is little information about the thermodynamics of the system copper (I)-thiosulfate [21, 22], it is known that three possible complexes can be formed in aqueous media:  $\text{CuS}_2\text{O}_3^-$ ,  $\text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ . The former complex is only produced when the concentration ratio between thiosulfate and copper is very high, so under our experimental conditions, we can avoid the formation of  $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ . Additionally, according to literature [21-23] the copper (I)-thiosulfate complexes can also lead to tetraionate ions as shown in equations 4 and 5:



In figure 2 the cyclic voltammograms of Cu-S, in the binary solution, during the forward scan, show a slight increase in current observed at about -200 mV that could be related to the electroreduction of a small amount of uncomplexed copper (II) ions, in agreement with results reported by S. Black [24], who found that at concentration ratio  $[\text{S}_2\text{O}_3^{2-}] / [\text{Cu}^{2+}] = 1.5$ , a portion of the copper is present as free  $\text{Cu}^{2+}$  ions, and the other portion as complexed  $\text{CuS}_2\text{O}_3^-$ . At higher negative potentials, beyond -800 mV, a couple of additional peaks appeared on the forward scan: the first one being associated to the formation of a binary phase  $\text{Cu}_{2-x}\text{S}$  according to reaction 6 [25]:

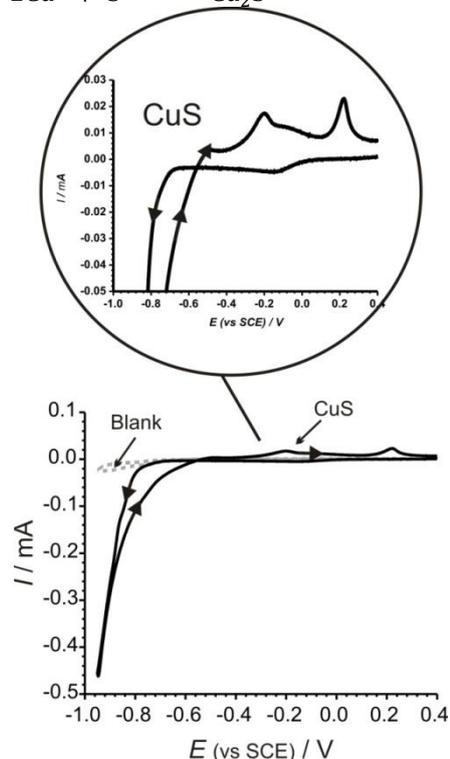


Figure 2. - Cyclic voltammograms of a mixture of  $\text{Cu}^{2+}$ ,  $\text{S}_2\text{O}_3^{2-}$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$  at pH 2.5 on  $\text{SnO}_2/\text{glass}$  substrate at a scan rate of  $20 \text{ mVs}^{-1}$ .

In this case, copper (I) ions are stabilized as  $\text{CuS}_2\text{O}_3^-$  which reacts with  $\text{S}^{2-}$  ions to produce  $\text{Cu}_2\text{S}$ . As the potential scan proceeds, a red brown precipitate is observed, confirming the formation of  $\text{Cu}_2\text{S}$ . The second signal is associated to the subsequent reaction of  $\text{Cu}_2\text{S}$  to produce  $\text{Cu}^0$  [26]. On the reverse scan, three oxidation waves were observed at -500 mV, -220 mV and +150 mV due to electroactive species formed during the forward scan.

For the binary In-S system, the electrolyte bath consisted in 5.0 mM  $\text{InCl}_3$  and 7.5 mM  $\text{Na}_2\text{S}_2\text{O}_3$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$  at pH 2.5. This leads to a colloidal sulfur species attributed to decomposition of  $\text{S}_2\text{O}_3^{2-}$  ions as mentioned before. Figure 3 shows a slight increase in the cathodic current at -640 mV attributed to formation of  $\text{In}_2\text{S}_3$  [27] according to reaction 7:

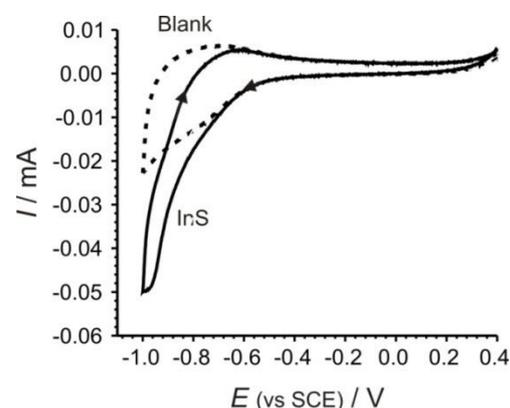
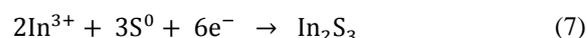
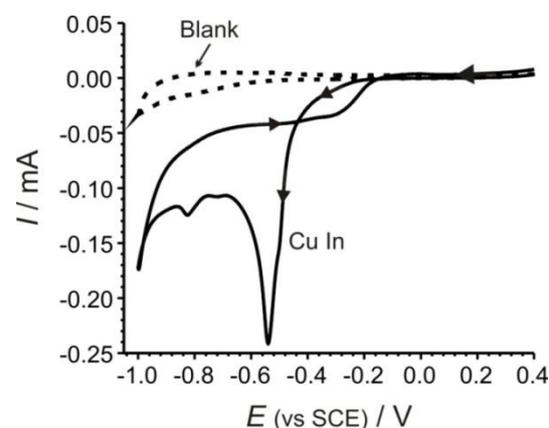


Figure 3. - Cyclic voltammograms on  $\text{SnO}_2/\text{glass}$  electrode.  $\text{In}^{3+}$  and  $\text{S}_2\text{O}_3^{2-}$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$  at pH 2.5 and a scan rate of  $20 \text{ mVs}^{-1}$ .

For the binary Cu-In system, the electrolytic bath consisted in 5.0 mM  $\text{InCl}_3$  and 5.0 mM  $\text{CuSO}_4$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$  at pH 2.5. Figure 4 shows that pure copper is first formed at -520 mV followed by a reduction peak at -820 mV associated to the electroplating of  $\text{In}^0$  and/or the possible formation of a poorly crystalline mixture of  $\text{Cu}_4\text{In} + \text{Cu}_9\text{In}_{11}$  as reported in literature [28, 29].



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Figure 4. - Cyclic voltammograms on SnO<sub>2</sub>/glass electrode of Cu<sup>2+</sup> and In<sup>3+</sup> dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5 at a scan rate of 20 mVs<sup>-1</sup>

are shown in figure 6. Composition found to be Cu<sub>1.00</sub>In<sub>1.00</sub>S<sub>1.50</sub> (figure 7).

### 3.3.- Cyclic voltammetry studies of ternary Cu-In-S system

Figure 5 shows the cyclic voltammograms obtained on SnO<sub>2</sub>/glass electrode for ternary Cu-In-S using as electrolytic bath 5.0 mM CuSO<sub>4</sub>, 5.0 mM InCl<sub>3</sub>, and 7.5 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5. The formation of the ternary phase could take place after the occurrence of different processes that makes difficult the proper location of the reduction waves. At -820 mV, a reduction wave which can be attributed to the reduction of In<sup>3+</sup> ions to indium metallic is observed [30]. In this case, a previous phase is formed (Cu<sub>2-x</sub>S) on the substrate which favor the deposition of metallic indium [31]. X-ray diffraction studies showed that Cu-In-S films deposited potentiostatically; contain metallic indium according to diffraction patterns results.

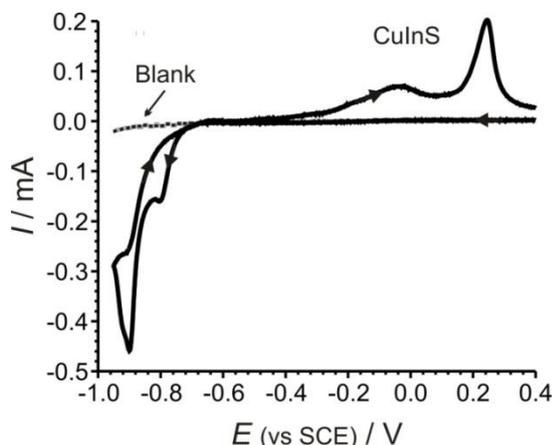
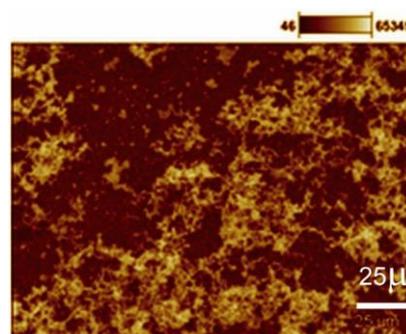


Figure 5. - Cyclic voltammograms on SnO<sub>2</sub>/glass electrode for Cu<sup>2+</sup>, Cu-S and Cu-In-S system dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5. Scan rate: 20 mVs<sup>-1</sup>

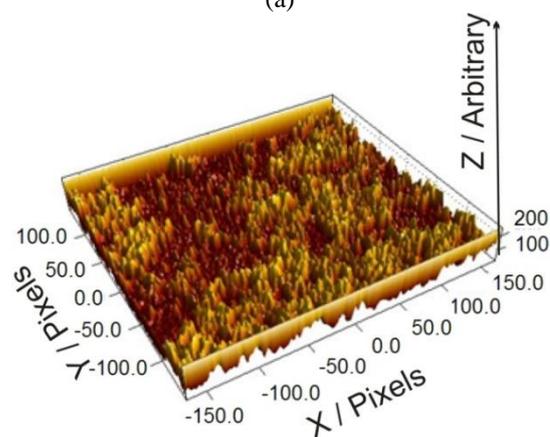
At values of potential more negative than -900 mV, a reduction wave was observed attributable to formation of a new phase. Since CuInS<sub>2</sub> could be produced through different mechanisms, it is difficult to relate this wave to a particular process only from the cyclic voltammetry results. These mechanisms could be associated mainly to the initial formation of Cu<sub>2</sub>S which favors the electroreduction of In<sup>3+</sup>, leading to the formation of the ternary semiconductor [9].

### 3.4.- Evaluation of the semiconductor by Scanning Electronic Microscopy

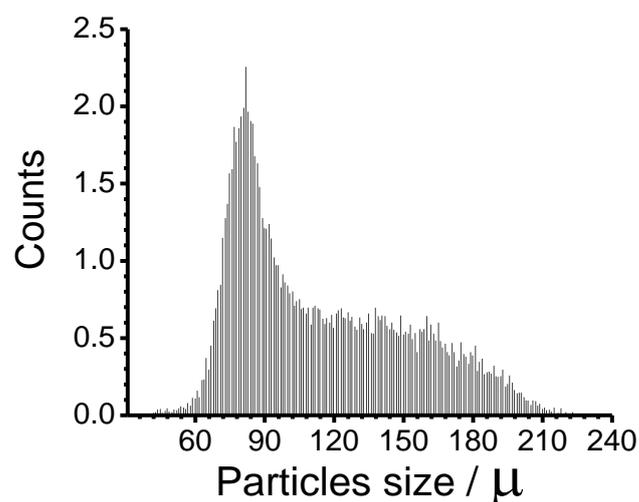
Scanning Electronic Microscopy (SEM) pictures of the ternary semiconductor film (synthesized at -1145 mV during 2 hours on SnO<sub>2</sub>/glass from 5.0 mM [Cu<sup>2+</sup>] = [In<sup>3+</sup>] and 7.5 mM [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] dissolved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at pH 2.5) Cu(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup>, a tridimensional view of the surface and the particles size distribution



(a)

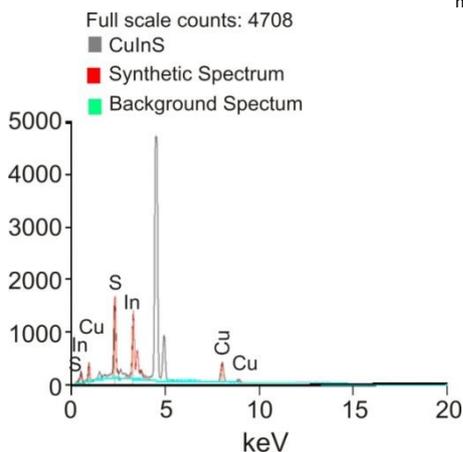


(b)



(c)

Figure 6. - SEM of CuInS deposited on SnO<sub>2</sub>/glass substrate at -1145 mV during 2 h (a) morphology (b) Tridimensional view (c) Particles size histogram



(a)

E (mV)	t (h)	atom %			Normalized composition
		Cu	In	S	
-1145	2	28.68	28.56	42.78	Cu <sub>1.00</sub> In <sub>1.00</sub> S <sub>1.50</sub>

(b)

Figure 7. - Energy Dispersive Spectroscopy (EDX) spectrum of (a) Cu-In-S film (b) Normalized composition of the semiconductor from figure 6. (b)

**3.5.- Composition of Cu-In-S films**

Pulsed electrolyses were carried out at different potentials during 2 hours (figure 8). The best composition of ternary semiconductor was obtained when using pulse amplitude of -1145 mV and a sulfur amount of 43%. The compositional data obtained in atomic percentage have been expressed in terms of molecularity ( $\Delta m$ ) and stoichiometry ( $\Delta S$ ), following equation 8 [32]:

$$\Delta m = \frac{x}{y} - 1 \quad \text{and} \quad \Delta S = \frac{2z}{x + 3y} - 1 \quad [8]$$

Where x, y, z, are referred to Cu<sub>x</sub>In<sub>y</sub>S<sub>z</sub>.

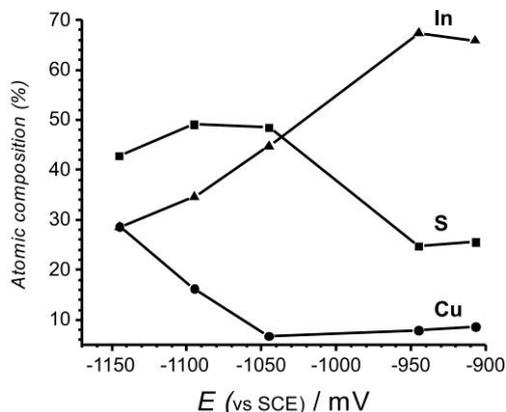


Figure 8. - Composition of ternary Cu-In-S films as a function of the applied deposition potential

According to the preceding definitions,  $\Delta m$  indicates the ratio cuprous sulfide to indium sulfide and  $\Delta S$  characterizes the excess of sulfur related to a material

with a given  $\Delta m$ . Figure 9 shows results of the thin films at -1145 mV starting with  $\Delta m$  equal to zero and  $\Delta S$  below zero, this means that although at this potential the stoichiometric ratio Cu/In is in a proper relation, a sulfur deficiency is observed, what means that a portion of the film is not combined with sulfur. The presence of elemental indium and Cu-In alloy was confirmed by X-ray studies (figure 10 b). If the deposition potential is within the range -907 mV to -1095 mV, films with  $\Delta m < 0$  and  $\Delta S < 0$  are obtained indicating that the synthesized samples are deficient in cuprous sulfide and sulfur, respectively.

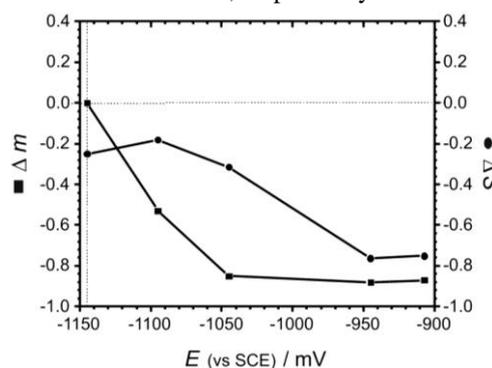


Figure 9. - Deviation from molecularity ( $\Delta m$ ) and stoichiometry ( $\Delta S$ ) as a function of the applied deposition potential for the electrodeposited films

Table 1 illustrates a more detailed interpretation of the composition changes represented in figure 8. The normalization of the atomic composition is very useful for this interpretation. It is to be pointed that the semiconductor synthesized at -1145 mV gives the composition ratio Cu/In = 1 with a slight deficiency of sulfur. To improve these results we should increase the amount of sulfur in the electrolytic medium before preparing the semiconductor or submitting it to an annealing treatment under sulfur atmosphere after its preparation.

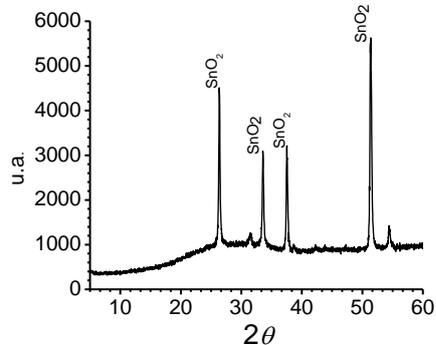
Table1. - Distribution of elements in the electrode surface deposited at different potential pulses.

E (mV)	t (h)	Atomic %			Composition
		Cu	In	S	
-907	2	8.61	65.85	25.55	Cu <sub>0,13</sub> In <sub>1,00</sub> S <sub>0,39</sub>
-945	2	7.91	67.34	24.75	Cu <sub>0,12</sub> In <sub>1,00</sub> S <sub>0,37</sub>
-1045	2	6.77	44.71	48.51	Cu <sub>0,15</sub> In <sub>1,00</sub> S <sub>1,08</sub>
-1095	2	16.21	34.58	49.12	Cu <sub>0,47</sub> In <sub>1,00</sub> S <sub>1,42</sub>
-1145	2	28.68	28.56	42.78	Cu <sub>1,00</sub> In <sub>1,00</sub> S <sub>1,50</sub>

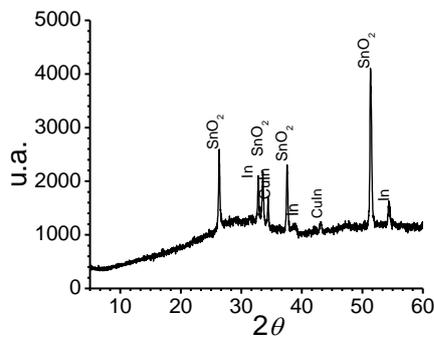
**3.6.- X-Ray Diffraction studies of CuInS<sub>2</sub>**

Figure 10 shows the X-Ray Diffraction (XRD) patterns of thin films Cu-In-S electrodeposited at -1145 mV during 2 hours with and without annealing. Figure 10 a: XRD pattern for SnO<sub>2</sub>/glass substrate, consisting only in one set of peaks. According to standard JCPDS 01-077-0450 cards, those peaks are attributed to the SnO<sub>2</sub> (Cassiterite). Figure 10 b shows the XRD patterns of the thin films synthesized without annealing, which is similar to that of SnO<sub>2</sub>/glass substrate but with a decrease in peaks intensity and a

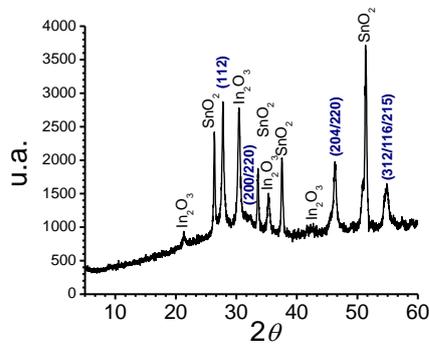
few new peaks. This demonstrates that CuInS<sub>2</sub> synthesized without annealing could be amorphous. It is because during the electrocrystallization process different reaction mechanisms are involved to obtain the crystalline phase.



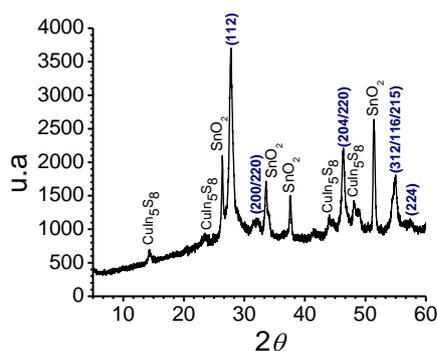
(a)



(b)



(c)



(d)

Figure 10.- X ray diffractograms of a Cu-In-S film deposited on SnO<sub>2</sub>/glass electrode at-1145 mV during

2h (a) bare electrode (b) no sulfur, no thermal treatment;(c) with thermal treatment under N<sub>2</sub> atmosphere, and (d) under sulfur atmosphere at 450 °C during 30 minutes

Annealing under either N<sub>2</sub> or sulfur atmosphere was performed to obtain the films in crystalline phase. Figure 10 c presents the XRD patterns of the CuInS<sub>2</sub> films annealed under N<sub>2</sub> atmosphere at 450°C for 30 minutes. As observed in figure 10 c, the patterns show the chalcopyrite structure of CuInS<sub>2</sub> (JCPDS No: 00-027-0159), but there is also sign of indium oxide (In<sub>2</sub>O<sub>3</sub>) (JCPDS No: 00-065-3170). Although the presence of indium oxide in the film is not easy to be justified, it is possible that, in the early stages of semiconductor deposition, formation of oxides and hydroxides of indium (In(OH)<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>) occurs as by-reactions, either by variation in local pH near the substrate surface or reaction with residual oxygen [33]. Figure 10 d represents XRD patterns of CuInS<sub>2</sub> films annealed under sulfur atmosphere at temperature of 450°C for 30 minutes. The diffraction patterns show characteristic peaks of the chalcopyrite structure (142d) of CuInS<sub>2</sub> indicating the formation of the semiconductor. In this case, the sulfur atmosphere removes surfacial hydroxides and improves crystallinity of CuInS<sub>2</sub> [34]. Besides, other low intensity peaks corresponding to CuIn<sub>5</sub>S<sub>8</sub> (JCPDS No: 00-024-0361) are observed, indicating a slight deviation in the stoichiometry of the semiconductor which is quite interesting because, by optimizing a few parameters, the single phase could be obtained and it would agree with the absorption described in 3.7 section.

### 3.7.- Optical absorption Studies

The fundamental edge may be determined from optical transmission measurement by observing the change of the absorption as a function of the incident energy. In general, measurements are made at nearly normal incidence beam, recording then the transmitted light intensities.

Figure 11 presents the optical transmission spectrum of CuInS<sub>2</sub> thin film annealed under sulfur atmosphere at 450 °C for 30 minutes. The absorption coefficient ( $\alpha$ ) was then evaluated from the optical transmittance (T) using equation 9, providing that the film thickness (d) is known.

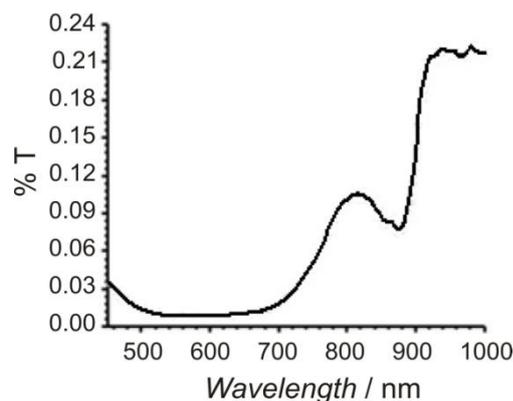
$$\alpha = \frac{\ln T^{-1}}{d} \quad (9)$$

The film thickness was estimated to be 25  $\mu\text{m}$  through transverse images by SEM. For the photon energy range shown in figure 11, the value of  $\alpha$  is close to  $10^5 \text{ cm}^{-1}$ , which is a very important figure for materials for higher efficiency in solar cells.

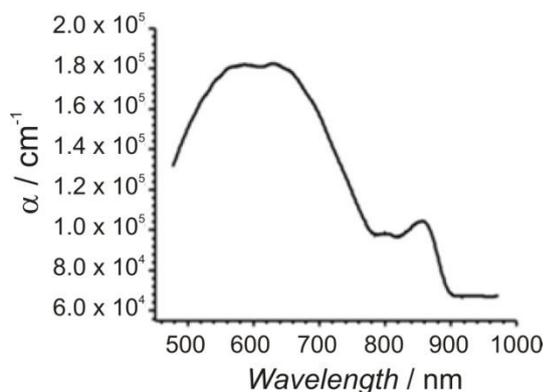
For direct band gap materials, the absorption coefficient is related to the energy gap according to equation 10:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (10)$$

Where A is a constant,  $h\nu$  is the photon energy, and  $E_g$  is the band gap energy. Therefore,  $E_g$  can be obtained by plotting  $(\alpha h\nu)^2$  vs.  $h\nu$ , as seen in figure 12. The fitted straight line shows that the film exhibits direct transitions corresponding to a band gap of about 1.53 eV, which is slightly smaller than the value reported in literature (1.55 eV) [1]. This can be interpreted by a slight deviation from stoichiometry of the atoms in the film that leads to defect states and therefore inducing smearing of absorption edges [35]. In the figure 11 a shoulder around 800 nm is observed and, from the X-ray results, this should be attributed to the small amount of the secondary phase of  $\text{CuIn}_5\text{S}_8$ . The calculation of the energy gap of the shoulder gives the value of 1.35 eV which is in very good agreement with the value reported [36] to this secondary phase corroborating the two experimental methods.



(a)



(b)

Figure 11.-Transmittance percentage (%T) vs. wavelength ( $\lambda$ ) and Absorption coefficient ( $\alpha$ ) vs. energy radiation ( $h\nu$ ) for a  $\text{CuInS}_2$  film deposited on  $\text{SnO}_2/\text{glass}$ .

#### 4. CONCLUSIONS

$\text{CuInS}_2$  thin films have been prepared by one-step electrodeposition and annealing process. The

voltammetric evaluation allowed optimization of variables for the synthesis of the  $\text{CuInS}_2$  semiconductor. Electrodeposited  $\text{CuInS}_2$  thin films were prepared from an aqueous solution of 5.0 mM  $\text{CuSO}_4$ , 5.0 mM  $\text{InCl}_3$  and 7.5 mM  $\text{Na}_2\text{S}_2\text{O}_3$  dissolved in 0.5 M  $\text{Na}_2\text{SO}_4$  at pH 2.5 on  $\text{SnO}_2/\text{glass}$  substrate. According to the composition analysis of electrodeposited material at a potential of  $-1145$  mV vs. SCE during 2 hours, a film was obtained with a stoichiometric ratio of  $\text{Cu}/\text{In} = 1$ , and near to a stoichiometric sulfur content. XRD analysis showed that, at the beginning, the obtained film is amorphous. To improve the crystallinity of these films, they were annealed in a sulfur atmosphere at  $450^\circ\text{C}$  for 30 minutes and the XRD studies show that the thin films  $\text{CuInS}_2$  were stoichiometrically obtained. Optical studies showed that films synthesized using annealing in sulfur atmosphere have a high absorption coefficient of  $10^5 \text{ cm}^{-1}$ , and an energy gap of 1.53 eV, matching with solar spectrum. All these features make it an excellent ideal absorber for thin film solar cells. The crystal structure of electrodeposited  $\text{CuInS}_2$  is tetragonal with space group of **I** (-4) **2d**, that is, chalcopyrite. A minority second phase of  $\text{CuIn}_5\text{S}_8$  observed can be diminished under an appropriate thermal annealing process. The electrodeposition is the cheapest way to produce future solar cells.

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