Electrochemical deposition of CuInS$_2$ thin films
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Abstract
Chalcopyrite thin films were one-step potentiostatically deposited onto stainless steel plates from aqueous solution containing CuSO$_4$, In$_2$(SO$_4$)$_3$ and Na$_2$S$_2$O$_3$. The ratio of (In$^{3+}$:Cu$^{2+}$) which involved in the solution and The effect of cathodic potentials on the structural had been studied. X-ray diffraction (XRD) patterns for deposited films showed that the suitable ratio of (In$^{3+}$:Cu$^{2+}$) = 6:1, and suitable voltage is -0.90 V versus (Ag/AgCl) reference electrode.

Key words
CuInS$_2$,
Electrical properties,
Solar cells,
chalcopyrite

Introduction: The ternary compound CuInS$_2$ with chalcopyrite structure has attracted considerable attention as a suitable material to fabricate low-cost, efficient solar cells. This is mainly due to its direct band gap energy of 1.55 eV at room temperature. [1].

Many deposition methods have been developed for the preparation of CuInS$_2$ thin films, such as sulfurization of electrodeposited Cu-In precursor, wet chemical route, chemical bath deposition, chemical vapor deposition, spray pyrolysis, ion plating, ion layer gas reaction (ILGAR) and co-evaporation [2]. Among the various deposition techniques, electro deposition is the most suitable for the commercial and large scale application. Electro deposition is an attractive technique and has widely been employed for the deposition of elemental, binary, intermetallic, ternary or even more complex compound and alloy thin films. It is an isothermal process mainly controlled by electrical parameters which are easily adjusted to control thickness, microstructure and composition [3].

The aim of this work is to study the voltage scan of H$_2$O decomposition and the voltage scan of electrodeposition for Cu, In and S; The structural properties for electrodeposited Cu-In-S films for different molar ratio (Cu/In) and different voltages have been also studied.

Experimental A three electrode-cell was used, where Ag/AgCl as the reference electrode, stainless steel (10 cm$^2$) as the working
electrode (cathode) and a graphite rod as the counter electrode (anode). The substrates and the counter electrode were cleaned with acetone, sodium hydroxide and followed by deionized water using ultrasonic bath. At first each component (Cu, In and S) electrodeposited from 4 mM CuSO$_4$, 4 mM In$_2$(SO$_4$)$_3$ and (400mM) Na$_2$S$_2$O$_3$:5H$_2$O respectively. Then electrodeposition membranes from bath consisted of (3 mM) CuSO$_4$, (1.5-9 mM) In$_2$(SO$_4$)$_3$ and (400mM) Na$_2$S$_2$O$_3$:5H$_2$O. The pH was adjusted to 2 using Tartaric acid and then to 1.50 using sulfuric acid. Different cathodic voltage were supplied (-0.6 , -0.7 and -0.9 V vs Ag/AgCl). The solution was stirred until the films electrodeposited. The films were electrodeposited at room temperature.

The deposited films were rinsed with deionized water and kept for further characterization. The films were analyzed using a Philips PZ 3710 x-ray diffractometer using monochromatic CuK$_{a1}$ radiation ($\lambda=1.5406$ Å) in a scanning angle range of 25-60$^\circ$.

**Results and Discussion**

Fig (1) shows the J-V characteristic of Hydrogen evaluation occurs at (-1.040 V, vs Ag/AgCl) which respect to the equation of half cell reaction: [4]

$$2 \text{H}_2\text{O} +2e \rightarrow \text{H}_2+2\text{OH}^- -0.8277 \text{ Volts Vs SHE}$$

It is clear that the Ag/AgCl reference electrode voltage =1.040-0.8277=0.212 mV. This value is very close to that at equation (2)

$$\text{AgCl} + e \rightarrow \text{Ag} + \text{Cl}^- 0.22233 \text{ Volts Vs SHE}$$

Fig. (1) the J-V characteristic of Hydrogen evaluation from H$_2$O decomposition at 25$^\circ$C, pH =1.5, (Scan Rate = 2 mV/s ).

Fig. (2) showed the J-V characteristic of (Sulfur) electrodeposition from 400mM Na$_2$S$_2$O$_3$ on stainless steel substrate at 25$^\circ$C, pH =1.5 (Scan Rate = 2 mV/s). Sulfur anions prepared from the following reaction:

$$\text{S}_2\text{O}_3^{2-}+6\text{H}^+4e\rightarrow2\text{S}+3\text{H}_2\text{O} \quad \text{...3}$$

The sodium thio sulfate play as a reducing agent.

Fig. (2) the J-V characteristic of (Sulfur) electrodeposition from 400mM Na$_2$SO$_3$ on SS Substrate at 25$^\circ$C, pH =1.5 (Scan Rate = 2 mV/s).

Fig. (3) Shows the J-V characteristic of (In) electrodeposition from 4 mM Indium Sulfate. Three peaks can noticed from it at -340,-590 and -690 mV versus Ag/AgCl with respect to the equations:

$$\text{In}^+ + e \rightarrow \text{In} -0.14 \text{ V vs. SHE} \quad \text{...4}$$

$$\text{In}^{2+} + e \rightarrow \text{In}^+ -0.39 \text{ V vs. SHE} \quad \text{...5}$$

$$\text{In}^{3+} + e \rightarrow \text{In}^{2+} -0.49 \text{ V vs. SHE} \quad \text{...6}$$
Fig. (3) the J-V characteristic of (In) electrodeposition from 4 mM Indium Sulfate on SS Substrate at 25°C, pH =1.5 (Scan Rate = 2 mV/s).

Fig. (4) shows the J-V characteristic of (Cu) electrodeposition from 4 mM Copper Sulfate on stainless steel Substrate at 25°C, pH=1.5.

Fig. (3) and (4) show that at voltage -700 the rate of (Cu) deposition is much greater than for (In) and it was not stable. While at -900 the rate of deposition of two is stable but it was still great. So the concentration of the composition must be chosen as (CuSO$_4$/In$_2$(SO$_4$)$_3$)<1.

This results agree with Raza et al (1996) who used 0.01M InCl$_3$ and 0.001 M CuCl$_2$ to electrodeposited CuInS$_2$ film [5], Kopach et al (2001) used 0.9 mM CuCl, 4.5 mM InCl$_3$ and 1.5 mM SeO$_2$ to electrodeposited CuInSe$_2$ film [6], Chraibi et al (2001) used 3mM of Cu$^{2+}$, 10mM of In$^{3+}$, 10mM of HSeO$_2$ to electrodeposited CuInSe$_2$ film [7] and Meglali et al (2008) used 10 mM of CuCl$_2$, 20mM of InCl$_3$ and 40 mM of SeO$_2$ to electrodeposited CuInSe$_2$ film [8]

Fig. (5) shows the variation of current density with time at electro deposition of CuInS$_2$ at -900 mV versus Ag/AgCl on SS plate. From this figure can notice that the current at the beginning decreasing with time and then being stable.

Fig. 5 The relation between J (mA/cm$^2$) versus the time in minute for CuInS$_2$ at -0.9V vs Ag/AgCl.

Current-time dependence due to mass transport in term of diffusion causes the concentration gradient in the vicinity of the electrode surface. This involves a gradual expansion of the diffusion layer associated with the depletion of the reactant and hence decreases the slope of the current profile. [9].

Fig. 6 shows that the X-ray diffraction for the stainless steel (314) plate which used as a substrate to deposited thin film on it. Table (1) shows the experiment and the standard peaks for Fe-Ni-Cr crystal and their intensities, it shows a perfect identical between them because the domain contain of SS-314 are Fe, Ni and Cr (see Table 2).

Fig. (6) XRD for stainless steel plate which uses as a substrate.
Table (1) The experiment peak for uses SS plate and the standard peaks for Fe-Ni-Cr crystal and their intensities [10]

<table>
<thead>
<tr>
<th>2θ exp.</th>
<th>d Exp. (Å)</th>
<th>Int. %</th>
<th>d Std. (Å)</th>
<th>Int. %</th>
<th>hkl</th>
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</thead>
<tbody>
<tr>
<td>43.592</td>
<td>2.075</td>
<td>67</td>
<td>2.08</td>
<td>100</td>
<td>111</td>
</tr>
<tr>
<td>50.766</td>
<td>1.797</td>
<td>100</td>
<td>1.80</td>
<td>45</td>
<td>200</td>
</tr>
<tr>
<td>74.616</td>
<td>1.271</td>
<td>97</td>
<td>1.27</td>
<td>26</td>
<td>220</td>
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</table>

Table 2 Chemical composition of stainless steel -314 alloy %.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>C max</th>
<th>Mn max</th>
<th>Si max</th>
<th>P max</th>
<th>S max</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>48-54</td>
<td>0.25</td>
<td>2.00</td>
<td>1.5-3</td>
<td>0.045</td>
<td>0.03</td>
<td>23-26</td>
<td>19-22</td>
</tr>
</tbody>
</table>

Fig. (7) shows XRD for thin film electrodeposited on SS from solution contain Cu:In molar ratio (1:1) for different applied voltage versus Ag/AgCl electrode. At -0.6 V and -0.7 V for electrodeposited film (Fig. 7-a and b) only the substrate peaks were observed but at (b) the intensities higher than at (a) which refers to Cu electrodeposited which peaks identical with these, because at this voltage the Cu anions was electrodeposited at high rate (see Fig. 4). At -0.9 V(Fig. 7-c) we can see two peaks for Covellite (CuS) phase.

Fig. (8) Shows XRD for thin film electrodeposited on SS plate from solution contain Cu:In molar ratio (1:2) for different applied voltage versus Ag/AgCl electrode (-0.6, -0.7 and -0.9 V).

Fig. (8-a) shows small intensities peaks for Cu$_{11}$In$_9$ appear at 2θ =34.28° and 44.74° with hkl{(400) and (021)} respectively.

In Fig. (8-b) the substrate peaks were noticed but theirs intensities higher than at Fig.(8-a) correspond of Cu phase, in addition to a small peak for CuInS$_2$ with hkl (112) located at 2θ = 28.0126, and others for Cu$_{11}$In$_9$ appeared at 20 =29.4, 29.6, 34.75, 38.77, 42.22 and 44.74 with hkl{(110), (402), (400), (203), (313), and (021)} respectively. The results in (a) and (b) shows deficiency samples from sulfur because no hydrogen evaluation from cathode at these voltage (see Fig.2). In Fig. (8-c) the peaks correspond to Cu-In alloy are disappear and the peak
correspond to (112) of CuInS$_2$ at $2\theta = 28.0126$ appear most clear than at others, this result correspond to hydrogen evaluation from cathode and then prepare sulfur anions by chemical reaction between hydrogen and HSO$_3^-$ anions (see Fig. 2. sulfur more electrodeposited at more negative potential) HSO$_3^- + 5H^+ + 4e^- \rightarrow S + H_2O \quad E^o(V) \text{ vs. SHE} = 0.420 \quad (...) [4]

These results are in agreement with Yunbin He (2003) [11], he studied the influence of the H$_2$S flow on the properties of CuInS$_2$ Thin Films prepared by Reactive Sputter Deposition and found that at low flow Cu-In alloy phases coexisting in the films. When the H$_2$S flow during sputtering increased the secondary Cu-In phases were suppressed, and nearly pure CuInS$_2$ phase films were obtained.

Fig. (9) shows the XRD for thin film electrodeposited from solution contain Cu:In molar ratio (1:6) at -0.9V versus Ag/AgCl electrode on SS substrate.

The pattern included two peaks at 20 equal to (27.875° and 46.402°) referred to (112) and (220-204) direction of chalcopyrite CuInS$_2$ respectively. This figure confirms that the preferential orientation is in the (112) direction.


Table (3) Comparison of observed and standard (d) values for different phases observed in films deposited in different voltages and Cu:In molar ratios[10].

<table>
<thead>
<tr>
<th>Cu/In</th>
<th>Supplied voltage vs. Ag/AgCl</th>
<th>Peak 20 (deg.)</th>
<th>Exp. d (Å²)</th>
<th>Int. %</th>
<th>Stan. d (Å²)</th>
<th>Int. %</th>
<th>phase</th>
<th>Plane (h k l)</th>
<th>JCPDS Card no.</th>
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<tr>
<td>-0.60</td>
<td>43.604</td>
<td>1.0758</td>
<td>2.08</td>
<td>FeNiCr</td>
<td>(111)</td>
<td>33-397</td>
<td></td>
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<tr>
<td></td>
<td>50.797</td>
<td>1.7973</td>
<td>1.80</td>
<td>FeNiCr</td>
<td>(111)</td>
<td>33-397</td>
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<tr>
<td>-0.70</td>
<td>43.504</td>
<td>2.0802</td>
<td>2.08</td>
<td>FeNiCr + Cu</td>
<td>(111)</td>
<td>4 - 836</td>
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<td></td>
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<tr>
<td></td>
<td>50.737</td>
<td>1.7993</td>
<td>1.80</td>
<td>FeNiCr + Cu</td>
<td>(200)</td>
<td>33-397</td>
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<tr>
<td>1:1</td>
<td>-0.90</td>
<td>43.549</td>
<td>2.0782</td>
<td>CuS</td>
<td>(103)</td>
<td>6 - 464</td>
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<td></td>
<td>50.746</td>
<td>1.7990</td>
<td>1.80</td>
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<td>31.790</td>
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<td>6 - 464</td>
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<td>48.124</td>
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<td>-0.60</td>
<td>43.996</td>
<td>2.0581</td>
<td>2.08</td>
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<td>(111)</td>
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<tr>
<td></td>
<td>50.971</td>
<td>1.7916</td>
<td>1.80</td>
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<tr>
<td>1:2</td>
<td>-0.70</td>
<td>34.278</td>
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<td>(200)</td>
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<td></td>
<td>44.744</td>
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<td>2.047</td>
<td>CuInS$_2$</td>
<td>(200)</td>
<td>41-883</td>
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<tr>
<td>-0.90</td>
<td>43.829</td>
<td>2.0655</td>
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<td></td>
<td>51.065</td>
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<tr>
<td>1:6</td>
<td>-0.90</td>
<td>27.952</td>
<td>3.1919</td>
<td>CuInS$_2$</td>
<td>(112)</td>
<td>27-159</td>
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<td></td>
<td>34.244</td>
<td>2.6185</td>
<td>3.198</td>
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<td>(112)</td>
<td>27-159</td>
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<td></td>
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<td>2.0622</td>
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<td>FeNiCr</td>
<td>(111)</td>
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<td></td>
<td>50.999</td>
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<td></td>
<td>27.875</td>
<td>3.1981</td>
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<td>27-159</td>
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<td></td>
<td>46.402</td>
<td>1.955</td>
<td>36</td>
<td>CuInS$_2$</td>
<td>(204,220)</td>
<td>27-159</td>
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</table>
Table (3) shows the comparison of observed and standard (d) values (from JCPDS) for different phases observed in films deposited in different voltages and different Cu:In molar ratios.

The grain size was calculated by Scherrer’s formula:

$$b = \frac{0.89 \lambda}{\Delta (2\theta) \cos (\theta)} \ldots (8)$$

Where $\lambda$=0.15406 nm for CuK$\alpha_1$,

$\Delta (2\theta)$=the full half width= 0.3023 deg. = 0.00527 rad. And $\theta$=27.9/2=13.95°

$b = 26.8$ nm

Electrodeposition normally leads to small particle size, mainly because it is a low temperature technique [17].

Lattice parameters (a) and (c) were calculated from X-ray d-spacings according to equation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \ldots \ldots \ldots (9)$$

Where h, k, and l refer to the Miller indices of individual reflections. The d-spacing of the (220) reflection was used to calculate (a)

$$\frac{1}{(0.5530)^2} = \frac{2^2 + 2^2}{a^2} + \frac{0^2}{c^2} \Rightarrow a = 0.5530$ nm

And the d-spacing of the (112) reflection was used, with the calculated lattice parameter a, to determine c.

$$\frac{1}{(0.31981)^2} = \frac{1^2 + 1^2 + 2^2}{(0.553)^2} + \frac{2^2}{c^2} \Rightarrow c = 1.11625$ nm

This method used by Banger et al (2002) [18].

The lattice parameters, the distortion parameter x (where x= 2–c/a), (given that a hypothetical c/a ratio of 2 would result in the absence of any tetragonal distortion) and the anion displacement parameter u (where u = 0.25+x) are presented in Table (4).

Comparison of the data collected from the CuInS$_2$ film shows they are in good agreement with the JCPDS reference values for single-crystal CuInS$_2$.

### Table 4

<table>
<thead>
<tr>
<th>CuInS$_2$</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>$\eta$=c/2a</th>
<th>X(mm)</th>
<th>u (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. values</td>
<td>0.5530</td>
<td>1.1116</td>
<td>1.0051</td>
<td>0.010</td>
<td>0.240</td>
</tr>
<tr>
<td>JCPDS values [67]</td>
<td>0.5523</td>
<td>1.1141</td>
<td>1.0086</td>
<td>0.017</td>
<td>0.233</td>
</tr>
</tbody>
</table>

**Conclusions**

The chalcopyrite CuInS$_2$ films were successfully deposited on SS using electrochemical technique. The structural of electrodeposited films were studied for different precursor concentration and different applied voltage.

It was found that the ratio of precursor concentration play an important role to successfully electrodeposited chalcopyrite CuInS$_2$ films and the best molar ratio of In:Cu=6:1 in the solution to electrodeposited chalcopyrite CuInS$_2$ films.

It was found that the applied voltage is also an important role in electrodeposited of CuInS$_2$ and the best voltage is -0.9 V versus Ag/AgCl.

Electrodeposited CuInS$_2$ film have chalcopyrite structure with preferential orientation at (112) direction located at 20= 27.875°.

**References**


[10] JCPDS-International Centre for Diffraction Data. All rights reserved PCPDFWIN v. 1.30 (N 1997)