ONE STEP ELECTRODEPOSITION OF $CuInSe_2$ THIN FILMS

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Formation of $CuInSe_2$ (CIS) thin films from aqueous solution containing citrate as complexing agent is reported. The surface morphology and the composition of the deposited films are characterized by scanning electron microscopy (SEM). The texture of the deposits and their compositions are analyzed by X-ray diffraction and transmission electron microscopy (TEM). Annealing of the films at 350°C in flowing argon electrodeposited at potentials in the range [-0.24, -0.4 (V vs Ag/AgCl)] resulted in the formation of alpha-Cu_2Se (JCPDS 24-1131) and CuSe (JCPDS 6-0427). On the contrary, annealing in the same conditions of the films electrodeposited between -0.4 and -0.6 V vs Ag/AgCl led to the formation of chalcopyrite $CuInSe_2$ (JCPDS 23-209) with alpha-Cu_2Se (JCPDS 24-1131) as secondary phase. The formation of $CuInSe_2$ films with a chalcopyrite structure and good stoichiometry is observed.

INTRODUCTION

$Cu(In,Ga)Se_2$ (CIGS) has become one of the most important semiconductor materials in developping polycrystalline thin film solar cell structures and can be used to make low-cost photovoltaic devices [1-2]. Solar cells based on $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) have reached conversion efficiencies as high as 16–17.5% [2-4] and a recent world record of 18.8% [5]. Several techniques have been used to prepare $CuInSe_2$ thin films. In this work, electrodeposition is studied. This technique is an attractive method. It is one of the suitable techniques to prepare low cost thin films. It is economic, technologically simple and allows the possibility of deposition over large surface areas [6,13]. However, the elaboration of a ternary compound is rather difficult due to the different values of equilibrium potentials for each constituent. The elementary deposition reactions for pure Cu, In and Se are the following (all the potentials are referred to the Normal Hydrogen Electrode (NHE)):

$Cu^{++} + 2e^- \Leftrightarrow Cu$

$$E = E^0_{Cu} + \frac{RT}{2F}\ln\left(\frac{a_{Cu^{++}}}{a_{Cu}}\right) \quad \text{or} \quad E = +0.342\ V + 0.0295 \log a_{Cu^{++}}$$

$In^{3+} + 3e^- \Leftrightarrow In$

$$E = E^0_{In} + \frac{RT}{3F}\ln\left(\frac{a_{In^{3+}}}{a_{In}}\right) \quad \text{or} \quad E = -0.338\ V + 0.0197 \log a_{In3+}$$

$HSeO_2^+ + 4H^+ + 4e^- + OH^- \Leftrightarrow H_2SeO_3 + 4H^+ + 4e^- \Leftrightarrow Se + 3H_2O$

$$E = E^0_{Se} + \frac{RT}{4F}\ln\left(\frac{a_{HSeO_2^+}}{a_{Se}}\right) + 3\frac{RT}{4F}\ln a_{H^+}$$

or $E = +0.74\ V + 0.0148 \log a_{HSeO2+} - 0.043\ pH$

Where a_{Cu++} , a_{In3+} , a_{HSeO2+} are the activities of the ions in the solution; a_{Cu} , a_{In} , a_{Se} are the activities of the elements in the solid phase (equal to 1 if a pure metal is deposited), a_{H+} is the activity of the hydrogen ions, and F is the Faraday constant. The equilibrium electrode potentials for Cu, In and Se are quite different. In order to deposit the three elements simultaneously, the individual potentials must be brought closer by using a complexing agent or by adjusting the concentrations of individual ions and the pH of the electrolyte. Ueno et al. [14] and Sahu et al. [15] electrodeposited Cu-In-Se from an aqueous electrolyte without complexing agents. Bhattacharya [7], Pottier et al. [16], Thouin et al. [17] and Tzvetkova et al. [18] used triethanolamine and ammonia, citrate ions, citric acid or thiocyanate as complexing agents for the $CuInSe_2$ electrodeposition. The authors reported that the complexing agent had no effect on indium ions but formed a stable complex with cuprous ions. In our previous paper (Chraibi et al.) [19] we studied the effect of sodium citrate, as complexing agent, on the electrodeposition potential and the surface morphology of pure copper, indium, selenium and of the ternary alloy. We reported that citrate ions form complexes with both Cu^{2+} and $HSeO_2^+$ ions,

but the indium deposition does not seem to be affected. The results showed that citrate ions may be used as a suitable complexing agent for the electrodeposition of $CuInSe_2$.

In this paper, electrodeposition of $CuInSe_2$ thin films depending on the deposition potential is studied. The films were plated on a titanium substrate from an aqueous solution containing $CuSO_4$, $In_2(SO_4)_3$, H_2SeO_3 and citrate. A detailed X-ray, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization was then performed of the as-deposited films and of the same films after heat treatment in a flowing argon atmosphere, the effect of annealing on the mean crystallite size of the $CuInSe_2$ films also being examined.

EXPERIMENTAL PROCEDURE

Electrodeposition was carried out using a classical three-electrode potentiostatic system with a saturated Ag/AgCl (+ 222 mV/NHE) electrode as reference electrode and a platinum sheet as counter electrode.The anode and cathode compartments were separated by a fritted membrane. Titanium plates (0.9×1 cm^2) were used as working electrodes. An EG&G Princeton Applied Research potentiostat/ galvanostat Model 273A with an IBM PC AT computer interface was used to control the electrodeposition process and to monitor the current and voltage profiles. The plates were degreased in an ultrasonic bath filled with alcohol and etched in a 25% fluorhydric - 75% nitric acids mixture, rinsed with bi-distilled water and then dried at room temperature. All experiments were performed at room temperature (18-20 °C) either from stagnant solutions or from solutions stirred by using a rotating disc electrode (RDE). The polarization curves were investigated potentiodynamically at a sweep rate of $10mV.s^{-1}$ and constant stirring between 250 and 1000 rpm.
The surface morphologies of the deposited films were characterized by scanning electron microscopy (SEM, JEOL: JSM- 820), and the compositions of the films were determined with an energy dispersive X-Ray microanalyzer (EDX, Tracor Northern-5525). Cristallinity and texture of the deposits were analyzed by means of a powder X- Ray (Cu- Kα) diffraction (XRD, SIEMENS: D500).

RESULTS AND DISCUSSION

1. Potentiostatic depositions

The $CuInSe_2$ thin films are prepared by electrodeposition from an aqueous solution containing Cu^{2+}, In^{3+}, $HSeO_2^+$ ions and citrate. the complexing agent (Trisodium citrate) allows to bring closer the electrodeposition potentials of copper, selenium and indium.
All films are deposited at potentials ranging between -0.24 and -0.7 V vs Ag/AgCl, with an electrode rotation speed between 250 and 350 rpm. This ternary alloy deposition is performed from aqueous solution containing 3mM of Cu^{2+}, 10mM of In^{3+}, 10mM of $HSeO_2^+$ and 50mM of citrate. The pH is adjusted at 2.5 by H_2SO_4 additions. Figure 1 shows a typical polarization curve for $CuInSe_2$. Two potential regions are observed from -0.12V vs Ag/AgCl to -0.42V vs Ag/AgCl (region I) and from -0.42V vs Ag/AgCl to -0.75V vs Ag/AgCl (region II). According

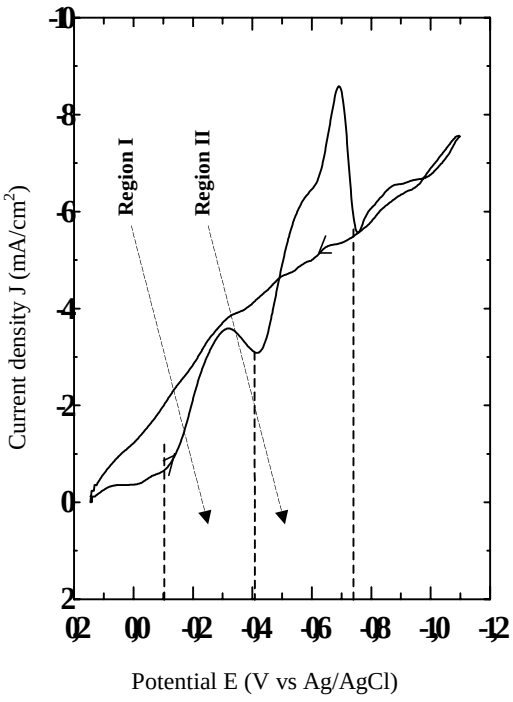


Figure 1: Polarization curve of $CuInSe_2$ thin films deposited from aqueous solution containing 3mM of Cu^{2+}, 10mM of In^{3+}, 10mM of $HSeO_2^+$ and 50mM of citrate at pH 2.5, sweep rate 10mV/s and electrode ro

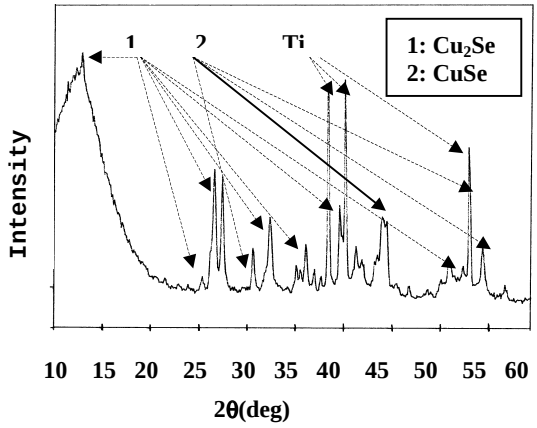


Figure 3: XRD spectra of thin films electrodeposited at -0.39 V vs Ag/AgCl, pH 2.5, 250rpm, from: 3mM of Cu^{2+}, 10mM of In^{3+}, 10mM of $HSeO_2^+$and 50mM of citrate and annealed in flowing Ar at 350°C during 15 min

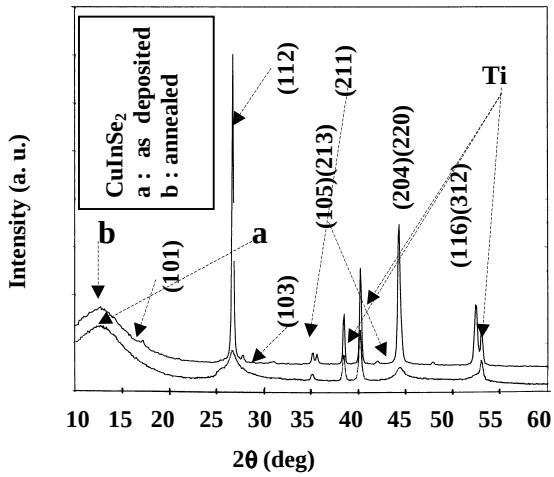
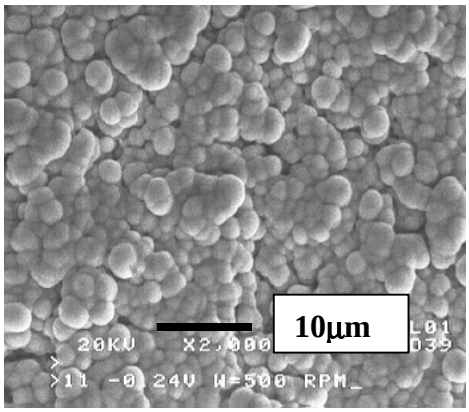
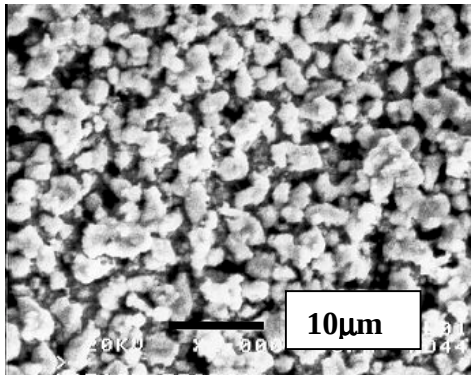


Figure 4: XRD spectra of $CuInSe_2$ thin films deposited at -0.57 V vs Ag/AgCl, pH 2.5, 250rpm, from: 3mM of Cu^{2+}, 10mM of In^{3+}, 10mM of $HSeO_2^+$and 50mM of citrate:



(a)



(b)

Figure 5**:** SEM micrographs of thin film electrodeposited at -0,24 V/ (Ag/AgCl), rotation speed 250 turns per minute, (a): as deposited, (b): annealed in flowing argon at 350 degrees during 15 min

to EDX and x-rays diffraction analysis the first range of potential makes it possible to make deposits of a binary alloy Cu-Se such as CuSe and / or Cu_2Se. On the other hand the second range of potential allows obtaining ternary alloy. Indeed, diagrams of x-rays diffraction show that the films obtained at the potential -0,24V / (Ag/AgCl), after annealing under argon at the temperature of 350 degrees present the Cu_2Se phase (Figure 2). The films electrodeposited at -0,39 V / (Ag/AgCl) present after annealing under argon during 15 minutes at the temperature 350 degrees and ω = 250rpm, a mixture of the two phases Cu_2Se and CuSe (Figure 3). Figures 5 and 6 show thin film SEM photographs deposited at -0,24 and -0,39 V vs Ag/AgCl for ω = 250rpm, before and after annealing under argon at 350 degrees during 15 minutes.

Electrodeposition at potentials -0,48 and -0,5 V va mixture of the Cu_2Se, CuSe and $CuInSe_2$ phas 2.

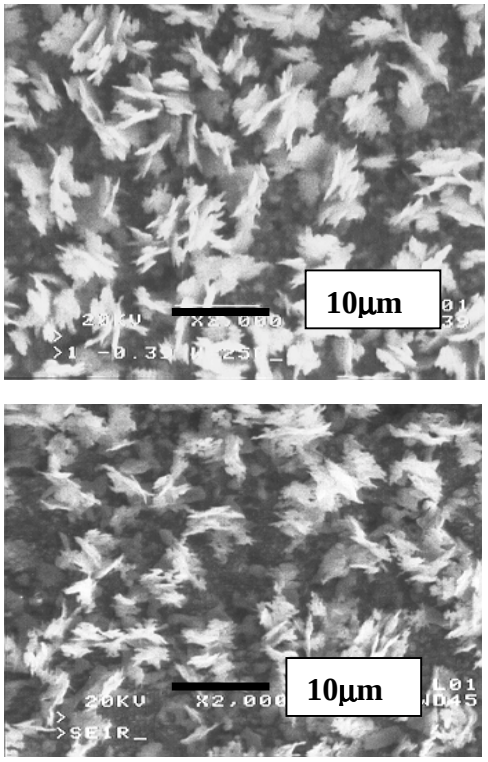


Figure 6**:** SEM micrographs of thin film electrodeposited at -0,39 V/ (Ag/AgCl), rotation speed 250 rpm, (a): as deposited, (b): annealed in flowing argon at 350 degrees during 15 min

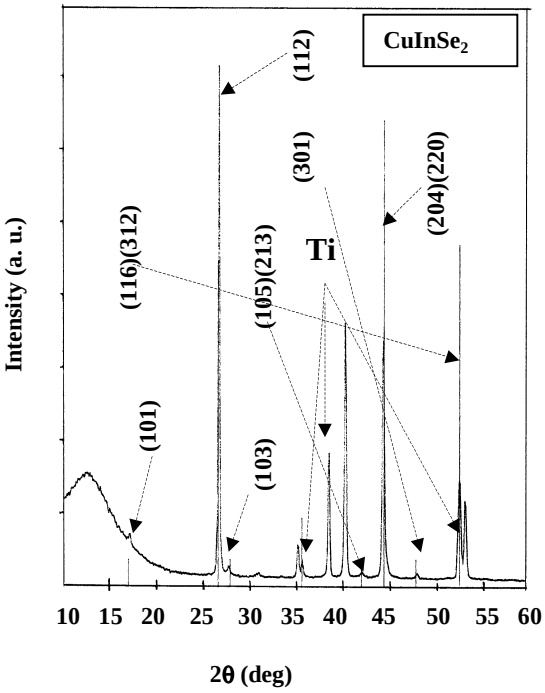


Figure 8 : X-ray diffraction of $CuInSe_2$ thin film electrodeposited at -0,57 V/ (Ag/AgCl), ω = 250 rpm and annealed at 350 °C in flowing argon during 15 min

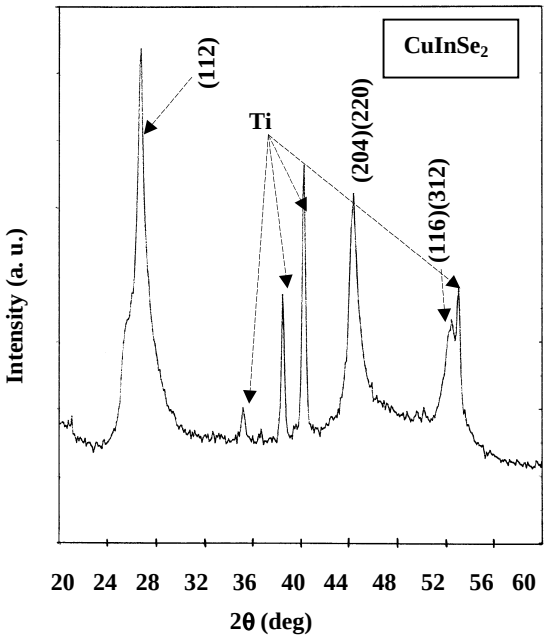


Figure 7 : X-ray diffraction of as deposited $CuInSe_2$ thin film electrodeposited at -0,57 V/ (Ag/AgCl), ω = 250 rpm

Characterizations with X-rays

The deposits of $CuInSe_2$ for more the share were characterized by x-rays diffraction before and after annealing under an atmosphere of argon at a temperature of 350 degrees and for one length of time equal to 15 minutes. The electrodeposited films present before annealing wide

peaks of low intensity corresponding to the reflexions of the (112), (204)(220) and (116)(312) plans of $CuInSe_2$ (Figure 7). The x-rays diffraction diagrams for these films do not present any characteristic line because the films deposited are amorphous or nanocrystalline. This is due to the small degree of crystallinity of these films. A thermal processing proves to be necessary to obtain well crystallized films. The peaks observed before annealing can correspond to the two phases of $CuInSe_2$ to knowing sphalerite and chalcopyrite. When the electrodeposited films have undergoes a thermal processing during 15 minutes at 350°C and under atmosphere of argon, small peaks corresponding to the (101), (103), (211), (105)(213) and (301) plans appear in the x-rays diffraction diagrams (Figure 7). The peaks (101), (103) and (211) are specific to the chalcopyrite phase of $CuInSe_2$ [JCPDS 23-209]. Figure 7 also shows that after annealing the intensity of the peaks of diffraction increases clearly and the full width at half maximum (FWHM) becomes narrower. Let us note that this diagram (Figure 8) highlights well the fact that the grains of $CuInSe_2$ grow following the preferential direction (112).

The size of the cristallites, determined by the Sherrer's formula from the XRD analysis of as deposited and heat treated $CuInSe_2$ films grows from 8.56 nm to 141 nm (analysis of the (112) peak width).

3. TEM characterizations

To confirm the existence of only the chalcopyrite phase of $CuInSe_2$ within our films, we made analysis of electronic diffraction by transmission with the TEM. The identification by the x-rays diffraction is made difficult by the overlapping of the peaks corresponding to the various phases. Figure 9 shows electronic diffractions in transmission obtained on films deposited at -0,5 V vs Ag/AgCl after annealing during 15 minutes under argon at the temperature 350 degrees. Table 1 represents the interreticular distances of the rings with the corresponding Miller indexes and the various phases obtained after electronic diffraction analysis with the TEM of thin films electrodeposited at the potentials -0.48 and -0.5 V vs Ag/AgCl and ω = 250 rpm after annealing at 350 degrees in flowing argon during 15 minutes. Figure 10 shows the rings of diffraction of a $CuInSe_2$ film before annealing. These rings are relatively fuzzy because of the bad crystallinity of the film. The three rings observed gave by direct measurement to the microscope, the d values (interreticular distances) which correspond to those given by JCPDS (23-209) card. Figure 11 shows the electronic diffraction photograph of a thin film electrodeposited at the potential -0.57 V vs Ag/AgCl after annealing under argon during 15 minutes at the temperature 350 degrees, this photograph represents the chalcopyrite phase of $CuInSe_2$ (Table 2). After having undergoes an annealing at temperature 350°C during 15 minutes under an atmosphere of argon, the films of $CuInSe_2$ deposited at -0.57 V / (Ag/AgCl) present in addition to the three rings observed without annealing, other rings clearer (Fig.10) with the corresponding diffraction points. Analysis of the deposit carried out at the potential -0.62 V vs Ag/AgCl also led to the mixture of the Cu_2Se, CuSe and $CuInSe_2$ phases. We can thus conclude that the $CuInSe_2$ phase can be produced in a range of potential ranging between-0.45 V and -0.7 V vs Ag/AgCl. The best should be stoichiometric. We thus analyzed the elementary composition of films by x-ray fluorescence (EDX) (Table 3). They are obtained for potentials ranging between -0.5 V and -0.6 V and after thermal processing. The films deposited under these conditions are homogeneous and present broad crystals of $CuInSe_2$ with large grains (mean diameter 3 to 6 μm). This show that the crystallinity of film himself is being improved by thermal processing and confirm the result that we have find by the X-rays diffraction.

4. CONCLUSION

$CuInSe_2$ thin films are prepared by electrodeposition from an aqueous solution containing citrate ions as complexing agent.

Depending on the deposition potential we can make binary alloy like CuSe and / or Cu_2Se for more anodic potentials. Whereas the chalcopyrite phase of $CuInSe_2$ with a mixture of the secondary phases CuSe and Cu_2Se can be obtained for more cathodic potentials.

At the specific potential -0.57 V / (Ag/AgCl) which correspond to the inflection point on the polarization curve, only the chalcopyrite phase of $CuInSe_2$ is obtained.

Annealing of the $CuInSe_2$ films increases their grain size and improves their crystallinity. Good chalcopyrite $CuInSe_2$ films with a (112) preferential orientation suitable for the production of efficient solar cells are obtained.

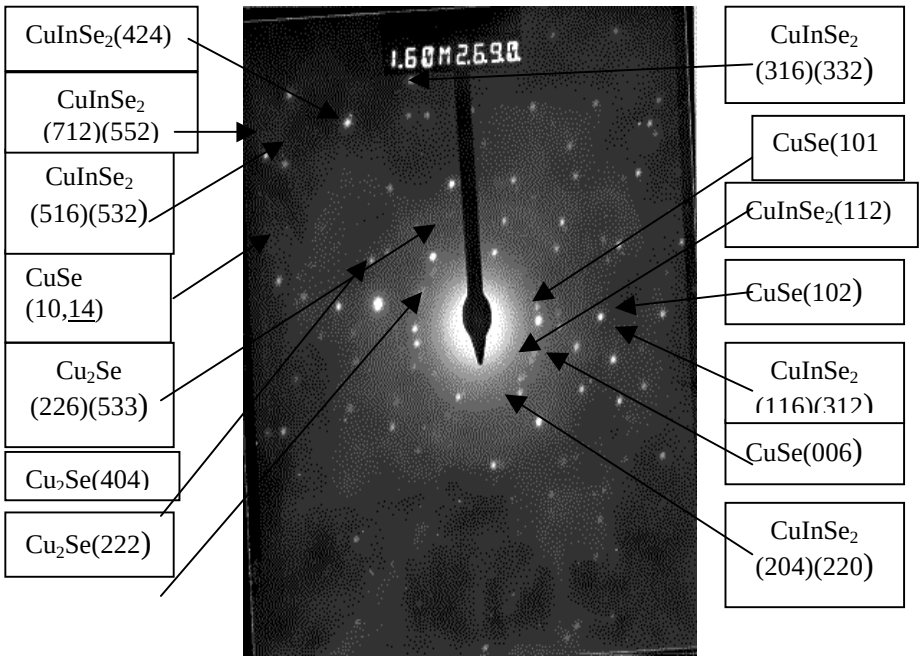
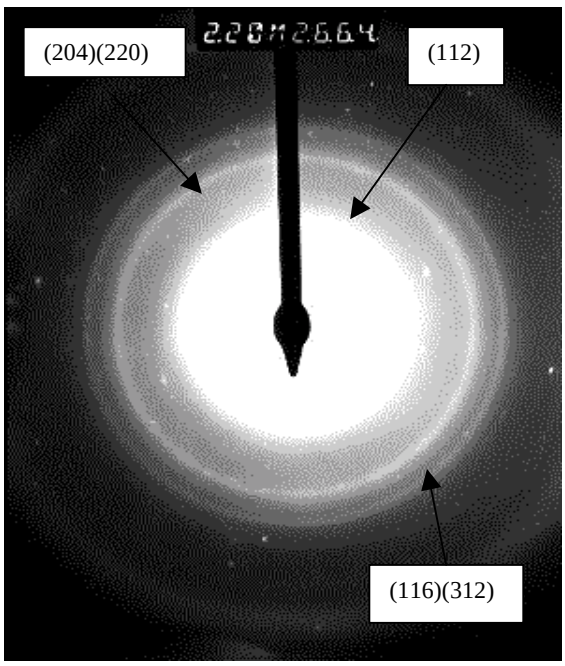


Figure 9: electronic diffraction of thin film electrodeposited at -0,5 V/ (Ag/AgCl), ω = 250 rpm and annealed in flowing argon at 350 °C during 15 min



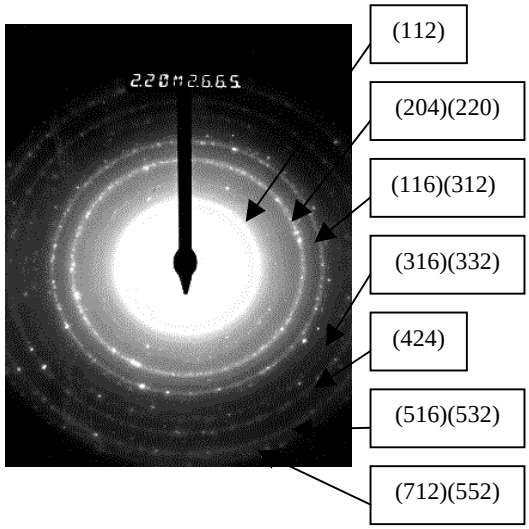


FIG.11: electronic diffraction obtained on a thin film electrodeposited at -0,57 V/ (Ag/AgCl), ω = 250 rpm after annealing in flowing argon at 350 degrees during 15 min

Figure 10: TEM photograph of as deposited thin film electrodeposited at -0,57 V/ (Ag/AgCl) and ω = 250 rpm

d_{hkl} (find)	d_{hkl} (JCPDS)	Phase	(hkl)	Int.(%)
2,06	2,06	Cu_2Se	(404)	100
2,06	2,04	$CuInSe_2$	(204)(220)	100
1,19	1,18	$CuInSe_2$	(424)	60
3,34	3,34	$CuInSe_2$	(112)	70
3,38	3,38	Cu_2Se	(222)	80
1,34	1,33	$CuInSe_2$	(316)(332)	35
1,16	1,16	CuSe	(10,14)	40
0,97	0,97	$CuInSe_2$	(516)(532)	30
1,75	1,74	$CuInSe_2$	(116)(312)	85
0,81	0,809	$CuInSe_2$	(712)(552)	30
3,21	3,18	CuSe	(102)	90
3,35	3,35	CuSe	(101)	60
2,88	2,88	CuSe	(006)	100
1,76	1,76	Cu_2Se	(226)(533)	70

Table 1: interreticular distances, Miller indexes and different phases obtained after TEM electronic diffraction analysis of thin films electrodeposited at the potentials -0,48 and -0,5 V/ (Ag/AgCl), ω = 250 rpm after annealing in flowing argon during 15 minutes at 350 degrees.

Anneau number	d_{hkl} (mesuré)	d_{hkl} (JCPDS) 23-209	Intensity (%)	(hkl)
1	3,35	3,34	70	(112)
2	2,06	2,04	100	(204)(220)
3	1,75	1,743	85	(116)(312)
4	1,34	1,327	35	(316)(332)
5	1,19	1,18	60	(424)
6	1,05	0,977	30	(516)(532)
7	0,81	0,809	30	(712)(552)

Table 2: chalcopyrite phase of $CuInSe_2$ obtained by diffraction of electrons on a thin film elecrodeposited at -0,57 V/ (Ag/AgCl) and annealed in flowing argon at 350°C during 15 min

Essai N°	1	2	3	4	5	6
Potential V vs Ag/AgCl	-0.24	-0.39	-0.48	-0.5	-0.57	-0.62
EDX (at%)Cu	65.7	58.6	40.3	36.6	24.6	28.5
EDX (at%)In	0.3	0.2	20.9	24.7	25.4	25.1
EDX (at%)Se	33.1	41.2	38.8	38.7	50	46.4
RX analysis ω=250 rpm	Cu_2Se	Cu_2Se	$CuInSe_2$	$CuInSe_2$	$CuInSe_2$	$CuInSe_2$
RX analysis ω=500 rpm	Cu_2Se	Cu_2Se + CuSe	$CuInSe_2$	$CuInSe_2$	$CuInSe_2$	$CuInSe_2$
TEM analysis			$CuInSe_2$+ Cu_2Se+ CuSe	$CuInSe_2$+ Cu_2Se+ CuSe	$CuInSe_2$	$CuInSe_2$+ Cu_2Se+ CuSe

Table 3: Results of electronic diffraction and X-rays analysis and microanalysis X (EDX) carried out on films electrodeposited at different potentials and annealed at 350 °C in flowing argon; ω = 250, 500 rpm

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