Revue des Energies Renouvelables Vol. 11 N°1 (2008) 19 – 24
DOI: https://doi.org/10.54966/jreen.v11i1.52

Characterization of $CuInSe_2$ thin films elaborated by electrochemical deposition

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(reçu le 10 Février 2008 – accepté le 30 Mars 2008)

Abstract - *In this paper, we report the elaboration and characterization of $CuInSe_2$ thin films prepared by electrochemical deposition technique. The thin films were deposited at room temperature using two electrodes cell configuration, then they annealed under argon atmosphere at 300 °C for 30 and 45 mn. The structural and optical properties of the films were characterized respectively by means of X-ray diffraction and transmission spectrophotometer measurements. The band gap of the samples was estimated using optical transmittance. All elaborated films show the tetragonal chalcopyrite $CuInSe_2$ with preferential orientation (112) plan. X- ray diffraction and calculation of grain size of the films show that the film annealed at 300 °C during 45 mn presents a good cristallinity, high grain size and its band gap is close to 1.1 eV.*

Résumé - *Dans cet article, nous rapportons l'élaboration et la caractérisation des couches minces de Cuivre Indium Sélénium ($CuInSe_2$) par la technique d'électrodéposition. Les couches minces ont été déposées à température ambiante en utilisant un système à deux électrodes. Après l'élaboration, les couches ont subi un recuit thermique sous atmosphère d'argon à une température de 300 °C durant 30 et 45 mn. Les propriétés structurale et optique de ces couches ont été caractérisées par la diffraction des rayons X (DRX) et les mesures de la transmittance optique. L'énergie du gap est estimée à partir de l'absorbance optique. Tous les films montrent la phase $CuInSe_2$ ayant la direction (112) comme axe privilégié de croissance. Les spectres de diffraction des RX et le calcul des tailles de grains montrent que le film qui subit un recuit à 300 °C durant 45 mn présente une meilleure cristallinité et une taille de grains relativement élevée, son énergie de gap est de l'ordre de 1.1 eV.*

Keywords: Copper indium diselined $CuInSe_2$ - Electrochemical - Thin films.

1. INTRODUCTION

A copper indium diselenide thin film ($CuInSe_2$) is a direct band gap material; it has 1.03 eV in band gap, high optical absorption coefficient (10^6 cm^{-1}), reasonable work function, good stability and largest efficiency (it achieved an efficiency of 17 %) [1, 2]. Therefore, these properties make $CuInSe_2$ a promising material for photovoltaic applications [3].

It is known that the electrical, optical, morphological and structural properties of this material are strongly influenced by the technique used for the elaboration and by the several experimental parameters.

Several techniques are used for elaborating this material, we cited: Close spaced vapour transport (CSVT) [4], RF sputtering [5, 6], Coevaporation [7], Spray pyrolysis [8, 9], Atomic layer deposition [10], Electrodeposition [11], etc. The last technique is one of the suitable techniques for the elaboration of low cost thin films [12].

In this work, the $CuInSe_2$ films were elaborated via the electrochemical deposition technique. They were deposited on tin oxide coated glass substrate (ITO) at fixed voltage, and then annealed at 300 °C under argon gas atmosphere during different times. The effects of annealing time on the structural and optical properties of the resulted films were studied respectively via the X-ray diffraction and the transmission spectrophotometer measurements.

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2. EXPERIMENTAL

Copper indium diselenide ($CuInSe_2$) thin films were electrochemically deposited using two electrode cell configurations. A platinum plate was used as the counter electrode (anode) and the ITO covered glass was used as the working electrode (cathode).

Cu-In-Se was electrochemically deposited from a solution containing 10 mM of $CuCl_2$, 20 mM of $InCl_3$ and 40 mM of SeO_2. This solution is dissolved in de-ionized water. The thin films were deposited at room temperature using deposition potential of 8 V during 15 mn, and then the as deposited films were annealed under argon atmosphere at 300 °C for 30 and 45 mn.

The structural and optical properties of the films were characterized respectively by means of X-ray diffraction and transmission measurement. The X-ray diffraction and optical transmission measurement of the films were carried out respectively by Philips PZ 3710 X-ray diffractometer using Cu $K\alpha$ radiation in scanning angle range of 0-70° and Shimadzu mode UV-3101 PC spectrophotometer.

The thickness T of the elaborated films was theoretically estimated as follow [13, 14]:

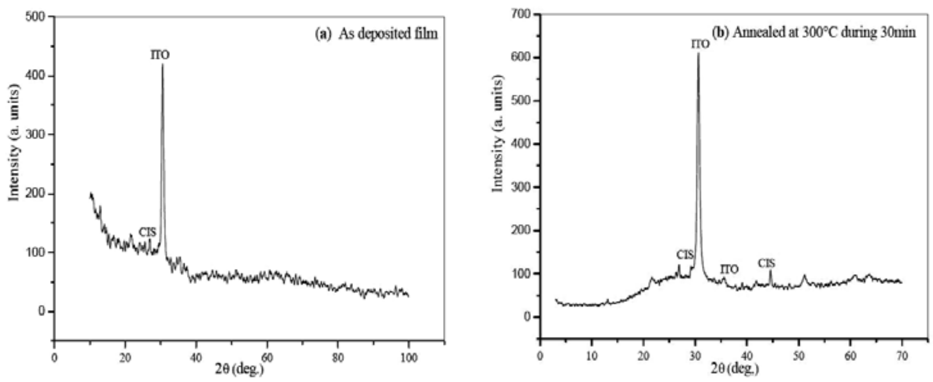
$$T = \frac{1}{nFA}\left(\frac{itM}{\rho}\right) \tag{1}$$

where $n = 13$ is the number of electrons transferred, F is the Faraday's number, A is the electrode area, i is the applied current, t is the deposition time, M = 336.28 g/mol is the formula weight and ρ = 5.77 g/cm^3 is the density.

3. RESULTS AND DISCUSSION

Figure 1.(a), (b) and (c) shows the X- ray diffraction patterns of the elaborated samples respectively for the as deposited and annealed samples at 300 °C for 30 and 45 mn. All these spectra appear the peak located at $2\theta \approx 26.8°$, this peak is the most intense peak given in the JCPDS file for $CuInSe_2$ phase [15] and is corresponding to the (112) plan.

On the other hand the films annealed at 300 °C for 30 mn (Fig. 1.(b)) and 45 mn (Fig. 1.(c)) appears the peak situated at $2\theta \approx 43°$, which corresponds to the second intense peak of the $CuInSe_2$, they correspond to the (204)/(220) plan. We note that the peak corresponding to (204)/(220) plan in the as deposited film is absent (Fig. 1.(a)).



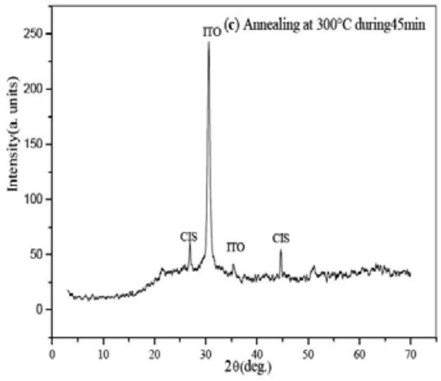


Fig. 1: XRD patterns of Cu-In-Se as deposited on ITO coated glass substrate by electrodeposition technique (**a**), and annealing at 300 °C for (**b**) 30 mn and (**c**) 45 mn

The intensity, d-spacing of (112) plan and the grain size of different elaborated thin films are recapitulated in **Table 1**. The grain size is calculated using the Scherre equation [16].

We note that, the film annealed during 30 mn present the high intensity of (112) plan and also the film annealed at 45 mn present the high grain size. Fig. 2. present the optical transmission respectively of as deposited film, annealed film at 300 °C for 30 and 45 mn. For all films there is a rapid decrease in transmittance value near the absorption edge.

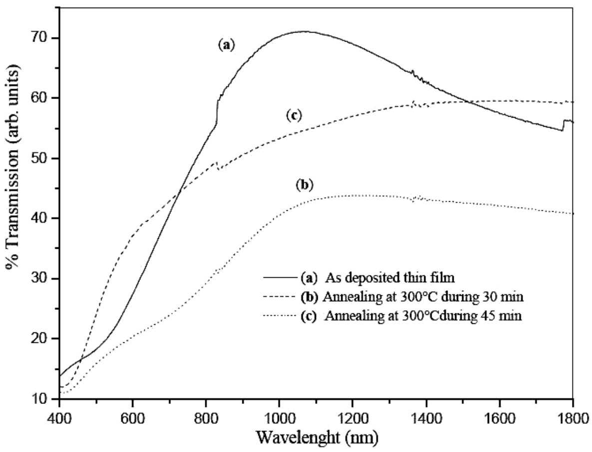


Fig. 2: Optical transmission versus wavelength of $CuInSe_2$ for (**a**) as deposited film, (**b**) annealed at 300°C during 30 mn, and (**c**) annealed at 300°C during 45 mn

It is well known that $CuInSe_2$ is a direct gap semiconductor, so the absorption coefficient in the region of strong absorption obeying the equation:

$$\alpha = \frac{A}{h\nu}\left(h\nu - E_g\right)^{1/2} \tag{2}$$

where α is the absorption coefficient, h is the Planck constant, ν is the radiation frequency, E_g is the band gap energy and A is a constant which depends on the nature of the radiation [17, 18]. The E_g value of the different thin films ratio are evaluated from the plot of squares of optical absorption coefficient $(\alpha h \nu)^2$ as function of photon energy $(h \nu)$ (Fig. 3. (a), (b) and (c)). The results are given in the last column of **Table 1**.

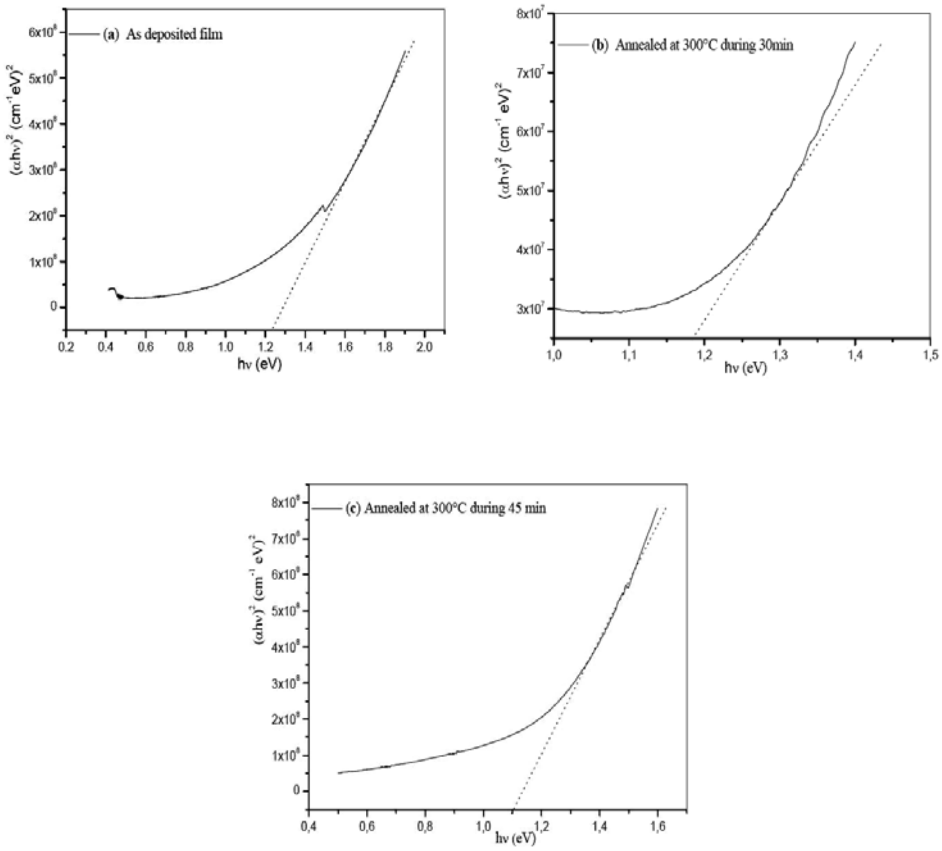


Fig. 3: Squares of optical absorption coefficient $(\alpha h \nu)^2$ versus photon energy $(h \nu)$

Table 1: The intensity and d spacing of (112) plan, grain size and band gap of elaborated films

	As deposited film	**Annealed at 300°C during 30 mn**	**Annealed at 300°C During 45 mn**
(112) plan intensity (a. units)	20.9	29.3	21.47
d_{112} (A°)	3.319	3.311	3.311
Grain size (nm)	112.65	272.27	291.72
Band gap energy (eV)	1.23	1.18	1.10

4. CONCLUSION

In this study, the $CuInSe_2$ thin films were electrochemically deposited using two electrode cell configurations; this configuration was successfully used to obtain $CuInSe_2$ thin films with good crystalline and high stability. All elaborated films show the tetragonal chalcopyrite CuInSe2 with preferential orientation (112) plan. We have found that the annealing time have great influence on the structural and the optical properties of the films. We note also that the film annealed at 300 °C during 30 mn presents the high intensity of (112) plan and the film annealed during 45 mn presents the high grain size, it is around 291.7A°. The band gap of the samples was estimated using optical transmittance; it is equal to 1.2 for as deposited film, and 1.1 eV for films annealed at 300 °C during 30 and 45 mn.

Acknowledgment

The authors would like to thank Mr. S. Khaled for their assistance in manuscript redaction.

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