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Structural and optical modeling of electro deposited $CuInSe_2$ thin films

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Abstract: The ternary semiconductor CuInSe2 is one of the most advantageous materials for the manufacturing of thin film solar cells. In this study, CuInSe2 thin films were prepared at room temperature using the electrodepositing method. The as-prepared films were found to be amorphous. The CuInSe2 films were crystallized in a tubular resistive furnace, and characterized by means of the the X-ray diffraction (XRD) and UV-VIS-NIR spectroscopy techniques. The parameters to optimize are the temperature and duration of the annealing time, and the Cu/In ratio in the precursors.
Keywords: Semiconductor, Chalcopyrite, thin layers, CuInSe2, Photovoltaic.

1 Introduction

The I-III-VI_2 semiconductors group that crystallize in the chalcopyrite structure are of considerable interest in solar applications. In these compounds, the ternary $CuInSe_2$ (CIS) is currently considered the most promising material as an absorbent in the photovoltaic conversion because of its energy bandgap (Eg ≈ 1 eV) and its relatively high absorption coefficient($\alpha = 10^4 - 10^5$ cm^{-1}) [1].

Indeed, heterojunction thin films using CdS and ZnO – based optical windows have a significant efficiency of about 14.1% [2], a remarkable stability and low manufacturing cost.Various techniques have been developed to prepare $CuInSe_2$ thin films such as plating, sputtering [3], co-evaporation [4, 5] etc. The plating methods are more beneficial than physical ones; it is much less expensive, and can be easily implemented on a large scale, and parts of complicated shapes can be covered.The plating can be performed at low temperatures, which limits the effects of interdiffusion between the layers.Electrodeposited materials also have a strong tendency to grow as epitaxial, crystalline orientation can be induced by the substrate [6, 7]. CIS films have some unique characteristics (bandwidth, absorption coefficient, diffusion length of minority carriers) specifically related to photovoltaic applications. So far, some works [8, 9] highligh the close link between the optical properties and the final yield of the solar cells.The absorption coefficient and the band-gap energy are considered as the most influential parameters in the development of semiconductor devices.These two parameters generally depend on the stoichiometry, defects and chemical parameters of the film growth [10]. This work aims to show how we can tune the structural and

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optical properties of electrodeposited $CuInSe_2$thin films while varying Cu/In ratio and temperature annealing.

2 Experimental techniques

Thin CIS films have a thickness of 1 µm were prepared by the electroplating technique.The latter consists, in general, to the reduction of metal ions in aqueous electrolytes, organic solvent, or molten salt.The deposit may, in principle, be accomplished through two different paths: A method of electroplating in which electrons are supplied by an external energy source. A process (autocatalytic) of electroless deposition in which a reducing agent in solution is the source of electrons[11]. This reaction occurs at the interface between the solution and the cathode.The simplest formula that governs the reaction at the cathode in aqueous media is (1):

$$M^{+n} + n\bar{e} \longrightarrow M \qquad (1)$$

The films were deposited on SnO_2:F –coated glass (taken as a cathode), the polarization of the electrodes will cause a migration of metal ions to the substrate. To form $CuInSe_2$ films, electrolyte solutions composed of various amount of $CuCl_2$, SeO_2 and $InCl_3$were prepared. To obtain intrinsic stoichiometric $CuInSe_2$ films, we adjust the $CuInSe_2$ in ratio and for this purpose the $CuCl_2$ concentration was varied between 5mM/l and 7mM/l, while SeO_2 and $InCl_3$ concentrations were kept constant, at 12 mM/l and 6 mM/l, respectively. The recommended pH for plating is 1.5 [12]. In the various $CuInSe_2$deposition tests, the value of the voltage of the reference electrode was taken equal to -700 mV for a plating period of 15 min.The endothermic reaction can be written as follows:

$$Cu^{2+} + In^{3+} + 2H_2SeO_3 + 8H^+ + 13\ e^- \longrightarrow CuInSe_2 + 6H_2O$$

The samples were dried in an oven at a temperature between 60° C and 70° C for a period ranging between 20 min and 30 min. The drying step improves the adhesion of the deposit and preserves the quality of the compound. The obtained films were found to be amorphous. In order to obtain crystallized films a heat treatment in nitrogen ambient was applied to all samples.

3 Results and discussions

3. 1 Structural characterization

The X-ray diffraction (XRD) patterns of the synthesized $CuInSe_2$ thin films crystallize in the chalcopyrite and sphalerite phases, characterized by (112), (220) and (116) main directions for Cu/In = 0.8 (Figure 1-a), and only in the chalcopyrite structure ((112) orientation)for Cu/In = 1 and Cu/In= 1.2 (Figure 1-b). The distortion ratio ***c/a***calculated from the lattice parameters ***a***and ***c*** calculated from the XRD patterns confirms that we are in presence of the chalcopyrite phase (Table 1) . Indeed, we see that the main peak intensity increases as a function of annealing temperature and is maximum for a temperature of 300°C for an annealing time ranging from 1 to 2 hours.

Table 1. Calculated crystal parameters

Thin layer	**a (Å)**	**c (Å)**	**c/a**
Chalcopyrite	5.78	11.61	2.00
sphalerite	5.75	11.65	2.02

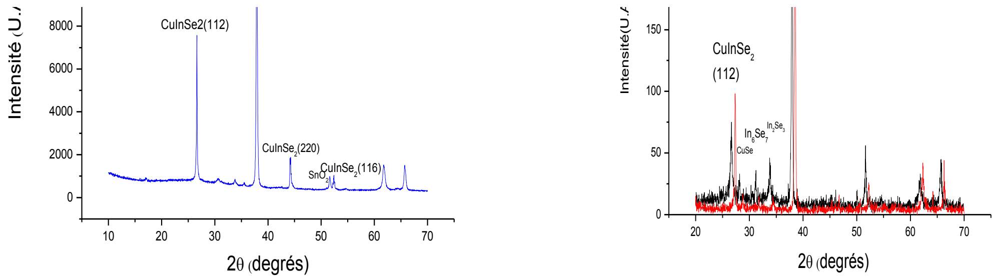

Fig. 1. X-ray Diffraction patterns of electrodeposited $CuInSe_2$ thin films on SnO_2.
(a) for Cu / In = 0.8 and (b) for Cu / In = 1 and 1.2. The annealing temperature and duration are 300°C and s, respectively

3.2. Optical modeling

Figure 2 depicts the transmission and reflection spectra of a $CuInSe_2$ film having a thickness of 1 µm. One may notice the absence of interference fringes in the spectra, which dues to diffusion phenomena. The film shows low transmission values in the visible range, and reaches about 22% at 950nm. The reflection spectrum has low values in the400 – 1800 nm spectral range, and begins increasing from 2000 nm. This demonstration the prepared $CuInSe_2$ films bahave as good absorber. The experimental curves of Figure 2 were used to evaluate the optical indices of the $CuInSe_2$ films using a computing program, where the model consists of considering a multilayered film composed of SnO_2 and $CuInSe_2$ having refractive indices and thicknesses$(\tilde{n}_1, d_1)$ and $(\tilde{n}_2, d_2)$, respectively.

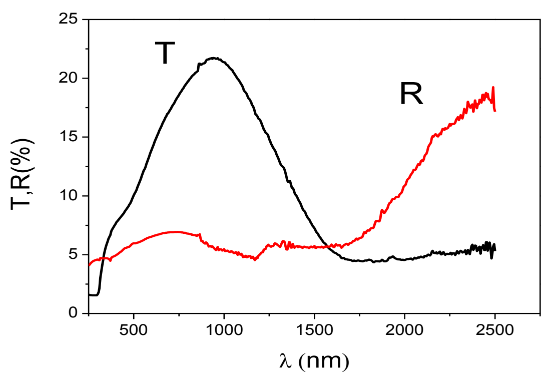

Fig. 2. Transmission and reflection spectra of a 1 µm thick$CuInSe_2$ film

In this situation, considering E_0^+ *and* E_0^- respectively the incident and reflected fields at the entrance of the system, E_{N+1}^+ the the output transmitted field and S the scattering matrix, which is the product of the transfer matrices associated with each layer expressed in terms of the reflection and transmission coefficients at each interface (I_i) and the matrix propagation (L_i) that depends on the complex phase of the wave introduced within each layer.

One can the write:

$$\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = S \begin{pmatrix} E_{N+1}^+ \\ 0 \end{pmatrix}$$

$$S = I_0\, L_1\, I_1\, L_2 I_2 L_3 \ldots\ldots\ldots I_{N-1} L_N$$

$$I_i = \frac{1}{t_i}\begin{pmatrix} 1 & r_i \\ r_i & 1 \end{pmatrix} \qquad L_i = \begin{pmatrix} e^{-i\beta_i} & 0 \\ 0 & e^{i\beta_i} \end{pmatrix}$$

$$r_i = \frac{r_i - r_{i-1}}{r_i + r_{i-1}}\ ; \quad t_i = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_{i-1}}$$

$$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$$

$$r_c = \frac{S_{21}}{S_{11}} \qquad t_c = \frac{1}{S_{11}}$$

r_c and t_c are the complex Fresnel coefficients related to the reflection and transmission, respectively.The expressions of the reflectivity and the transmission can be wriiten as:

$$R = |r_c|^2 \quad et \quad T = \frac{n_{N+1}}{n_0}|t_c|^2$$

Figures 3 (a) and 3(b) give the indices ***n*** and ***k*** of the $CuInSe_2$ thin film over the entire spectral range [250 – 2500] nm. One may notice a very small fluctuation of the refractive index of the $CuInSe_2$ films around 2.25. Similarly the theoretical values of the refractive index ***n*** and the extinction coefficient ***k*** well fit the experimental onesusing the Cauchy model (Figure 3):

$$n = a + b/\lambda^2 + C/\lambda^4$$

$$k = a/\lambda + b/\lambda^3 + c/\lambda^5$$

The optical parameters (***n***,***k***) were calculated by solving the following nonlinear equations:

$$\begin{cases} R_{exp} - R_{th}\,(n, k, \lambda) = 0 \\ T_{exp} - T_{th}\,(n, k, \lambda) = 0 \end{cases}$$

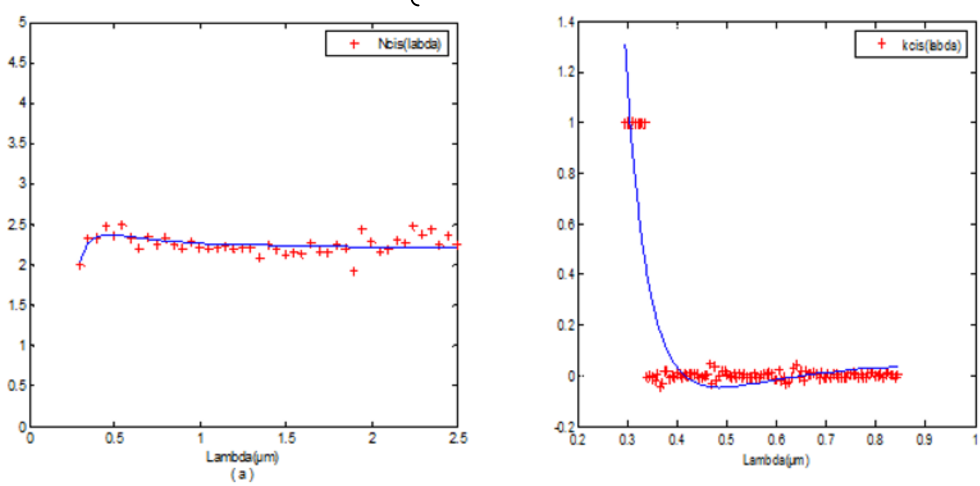

Fig. 3. Variation of the refractive index n (a) and extinction k (b) of CuInSe2 thin layer. The annealing temperature T=300 °C, annealing duration = 2 hours, and Cu/In = 1) (*: Experiment, __: Theory).

The previously determined values of ***n*** and ***k***, have yielded good agreement between experimental and theoretical values of R and T (Figure 4) over the entire spectral range [250-2500] nm.The absorption edge determines the band-gap energy of the film using the following equation:

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

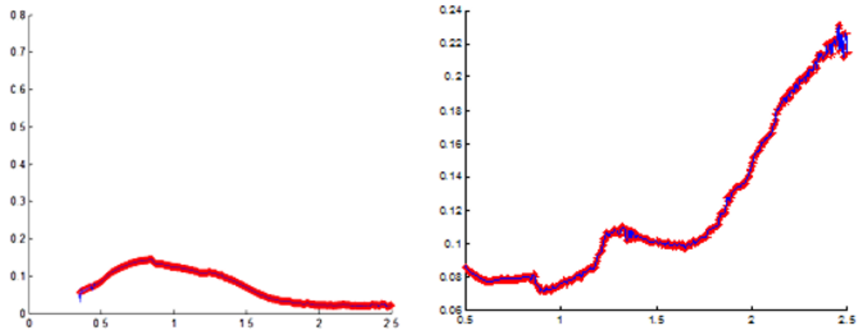

Fig. 4 Transmission and reflection spectra of $CuInSe_2$films. The annealing temperature T=300 °C, annealing duration = 2 hours, and Cu/In = 1) (***) experimental and theoretical (___) de.

The band-gap energy of electrodeposited $CuInSe_2$ is about 1.35 eV, and is not practically affected by the annealing temperature (Figure 5). The resulting gap is ideally suitable for photovoltaic conversion of solar energy.

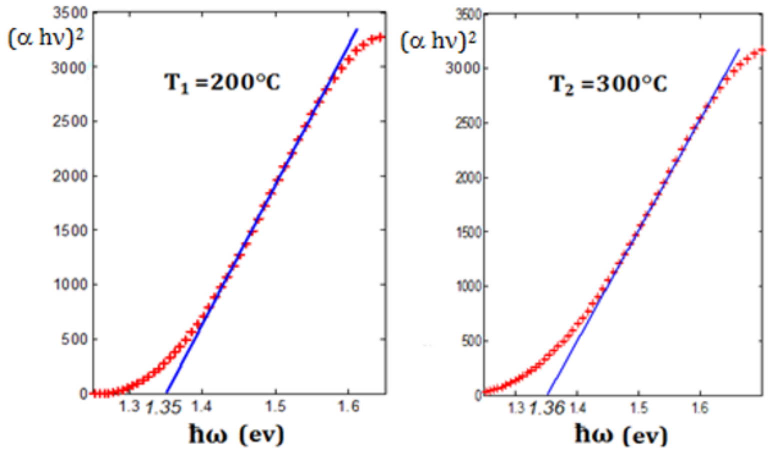

Fig. 5. Variation of $(\alpha\, h\nu)^2$ versus the incident photon energy for annealing temperatures equal to 200 °C and 300 °C

4 Conclusion

Crystallized chalcopyrite $CuInSe_2$ films characterized by the main (112)crystallographic orientation were electrodeposited on SnO_2 substrates. The intensity of the (112) XRD line reaches a maximum at a temperature of 300 °C for annealing periods ranging from one to two hours.The best quality structure corresponds to aCu/In ratio in liquid solution equal to 1 and 1.2.The optical modeling showed that the electrodeposited $CuInSe_2$has a quasi-constant refractive index of about 2.25.The extinction coefficient k, in turn, decreases in the spectral [250 - 1000] nm range and incrases in the free carrier absorption zone between [1000 -2500] nm. The bad-gap energy of the $CuInSe_2$films is about 1.35 eV.

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