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# Preparation and characterization of $CuInSe_2$ electrodeposited thin films annealed in vacuum

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ABSTRACT

The effect of the annealing temperature on the $CuInSe_2$ (CIS) electrodeposed films on FTO substrates has been investigated. Followed by different annealing, in vacuum and for different temperatures, X-ray diffraction has proved that the $CuInSe_2$ films have chalcopyrite structure oriented along the (1 1 2) direction with good crystallinity at 400 °C.

From the evolution of the full width at half maximum (FWHM) of the (1 1 2) peak, we have estimated the grain size versus the annealing temperature. The results show that the grain size increases from 0.45 to 0.75 μm with the annealing temperature. The morphological, optical and electrical properties of the CIS films have been investigated respectively, by the scanning electron microscopy (SEM), UV–vis spectroscopy and *I–V* characteristics. The band gaps of the CIS films also shows an evolution when the temperature is varied. In fact the band gap decreases from 1.24 eV at 250 °C to 0.98 eV at 450 °C. The electrical characterization of the junction Al/CIS/FTO shows an interesting Schottky rectifying behavior.

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## 1. Introduction

In the recent years, the ternary chalcopyrite compounds of the groups I–III–VI direct gap semiconductors have taken considerable attention for solar cell applications because of their material properties as an absorber layer for tandem solar cell [1]. They also have been used for the fabrication of light emitting diodes, optoelectronics and nonlinear optical devices [2]. It has been shown that, their band gaps goes between 0.8 and 2.0 eV when changing the compositions of the constituent elements in the structure and they can be grown either P or N type [3]. However, among chalcopyrite compounds, the CIGS thin film solar modules have shown good stability, high efficiency and low production cost [4–6]. Likewise, the $CuInSe_2$ (CIS) is one of the most promising photovoltaic thin films. It has been widely studied for its high absorption coefficient ($\alpha \approx 10^5\ cm^{-1}$) to the sunlight with a well-suited direct band gap of 1.08 eV and it has been used as absorber materials [7–9]. However, the possibility to control, modify and optimize the film properties relies on the well established knowledge of its physical properties. Some physical deposition techniques, as evaporation or molecular beam epitaxy, need high vacuum conditions with high production costs [10]. Hence, the low cost electrodeposition technique has been used intensively for the industrial growth for large semiconducting solar cells [11,12]. A great deal of efforts has been made to develop this technique with annealing process in vacuum [13].

In this work, the CIS thin layers have been prepared by electrodeposition and have been annealed in vacuum. We give in the next sections a description of the experimental preparation followed by an investigation of the structural, morphological, optical and electrical properties. The (*I–V*) measurement in dark has been applied on the Al/CIS/FTO junction.

## 2. Experimental CIS preparations

The CIS films have been electrodeposited on $1.5 \times 1.5\ cm^2$ glasses substrates coated with thin FTO films of 1200 nm of thickness. At the first step, the glass substrates were cleaned successively by acetone and methanol for 20 min for each one. Aqueous solutions containing the analytical reagents $CuCl_2$, $InCl_3$, $SeO_2$ and sodium citrate were prepared. The concentration of the solution was chosen to be 7 mM for the $CuCl_2$, 6 mM for $InCl_3$, 12 mM for $SeO_2$ and 0.4 M for the sodium citrate which was chosen to be a complexing agent [14]. The pH of the solution was adjusted to 1.68 by adding HCl. The electrodeposition was carried out with a Potentiostat–Galvanostat electrochemical instrument type Powerstat-05 CE purchased from Nuvant Systems Inc. It Includes 5-lead cables (three electrodes, sense and ground lead) and Lab View based EZware software that controls the cell potential or current. The Powerstat-05CE delivers

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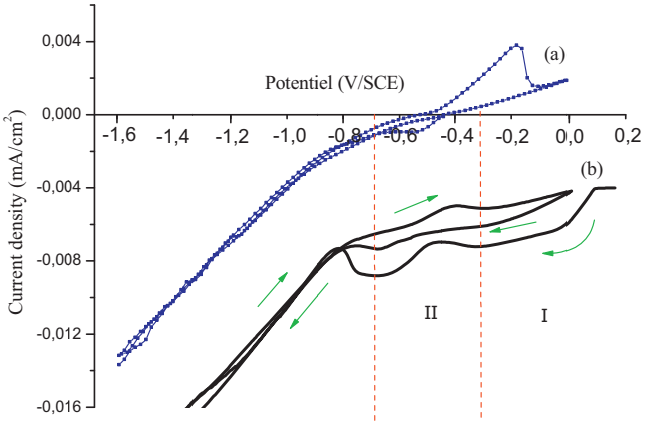


**Fig. 1.** Cyclic voltammogram of FTO/glass electrode in: (a) 0.4 M sodium citrate solution. (b) 7 mM $CuCl_2$, 6 mM $InCl_3$, 12 mM $SeO_2$ and 0.4 M citric acid solutions.

±5 A (±10 V versus reference), 3 μA resolution, 500 V/s scan rates and ±15 V compliance.

The typical cyclic voltammogram of the substrate in 0.4 M sodium citrate solution is illustrated in Fig. 1a. It shows that the electrode reacts with the electrolyte in a wide potential range from 0 to −1.6 V measured through an Ag/AgCl reference electrode. In the same way, the electrochemical behavior of the Cu-In-Se system with sodium citrate was studied by cyclic voltammetry on FTO/glass electrode as shown in Fig. 1b. Looking into the minimum of the reduction of metallic ions, two significant cathodic peaks are observed at potentials between −0.2 to −0.8 V. Two potential regions are observed from 0.2 to −0.32 V (region I) and from −0.32 to −0.7 V (region II). It is well known that the XRD analysis has proved the formation of binary alloys like CuSe and $Cu_2Se$ in region I and ternary in region II [15]. To depose the CIS films, the potential of the working electrode was maintained at a constant value fixed at −0.7 V during 20 min [16]. A thin dark-blue film was deposed on the FTO substrate. Finally, the sample was extracted from the cell and carefully washed with deionized water.

The annealing of the CIS films was done in enclosed vacuum space through different steps where we stabilize the temperature for 10 min for each increasing of 50 °C until the final temperature. This procedure was realized to minimize the exhausting of the Selenium from the sample [17]. The temperature of the samples was varied from 200 to 450 °C with heating rate process 20 °C/min. Finally, the samples were cooled down to the room temperature.

The morphological, the structural and the optical characterizations of the CIS thin films were carried out successively by a scanning electron microscope (SEM), X-ray diffractometer (XRD) and UV–vis spectrophotometer.

By evaporation, we have added disk shape of aluminum electrodes of 99.99% purity, on the surface of the samples with 2 mm diameter and 2 μm of thicknesses. The top and the bottom of the formed junctions Al/CIS/FTO are linked to two thin conducting wires. Their electrical properties were tested using AC/DC instrument by measuring their *I–V* characteristics.

## 3. Results and discussion

### 3.1. Morphology of the CIS surface film

Fig. 2 shows the scanning electron micrographs of two CIS thin films, annealed under vacuum, respectively at 250 and 400 °C. The two microstructures consist of dense layers with small crystallites and some large aggregates. The effect of the annealing temperature is visible on the aspect of the surface film. The first micrograph (Fig. 2a) reveals non-uniform grain sizes and non-homogeneous surface with mixture of smaller and larger clusters whereas for the second sample (Fig. 2b), we notice a reduction of clusters size giving a densely-packed and a nearly homogeneous surface [18]. This reduction reinforces the densification of the CIS films and reduces the leakage current due to grain boundaries. This type of film is favorable as absorber layer for the new generation of the photovoltaic solar cells [17].

### 3.2. Structural characterization

The XRD of the CIS films are illustrated in Fig. 3 for different temperatures. Except the marked peaks with triangles of FTO substrate, the dominant line in the spectra is found at 26.74°, it corresponds to the (1 1 2) reflection line. We have localized the principal other peaks which appear at the angles 44.29 and 52.49°, corresponding respectively to the Miller Indices (2 2 0) and (1 1 6) of the ternary CIS [19]. The two main diffraction peaks appearing for the as-deposed films (Fig. 3a), corresponding to (1 1 2) and (2 2 0), indicating the beginning of the formation of the CIS's seed with poor crystallinity [20].

After 30 min annealing in vacuum, the amplitude of the diffraction peaks increased and the full width at half maximum (FWHM) becomes narrow and favorites the (1 1 2) preferential orientation. All the observed peaks in the patterns are in agreement with the theoretical diffraction lines of the chalcopyrite structure [21,22]. Some weaker peaks appear in the XRD patterns (Fig. 3b) which are due to a disorientation of the structure during the heat treatment. In particular, we note the apparition of the peak (1 1 6) at

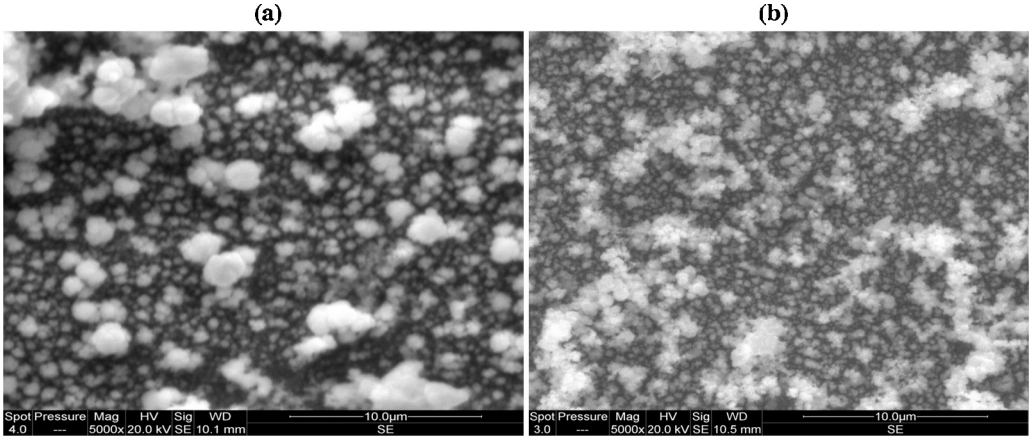


**Fig. 2.** SEM images of CIS thin films annealed at (a) 250 °C (b) and at 400 °C.