Structural and optical properties of CuInSe$_2$

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Thin films of polycrystalline CuInSe$_2$ were deposited on Pyrex substrates using a simple system of close spaced vapor transport (CSVT). The used CSVT system is an open horizontal reactor, this does not require vacuum, a gas flow is enough. During the growth phase, the CSVT system is continuously crossed by argon gas. A study on the influence of the source temperature and the deposition duration on the structural properties of the deposited films is reported. Analyses by X-ray diffraction have shown that these films are polycrystalline and have a chalcopyrite structure. The preferential orientation of the (112) plane was obtained for the films deposited at 550 °C. From the X-ray spectra we calculated the lattice parameters $a$ and $c$, the ratio $c/a$ was found to be close to 2. The characterization of the deposited films by an energy dispersion spectrometer (EDS) has shown that their chemical composition is quasistoichiometric with a ratio Cu/In varying from 0.96 to 1.10. Analysis with a scanning electron microscope (SEM) of the deposited films surface has shown that those slightly rich in indium present a more homogeneous morphology and smaller crystallites sizes than the films slightly rich in copper. The measurement of the photoconductivity of the prepared compound has allowed us to determine the value of its gap at room temperature. It was found to be close to 0.99 eV.

Keywords: Chalcogenide; Structural; Thin films.

1. INTRODUCTION

The ternary compound CuInSe$_2$ of a chalcopyrite structure is a very promising material for the fabrication of solar cells from thin films [1–5]. This material is distinguished by a high absorption coefficient of nearly $10^5$ cm$^{-1}$ [6] and a direct transition gap around 1 eV [7]. In addition its gap can be
increased to by introducing gallium into the CuInSe₂, which permits to obtain the Cu(In, Ga)Se₂ [8]. The use of these compounds (CuInSe₂ and Cu(In, Ga)Se₂) as absorbers for the fabrication of solar cells has allowed to obtain efficiencies of 15 % [9] and more than 20 % [10, 11], respectively. The success of these compounds depends strongly on the elaboration, at low cost, of CIS and CIGS thin films, since the deposition of these films represents a significant part in the total cost of the photovoltaic panel.

The aim of this work is to investigate the influence of the source temperature and the deposition duration on the structural and morphological properties of the CuInSe₂ thin films, deposited by the Close Spaced Vapor Transport (CSVT) technique.

2. EXPERIMENTAL

Thin films of CuInSe₂ were deposited on Pyrex substrates using the CSVT technique (Fig. 1). Contrarily to other CSVT systems used by other authors to deposit thin films of the CIGS compound [12–14], the present system is distinguished by the fact that we used it with an open reactor. In other words, we don’t need to use vacuum in the reactor, but a simple flow of argon through the reactor is enough. The Pyrex substrates used are flat, well-polished, very clean and well dried. The source is a powder of CuInSe₂ placed in a graphite crucible and pressed manually. This powder is obtained from the bulk CuInSe₂ which was prepared by the vertical Bridgman method [15], with elements having puri-ties of 5 N for Cu, In and 6 N for Se. The substrate is placed at the top of the crucible on 1 mm-thick Pyrex holds. The set is then placed at the center of the reactor. Some solid iodine grains are placed in their position close to one of the two entries of the reactor. Iodine is used as carrier gas. It allows the transport of CuInSe₂ of the crucible toward the substrate. A Kanthal “U” bar, placed under the reactor just below the crucible, allows the heating of the source and the substrate. The temperatures used for the source are 450 and 550 °C for durations of one hour and two hours.
3. RESULTS AND DISCUSSION

The thin films of CuInSe$_2$ prepared by the CSVT technique were characterized by EDS, and the results are reported. The chemical composition of the constituents is obtained after analysis of five different positions of each studied film. The ratio Cu/In comprised between 0.96 and 1.10 shows that the obtained samples present a quasi-stoichiometry. The sample C1 is slightly rich in copper, whereas, C2 and C3 are slightly rich in indium. Similar results were reported by Zouaoui et al. [13] on thin films of CuInSe$_2$, deposited by CSVT method with closed reactor under vacuum. The iodine quantity in the deposited films decreases with the increase of the temperature and the deposition duration. It passes from 5 at\% for $T_{\text{Source}}$ 450 °C (C1) to less than 0.5 at\% for $T_{\text{Source}}$ 550 °C (C3). Meeder et al. [16] showed that the surface of the ternary CGS films, deposited by CVD process on two steps and open tube, can be contaminated by the iodine used as transport agent in the process of the film's growth. This presence of iodine in the deposited films is more pronounced in the films with stoichiometric composition or rich in copper [17]. This is in agreement with the results obtained, which showed that the films slightly rich in copper are much more contaminated by iodine than those slightly rich in indium. On the other hand, it was shown by Sander et al. [18] that high temperature treatments permit to reduce the iodine from the surface of the films.

Figure 2 Surface morphology of the sample C1.
The morphological study was carried out with a Scanning Electron Microscope (SEM). This analysis has shown that the films slightly rich in indium (C2 and C3) present a more homogeneous morphology than the films slightly rich in copper (C1), with smaller size and better jointed crystalite, giving it a more compact and less rough aspect (Figs. 2 and 3). Similar results for the surface morphology of CIS films have been found by Klenk et al. [19] and Al-Bassam [20]. Schock and Rau [21] showed that the Cu-poor CuInSe$_2$ and Cu(In, Ga)Se$_2$ films maintain excellent semiconducting properties.

The results of the characterization by X-ray diffraction of the thin films deposited at the source temperatures of 450 and 550 °C during 1 and 2 hours are shown in Figs. 4, 5, 6. The structural analysis shows that the films C1 and C2 are polycrystalline, with the presence of some binary phases.
Cu$_2$Se, CuSe$_2$ and In$_6$Se$_7$ beside the main phase CuInSe$_2$ (Figs. 4 and 5). The binary CuSe$_2$ presents a strong intensity in the spectrum of the film C1 and disappears from the spectrum of C2. The film slightly rich in copper (C1) shows the presence of the binary phases Cu$_2$Se and CuSe$_2$ that are more intense than In$_6$Se$_7$. Guillén et al. [22] have showed that for a ratio Cu/In > 1, the secondary phase Cu$_2$Se can coexist with the ternary phase CuInSe$_2$. For the film slightly rich in indium (C2), it is the binary phase In$_6$Se$_7$ which is predominant. In the spectrum of the film C3 deposited at 550 °C during 2 hours (Fig. 6), we notice the disappearance of the binary phase peaks. This spectrum shows only the peaks of the CuInSe$_2$ compound with planes of orientations (112), (204, 220) and (116, 312) of strong intensity. The X-rays diffraction spectra show that the plane of orientation (112) has a very low intensity for the film C1 deposited at 450 °C. On the other hand, the films C2 and C3 which were deposited at 550 °C show a preferential orientation according to the direction (112). Kanan et al. [14] have indicated that the planes of orientation (112) are desirable for the photovoltaic conversion. From the X-rays spectra we calculated the lattice parameters $a$ and $c$. The obtained results (Table 1) are in good agreement with those reported in the literature [23]. The presence of the peaks characterizing the chalcopyrite structure ((101), (211), (301), (305)) and the ratio of the lattice parameters $c/a = 2$, show that the deposited films have a chalcopyrite structure.

![Figure 5](image)

**Figure 5** X-ray diffraction pattern of the sample C3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters</th>
<th>$c/a$ ratio</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
</tr>
<tr>
<td>C1</td>
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<td>11.7581</td>
</tr>
<tr>
<td>C2</td>
<td>5.7723</td>
<td>11.7363</td>
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<tr>
<td>C3</td>
<td>5.7530</td>
<td>11.5693</td>
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</table>
4. CONCLUSIONS

Thin films of CuInSe₂ were deposited using a simple and low-cost open reactor CSVT. The preferential orientation according to the plan (112) was obtained for the films de- posited at the source temperature of 550 °C. The use of an energy dispersion spectrometer for the analysis of the constituent chemical composition of the deposited films has shown the quasi-stoichiometry of our films with a ratio Cu/In varying from 0.96 to 1.10. The structural studies of the deposited thin films showed that these layers are polycrystalline and of chalcopyrite structure. This technique has allowed us to deposit, at 550 °C during 2 hours, thin films that are homogeneous, compact and of good crystallographic qualities. The measurement of the photoconductivity of the prepared films has allowed us to determine the value of its gap at room temperature. It was found to be close to 0.99 eV.

References
