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Preparation and Study of $CuInSe_2$ Thin Films Obtained by the Technique of Close-Spaced Vapour Transport with Open Reactor

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Abstract: In this study, a low cost simple improved system of Close-Spaced Vapour Transport (CSVT) technique consisting of using a horizontal and open reactor was designed; thin films of $CuInSe_2$ were successfully prepared. Unlike the configuration with closed reactor, the present design does not require vacuum, a continuous argon flow in the reactor is enough during the films growth. Analysis by X-ray diffraction made it possible (i) to study the crystalline structure of the deposited $CuInSe_2$ thin films (ii) to determine the various crystallization planes and (iii) to detect various involved phases. It was found that all deposited thin films have polycrystalline and chalcopyrite structures. Moreover, the thin films deposited at 550°C present a preferential (112) orientation. A scanning electron microscope associated with an energy dispersion spectrometer was used to study the morphology of the films surface and to determine the chemical composition of their constituents. The analysis of the results not only confirmed the above thin films polycrystallinity but also showed the quasi-stoechiometry of the thin films with a Cu/In ratio varying from 0.91 to 1.10.

Key words: CSVT, $CuInSe_2$, thin films, open reactor, chemical vapour deposition, chalcopyrite structure

INTRODUCTION

Thin films of $CuInSe_2$ (CIS) compound, with a direct gap and a high absorption coefficient is one of the most recommended materials for the fabrication of the solar devices absorber. Conversion efficiencies of 15% for solar cells containing $CuInSe_2$ were reported. This value can be increased up to 19% by using $Cu(In,Ga)Se_2$ (CIGS) as absorber. This quaternary compound is obtained by introducing Gallium into ternary $CuInSe_2$. CIS and CIGS thin films are usually deposited by various techniques, namely, RF sputtering (Muller *et al*., 2006), co-evaporation (Chityuttakan *et al*., 2006; Kwon *et al*., 1998), electrodeposition (Guillén and Herrero, 1998; Huang *et al*., 2004), metalorganics chemical vapor deposition (Orsal *et al*., 2000), closed spaced selenezation (Adurodijia *et al*., 1998), electron beam and flash evaporation (Casteneda and Rueda, 2000), chemical spray pyrolysis (Shirakata *et al*., 2005), UV laser ablation (Tverjanovich *et al*., 2006) and close-spaced vapour transport (Guenoun *et al*., 1998; El Haj Moussa *et al*., 2002; Kannan *et al*., 2004). However, the competitiveness of these compounds depends strongly on the elaboration, at low cost, of CIS and CIGS thin films, since the deposition of these films represent a significant part in the total cost of the photovoltaic arrays. In order to obtain competitive layers, we propose the design and the realisation of a simple and low cost system of CSVT.

MATERIALS AND METHODS

Figure 1 shows the proposed system of the CSVT with a horizontal and open reactor used for the deposition of $CuInSe_2$ thin films. The reactor consists of a principal quartz tube of 40 cm in length and 3.5 cm in interior diameter, positioned horizontally, which can be closed by two removable lids. The input lid comprises two arrivals with valves, which are used to control the rate argon flow in the reactor, with or without iodine. The second lid comprises an exit with valve for exit of gases and an opening for the passage of thermocouple wires towards the source and the substrate. To reduce temperature losses, the principal enclosure of the reactor is surrounded by refractory bricks. The pyrex substrates used are flat, well polished, very clean and well dried. The source is a powder of $CuInSe_2$ placed in a graphite crucible and pressed manually. This starting powder is obtained from the synthesis of $CuInSe_2$ manufactured

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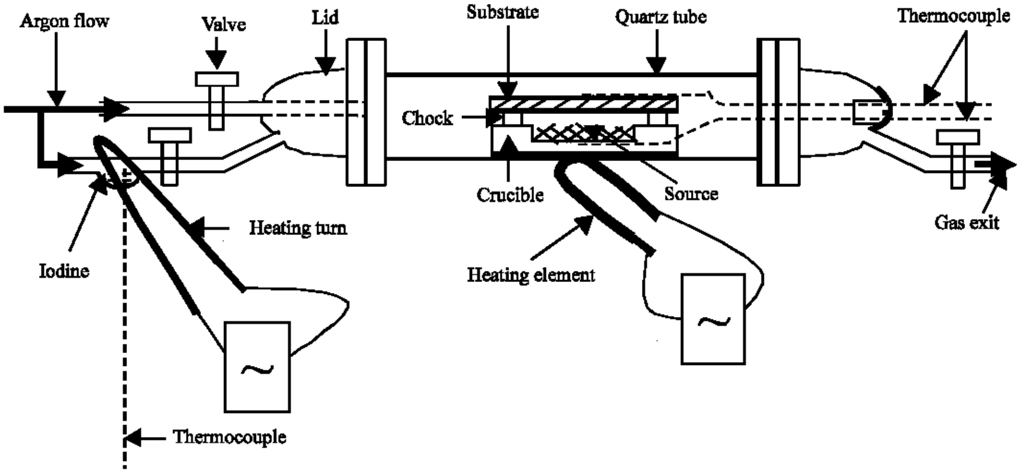

Fig. 1: Schematic diagram of the CSVT reactor

Table 1: Chemical composition of $CuInSe_2$ films determined by EDS

Sample	Deposition conditions	Cu (%)	In (%)	Se (%)	I (%)	Cu/In	Se/(Cu+In)
CIS 1	450°C, 1 h	23.32	21.26	49.58	5.84	1.10	1.10
CIS 2	450°C, 2 h	23.10	21.39	51.85	3.36	1.08	1.16
CIS 3	500°C, 1 h	22.28	24.41	51.53	1.78	0.91	1.10
CIS 4	550°C, 1 h	25.33	25.73	48.29	0.65	0.98	0.95

Table 2: Lattice parameters (a and c) for $CuInSe_2$ thin film

Sample	a (Å)	c (Å)	c/a
CIS 1	5.7922	11.7581	2.03
CIS 2	5.7530	11.7033	2.03
CIS 3	5.7752	11.6038	2.01
CIS 4	5.7723	11.7363	2.03

[a]Side length of the elementary unit basis, [c]Height of the elementary unit

with elements having purities 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 crucible 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. A U - bar of Kanthal resistance, placed under the reactor just below the crucible, is used to heat both the source and the substrate.

The temperature of the source for the step of growth is 450, 500 and 550°C for deposition time of 1 and 2 h (Table 1); that of the substrate is approximately 70°C lower than that of the source. Heating whorls make it possible to heat and maintain the temperature of iodine at 50°C. At the beginning of the deposition, the rise in temperature of the source and substrate are carried out under argon flow. When the temperature of the source reaches the growth value, the temperature of iodine is maintained at 50°C, the valve isolating iodine from the principal enclosure of the reactor is opened and that of the second entry is closed. The iodine vapour is carried by the argon flow until the source where the reaction can start. A Scanning Electron Microscope (SEM), associated with an Energy Dispersion Spectrometer (EDS) were used respectively to study the morphology of the films surface and to determine the chemical composition of their constituents. An X-ray diffractometer with a copper Kα radiation (λ = 1, 54051 Å) was used to analyze the crystalline structure of $CuInSe_2$ thin films deposited and to determine the various plans of crystallization as well as the various involved phases.

RESULTS AND DISCUSSION

Composition of the films: The thin films of $CuInSe_2$ prepared by the CSVT technique were characterized by EDS and the results are reported in Table 1. The chemical composition of the constituents is obtained after analysis of five different positions from each studied films.

The results obtained show that the films are quasi-stoechiometric with $0.91 \leq Cu/In \leq 1.10$ and $0.95 \leq Se/(Cu+In) \leq 1.16$. The films CIS 1 and CIS 2 are slightly rich in copper, whereas, CIS 3 and CIS 4 are slightly rich in indium. Similar results were reported by Zouaoui *et al.* (1999) on thin films of $CuInSe_2$, deposited by CSVT method with closed reactor under vacuum. The iodine quantity in the obtained thin films (CIS 1 to 4) decreases with the increase in the temperature and the deposition time. It passes from 5% for T_{source} = 450°C (CIS 1) to almost 0.5% for T_{source} = 550°C (CIS 4). Moreover, thin films of $CuInSe_2$ were deposited under iodine at room temperature. The comparison of the chemical compositions of the constituents of the layers deposited showed that the quantity of iodine is lower when the iodine is heated. In other words, when iodine is heated, its contamination effect is lower in the deposited layers of $CuInSe_2$. Meeder *et al.* (2003a) showed that the surface of the ternary CGS thin films, deposited by CVD process on two steps and opened tube, can be contaminated by the iodine used as transport agent in the process of the films growth. This presence of iodine in the films deposited is more pronounced in the films with stoechiometric composition or rich in copper (Meeder *et al.*, 2003b). This is in agreement with the results obtained, which showed that the films slightly rich in copper (CIS 1 and 2) are much more contaminated by iodine than those slightly rich in indium (CIS 3 and 4).

The analysis by SEM of the surface of samples CIS showed that the films are homogeneous and polycrystalline.

Characterization by X-ray: The results of the characterization by X-ray diffraction of the $CuInSe_2$ thin films, deposited at the source temperatures of 450, 500 and 550°C during 1 and 2 h are shown in Fig. 2-5. The X-ray spectra show that the plans of orientation (112) and (103) have a very low intensity for the films deposited at 450°C during 1 h (CIS 1) and they increase slightly for a temperature of 500°C (CIS 3). However, at 550°C (CIS 4), the $CuInSe_2$ thin films deposited, show an increase in the intensity of the peak (103) and a preferential orientation according to the direction (112). Similar results were reported in the literature (Kannan *et al.*, 2004; Kessler *et al.*, 2003). Kannan *et al.* (2004) indicated that the planes of orientation (112) are desirable for photovoltaic conversion.

The comparison of the X-ray spectra of samples CIS 1 and CIS 2 shows that the increase in the deposition time is favorable to the rise of the peaks intensity of (112) and (103). Lundberg *et al.* (2003) showed that the intensity of the preferential orientation of the grains increases with the deposition time for CIGS thin films obtained by co-evaporation.

In addition of the planes of orientation (112), (103), (204), (220), (116), (312), (323), (400), (316) and (332) of the ternary compound $CuInSe_2$, most of the chalcopyrite structure peaks (101), (211), (301) and (305) are in the films X-ray spectra (Fig. 2-5).

The structural analysis confirms the observations made with the SEM and indicates that the films are indeed polycrystalline, with the $CuInSe_2$ as the principal phase and the inclusions of Cu_2Se, $CuSe_2$ and/or In_6Se_7. The presence of these latter can be due to the non stoechiometry of present thin films. Indeed, the chemical compositions of the samples are only quasi-stoechiometric ($0.91 \leq Cu/In \leq 1.10$). The films slightly rich in copper (CIS 1 and 2) show that the presence of Cu_2Se and/or $CuSe_2$ are more important than those of In_6Se_7. For the films slightly rich in indium (CIS 3 and 4), the presence of In_6Se_7 is dominant.

From the X-rays spectra, the lattice parameters a and c were calculated and are shown in Table 2. These results are in good agreement with those reported in the literature (Lam and Shih, 1998).

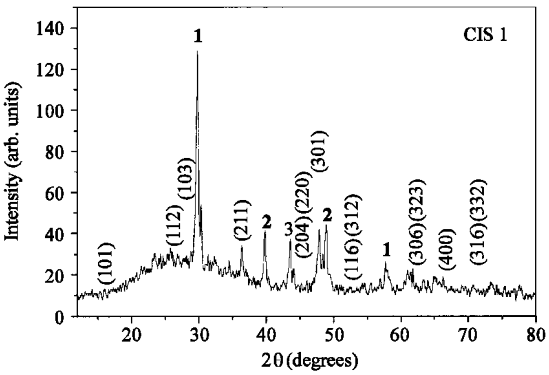

Fig. 2: X-ray diffraction patterns of $CuInSe_2$ thin films. Secondary phase: 1. $CuSe_2$, 2. In_6Se_7, 3. Cu_2Se

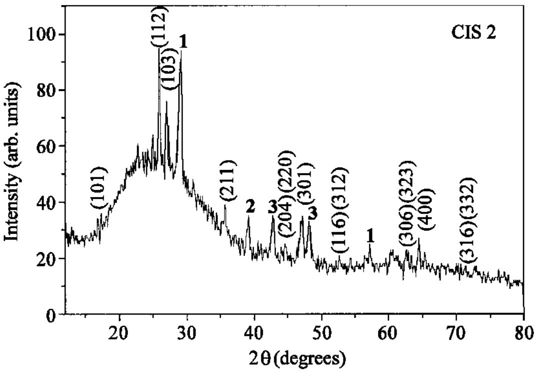

Fig. 3: X-ray diffraction patterns of $CuInSe_2$ thin films. Secondary phase: 1. $CuSe_2$, 2. Cu_2Se, 3. In_6Se_7

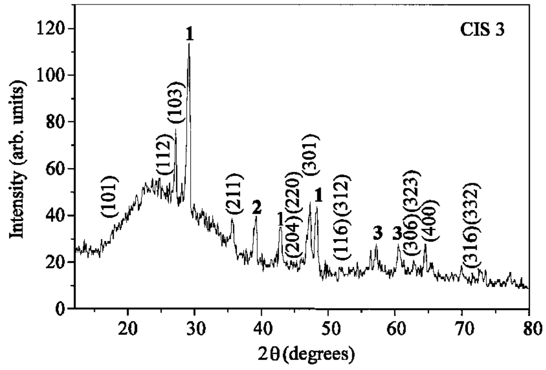

Fig. 4: X-ray diffraction patterns of $CuInSe_2$ thin films. Secondary phase: 1. In_6Se_7, 2. Cu_2Se, 3. $CuSe_2$

The presence of the peaks characterizing the chalcopyrite structure and the ratio of the lattice parameters c/a ≈ 2 show that deposited films have a chalcopyrite structure.

The obtained results are in good agreement with those reported by other CSVT techniques (Guenoun *et al.*, 1998; El Haj Moussa *et al.*, 2002;

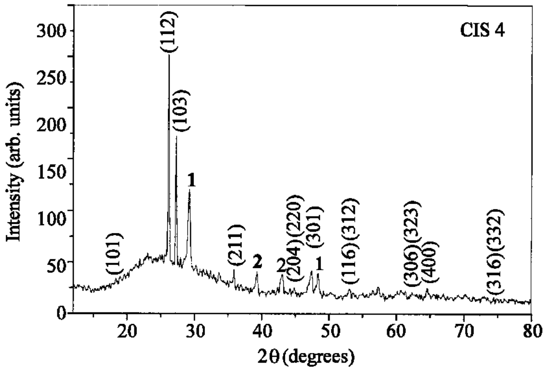

Fig. 5: X-ray diffraction patterns of $CuInSe_2$ thin films. Secondary phase: 1. In_6Se_7, 2. Cu_2Se

Kannan *et al.*, 2004). However, the present CSVT system with opened reactor possesses the advantage of being simpler than the others; it allows sample preparations with much lower costs.

CONCLUSION

A simple and low cost CSVT system was designed and fabricated. The structural studies of $CuInSe_2$ thin films deposited by this CSVT system with opened reactor, showed that these layers are polycrystalline and of chalcopyrite structure. The preferential orientation according to the plan (112) was obtained for the films deposited at the source temperature of 550°C. From the X-ray spectra, we calculated the lattice parameters a and c; the c/a ratio was found to be approaching 2. The characterization with the EDS of the films deposited, showed that their chemical composition is quasi-stoechiometric, with a Cu/In ratio varying from 0.91-1.10. The SEM analysis of the surface of the films showed that they are homogeneous and polycrystalline.

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