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DEVELOPMENT OF A VACUUM CSVT LOW COST TECHNIQUE TO DEPOSIT $CuInSe_2$ THIN FILMS

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ABSTRACT

Copper Indium Diselenide ($CuInSe_2$) thin films were deposited by a vacuum free Close-Spaced Vapour Transport (CSVT) process. The equipment requires a horizontal open quartz tube reactor, using iodine vapour as a transport agent. The process deposition was made without vacuum. The films were deposited on glass substrate heated at temperatures of 380°C, 425°C and 470°C. The deposition time was about one hour. Characterizations by means of compositional and structural analysis were carried out. The composition of the films obtained was determined by Energy Dispersive Spectrometry (EDS) coupled to a scanning electron microscope. This analysis provided a good stoichiometric composition. The structural characterization of the Copper Indium Diselenide films was studied by X-ray diffraction (XRD). The spectra revealed that all the films were polycrystalline in nature with chalcopyrite structure. These spectra showed secondary phases in the films and additional peaks with weak intensities. The preferred orientation along (112) direction suitable for $CuInSe_2$ films to be employed as solar cells was observed at substrate temperature of 470°C.

KEYWORDS: Vacuum free CSVT, $CuInSe_2$, thin films.

INTRODUCTION

The increasing use of solar energy calls for the development of a technique to produce photovoltaic cells (*Delahoy et al., 2004; Diehl et al., 2005*) in abundance. The interest for Copper Indium Diselenide ($CuInSe_2$) thin films lies in its direct band gap of about 1.04 eV and its large absorption coefficient within the range of $10^4 - 10^5 cm^{-1}$ (*Moudakir et al., 2004; Siebentritt, 2002*). Besides theses properties, the $CuInSe_2$ thin films can be produced both n- or p-type conducting (*Massé et al., 1997*).

Several $CuInSe_2$ thin films processing techniques have been investigated, such as chemical bath deposition (*Dhanam et al., 2002*), RF sputtering (*Yamaguchi et al., 1992*), metalorganic chemical vapour deposition (MOCVD) (*Artaud et al., 1998*), three source co-evaporation (Hama et al., 1991), electron beam evaporation (*Castañeda et al., 2000*), close spaced selenization (*Adurodija et al., 1998*), and close-spaced vapour transport (CSVT) (*Massé et al., 2004, 2002, 1997; Kannan et al., 2004; El Hadj Moussa et al., 2002*),

Our area of interest is devoted to the use of a vacuum free CSVT technique with a horizontal open tube reactor to deposit $CuInSe_2$ thin films.

In this paper, we present the preparation of $CuInSe_2$ thin films by this CVST technique and the results on the composition and structural characteristics of the films as a function of substrate temperature at which the films are deposited.

MATERIALS AND METHODS

For the experiment, we designed and fabricated vacuum free CSVT system. The experimental set up is shown in Figure 1. The quartz reactor has an inner diameter of 35 mm and a length of 400 mm. The source was formed of pressed or hand pressed $CuInSe_2$ powder put in a quartz crucible, and the substrate (pyrex glass) was above the source and separated from it by a quartz or glass spacer (thickness: 1 – 2 mm). The substrate and the crucible containing the source were heated by a U-form Kanthal resistor.

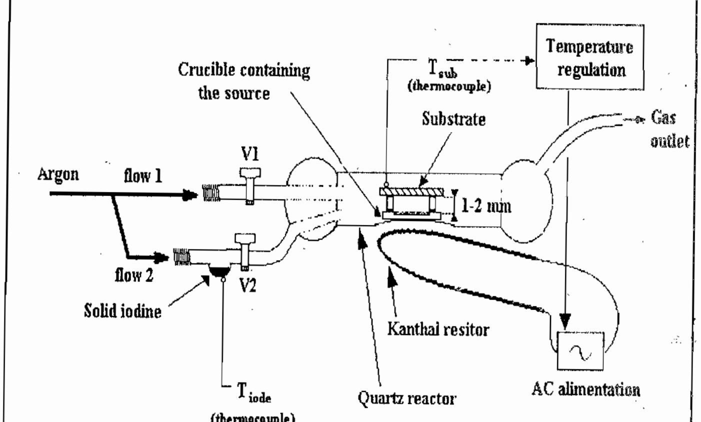

Figure 1. Schematic diagram of horizontal CSVT open reactor system

The source temperature was indicated by a regulator and the temperature of the upper face of the substrate was directly measured using a chromel-alumel thermocouple. As the substrate was 1 mm thick, the temperature above and below the substrate was practically the same during the experiments. Solid iodine used as a transport agent was outside the reactor and isolated by a valve V2. Before deposition of $CuInSe_2$ thin films, valve V1 was opened and V2 closed. Therefore, no iodine vapour was present in the reactor. Argon-flow 1 removed the air from the reactor, while the source was heated until the desired temperature for the deposition. After the stabilized source temperature, V1 was

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closed and V2 opened. The reaction process began as argon-flow 2 transported iodine vapour into the reactor and then invaded it. Solid iodine could be at room temperature or heated by an electrical filament to the temperature of 50°C, measured by chromel-alumel thermocouples. The desired temperature of the deposition was the source temperature. This temperature was in the range of 400 to 600°C. The iodine vapour decomposed the surface of the source and transported the elements to the bottom of the substrate which was colder than the source of about 50-100°C. These elements settled and reconstituted the composite. After the deposition time of about one hour, V2 was closed during cooling period. Therefore, no more iodine vapour was transported into the reactor.

RESULTS AND DISCUSSION

Compositional analysis

$CuInSe_2$ thin films were deposited on glass substrate with thickness of about 1 □m during evaporation time of one hour. The films obtained were noted S-1, S-2 and S-3. The source was a powder of $CuInSe_2$ hand pressed.

Table 1 shows a typical composition of the films prepared at various substrate temperatures, starting from

Table 1: EDS composition of the deposited $CuInSe_2$ films.

Films deposited	Source temp.	Substrate temp.	Iodine temp.	at. % Cu	at. % In	at. % Se_2	at. % I
S-1	450°C	380°C	50°C	23.32	21.26	49.58	5.84
S-2	500°C	425°C	50°C	23.39	24.37	48.62	3.62
S-3	550°C	470°C	50°C	25.23	25.73	48.29	0.65

380°C. The composition was given by Energy Dispersive Spectrometry (EDS) coupled to a scanning electron microscope. The amount of iodine in the films decreased as the substrate temperature increased. Similar observation has been made by several researchers (*Massé et al., 1997, Zouaoui et al., 1999*) following the study of some chalcopyrite compounds fabricated by CSVT also, but using different relevant growth conditions. We noted that with the rising of substrate temperature, the amount of copper and indium increases but the amount of diselenide decreases. These results are in disagreement with those presented by Zouaoui (*Zouaoui et al., 1999*). The difference could be due to the presence of secondary phases in our films. Besides, the absence of iodine in the films was observed at substrate temperature of above 470°C. The observed temperature (470°C) was higher than the one (410°C) reported by the CSVT technique under vacuum (*Massé et al., 1997, Zouaoui et al., 1999*).

Structural analysis

Structural analysis was made by X – ray diffraction (XRD) using a powder diffractometer (θ, 2θ geometry) with CuK_α radiation (λ = 1.54051 Å). The spectra are shown in Figures 2 – 4.

Table 2. Main diffraction peaks observed for $CuInSe_2$ phase

Sample	Observed Peaks
S-1	(211) (204, 220) (301) (305, 323)
S-2	(211) (301) (305, 323)
S-3	(112) (103) (211) (301)

The diffraction peaks observed for $CuInSe_2$ films deposited at substrate temperatures of 380°C, 425°C and 470°C revealed that the films were polycrystalline in nature of chalcopyrite structure.

The main diffraction peaks observed for $CuInSe_2$ phase are indicated in table 2. The peak (112) is observed in all the films. However, the intensity of this peak is very weak in the films deposited at substrate temperatures of 380°C and 425°C. In sample S-3, this peak is prominent showing a preferred orientation along (112) direction. We have already noted that at substrate temperature of 470°C, the amount of iodine is negligible in the films. So, it could mean that the preferred orientation along (112) direction appeared when there was no presence of iodine in the films. Similar result was reported in the literature (*Kannan et al., 2004*).

Furthermore, the XRD spectra show secondary phases in the films. At substrate temperature of 380°C, the secondary phases were identified to be Copper Diselenide ($CuSe_2$) and Indium Selenide (In_6Se_7) with the peak noted respectively 1 and 2 in Figure 2. At substrate temperature of 425°C, the secondary phases were identified to be In_6Se_7, Copper Selenide (Cu_2Se) and $CuSe_2$ with the peak noted respectively 1, 2 and 3 in Figure 3. At substrate temperature of 470°C, the secondary phases were identified to be In_6Se_7 and Cu_2Se with the peak noted respectively 1 and 2 in Figure 4. The peak due to In_6Se_7 was noted to be present on all the recorded XRD spectra. Such observations have been reported by Zouaoui (*Zouaoui et al., 1999*). Additional peaks were also detected but their weak intensities did not permit us to clearly identify them.

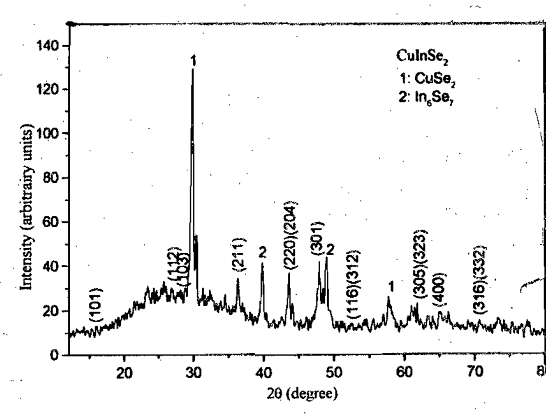

Figure 2. XRD spectrum of sample S-1

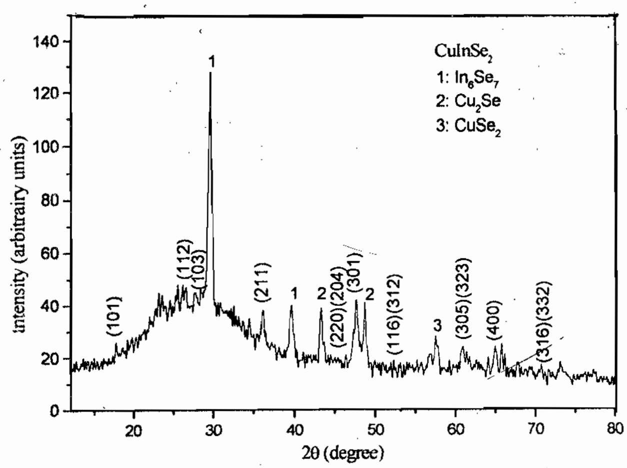

Figure 3: XRD spectrum of sample S-2

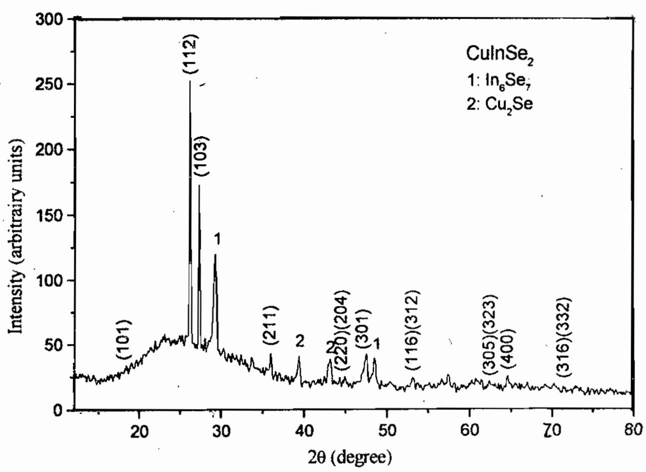

Figure 4 : XRD spectrum of sample S-3

CONCLUSION

During our experiment, we developed new low cost CSVT technique. It requires inexpensive equipment for its implementation. $CuInSe_2$ thin films were deposited by this technique for photovoltaic solar cells. The XRD study confirmed that the deposited films were polycrystalline in nature of chalcopyrite structure. EDS study of the deposited films exhibited a good stoichiometric composition. The quality of these results depended strongly on the substrate temperature. The preferred orientation along the (112) direction suitable for $CuInSe_2$ films to be employed for photovoltaic solar cells was observed at substrate temperature of 470°C. Above this temperature, the trace of iodine in the films disappeared. The characteristics of the films obtained by the vacuum free CSVT technique were encouraging since they corroborated with those reported by several group of researchers employing different CSVT deposition techniques. However, experiments and detail structural study should be carried out to optimise this growth process.

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