Structural and optical properties of $CuIn_{0.74}Ga_{0.26}Se_2$ and $CuIn_{0.76}Ga_{0.24}Se_2$ thin films

M. CHANDRAMOHAN, T. VENKATACHALAM*
Department of Physics, Coimbatore Institute of Technology, Coimbatore - 641 014, India

High quality thin films of $CuIn_xGa_{1-x}Se_2$ were deposited on well cleaned glass substrates by chemical bath deposition technique. The composition, structural and optical properties of two representative films (bath temperatures 300 and 323 K) were carried out by using EDAX technique, X-ray diffractogram and spectrophotometer respectively. From the EDAX results, the Stoichiometric formulae of the films 1 and 2 were identified as $CuIn_{0.74}Ga_{0.\ 26}Se_2$ and $CuIn_{0.76}Ga_{0.24}Se_2$. The XRD results reveal that the films are chalcopyrite type structure with the lattice parameters 5.725 Å (a) and 11.462 Å (c). The optical transmission spectra for the films were recorded from the spectrophotometer. The transmission data was used to determine the energy band gap values which were calculated to be 1.23 and 1.15 eV.

(Received December 15, 2009; accepted January 19, 2010)

Keywords: Chemical bath deposition, Thin films, CIGS, Solar cells, Band gap, Semiconductor

1. Introduction

The best solar cells based on $CuIn_{1-x}Ga_xSe_2$ (CIGS) materials with $x < 0.3$ have reached efficiencies in the range of 19 % [1-3]. Thin films of CIGS are considered as the most promising material for low cost and high efficiency, because of their high absorptivity ($>10^5$ cm^{-1}) and stability against photo degradation. The $CuIn_{1-x}Ga_xSe_2$ quaternary alloy is a direct band gap semiconductor with the gap energies varying from 1 eV (for x = 0) to 1.7 eV (for x = 1); thus it allows tailoring of optical band gap for optimum solar cell conversion [4, 5]. CIGS thin films have been deposited using various techniques including physical evaporation [6-8], rapid thermal process [9], selenization of sequentially stacked precursors [10]. All these vacuum deposition techniques are carried out to be heavy and expensive. It is found that electro deposition techniques are low cost, potentially suitable to obtain good quality, large area CIGS precursor films and they are suitable for growing large area thin films economically. A better understanding of the quaternary formation processes is essential for optimizing these films for solar cell fabrication. We present the results of investigation of the structural and optical properties of chemical bath deposited $CuIn_{1-x}Ga_xSe_2$ thin films.

2. Experimental details

The constituent atoms of CIGS molecules are co-deposited from the solution onto the well cleaned substrates with the help of their ions in reaction mixer. The reaction mixer used for preparing CIGS thin films consists of $CuCl_2$, LiCl, $GaCl_3$, H_2Se0_3, and $InCl_3$ substances of analytical grade chemicals (99.99% Sigma Aldrich) [3]. The mixer was prepared by taking each 10 ml of above solutions in 100 ml beaker. The pH value of mixer was measured with the help of digital pH meter and it was found to be 2 ± 0.05. Two well-cleaned glass plates (37.5 mm x 12.5 mm x 1 mm) were suspended vertically with the help of substrate holder and dipped into the beaker containing the reaction mixture. The beaker containing the reaction mixture and glass substrates were placed in water bath, was stirred with the help of magnetic stirrer as shown in Fig. 1.

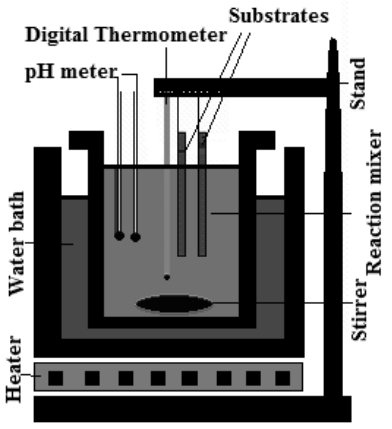

Fig. 1. Schematic diagram of chemical bath deposition.

The deposition bath turned pure white and then to colorless as the time progress. The deposition was carried-out at two different temperatures (300 K, and 323 K) by taking two different time of deposition (60 min and 120 min). The mixture with glass substrates was kept at one particular temperature and stirred continuously, while stirring the solution; the substrates were taken out at the intervals of 60 minutes. The glass plates were dried in open air in order to evaporate the moisture content. The structural analysis of the films are carried out using a

computer controlled X-ray diffractometer system model JDX 8030 (Japan) with Ni filter and Cu Kα radiation. The scanning is carried out using θ-2θ scan coupling mode the ratings being 40 kV, 20 mA. The particle size, dislocation density, lattice parameter, strain, lattice spacing and dislocation density values for the various films have been calculated using the relations. The crystalline sizes (D) are calculated using the Scherrer's formula from the full width at half maximum (β) using the relation $D = \frac{0.9\lambda}{\beta \cos\theta}$. The strain (ε) is calculated from the slope of β cosθ versus sinθ plot using the relation $\beta = \frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta$. The dislocation density (δ) is evaluated from the relation $\delta = \frac{1}{D^2}$. The width of the peaks decreases as the deposition temperature increases. This could be due to reduced strain within the film or an increase in grain size indicating a better crystalline perfection. The lattice parameters (a and c) of the crystal are determined by using the relation $\frac{a^2}{h^2+k^2} + \frac{c^2}{l^2} = \frac{1}{d^2}$, where (hkl) is the miller indices of the peaks. Micro structural investigations of thin films on glass substrate are carried out using Scanning Electron Micrograph (SEM JOEL – Japan). Compositions of the films are determined by EDAX measurements (JOEL –Japan). Thicknesses of all the films are measured by using multiple beam interferometer technique. The optical studies are made on the films deposited on glass substrates in the wavelength range from 190 to 2500 nm at room temperature by using spectrophotometer (JASCO-370V). The absorption coefficient **α** is estimated from the optical transmittance spectra using the relation $\alpha = \frac{2.303 \log(\frac{1}{T})}{t}$ where T is the transmittance (in %) and t is the thickness of the film. All such graph satisfies the condition for a direct transition in the excitation process i.e. $\alpha = (E_v - E_i)^{1/2}$ for allowed direct transition, where E_v is the top of the valence band and E_i is energy of the initial state from which the transition is made.

3. Results and discussion

All the films deposited on well cleaned glass substrate are smooth, uniform, adherent and white in color. The darkness increases with increase in thickness of the thin films. Fig. 2 shows XRD graphs of the thin films (deposition temperatures 300 K and 323 K) of thicknesses 150 Å, and 370 Å respectively. The predominant peaks in XRD graph of CIGS thin films could be probably associated with (101), (112), (103), (211), and (105) reflections of the chalcopyrite structure [4, 5, 11] (JCPDS card 35–1102) [12].

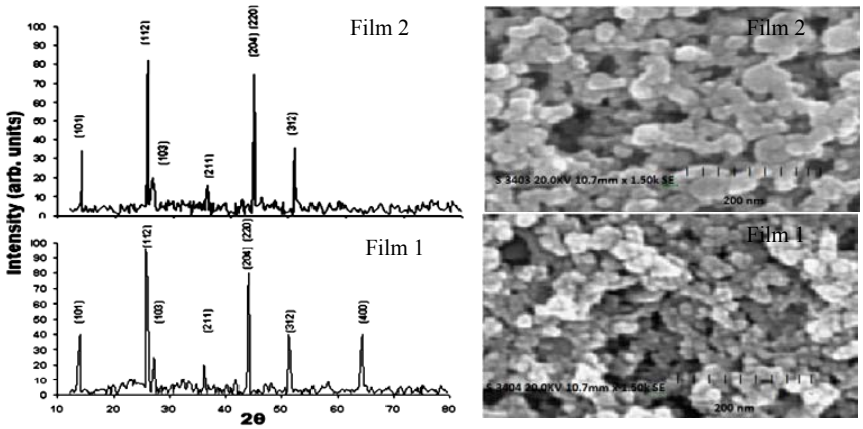

Fig. 2. X-ray diffraction pattern and SEM images of CIGS thin films.

The peak intensities of all the film increases with increase in deposition temperature, it is due to increase in the crystalline nature of the film. The lattice parameters, particle sizes, strain and dislocation densities of thin films deposited are given in Table 1.

Table 1.

Film number	Lattice parameter (Å)		Particle size (D) (Å)	Strain (ε) ($x10^{-4}$ lines^{-2} m^4)	Dislocation density (δ) ($x10^{-4}$ lines^{-2} m^2)
	a	c			
1	5.725	11.447	395	1.708	6.343
2	5.733	11.466	445	0.409	5.047

It is found that the size of the particle increases with the bath temperature in all the films. These results are in agreement with the SEM results. The compositions of the films are identified from the EDAX measurements (Fig. 3) and their data are tabulated (Table 2). The particle sizes in SEM micrograph of all the alloys are measured and the mean values of the particle sizes are found to be 410 Å (film 1), and 550 Å (film 2) which are very close to the

XRD results [4, 5, 11]. The optical transmittance spectra of thin films are as shown in Fig. 4. All the films exhibit direct band gap structure and their band gap values are found to be 1.23 eV (film 1), and 1.15 eV (film 2).

Table 2

Film number	Cu (%)	In (%)	Ga (%)	Se (%)	Molecular formula
1	19.6	26.2	5.6	48.6	$CuIn_{0.74}Ga_{0.26}Se_2$
2	19.5	26.8	5.1	48.6	$CuIn_{0.76}Ga_{0.24}Se_2$

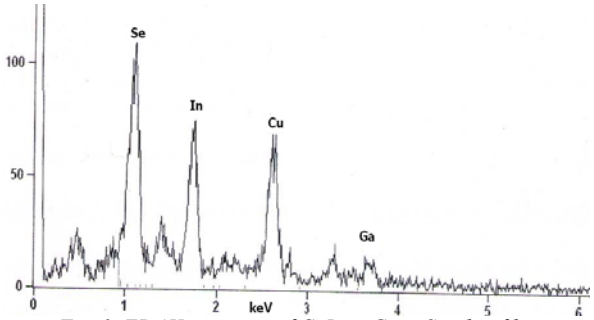

Fig. 3. EDAX spectrum of $CuIn_{0.74}Ga_{0.26}Se_2$ thin film prepared with bath temperature 300 K.

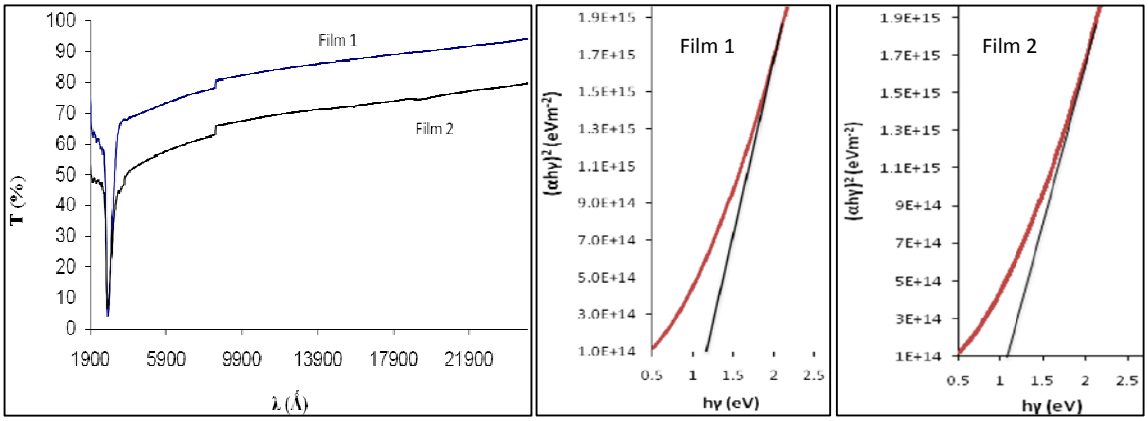

Fig. 4. Transmittance spectra versus wavelength and $(\alpha h\gamma)^2$ versus hγ curves of CIGS thin films.

5. Conclusions

Good quality thin films of the CIGS have been prepared by a chemical bath deposition method with two different bath temperatures and two different deposition times. X-ray analysis revealed that the films are crystalline in nature with chalcopyrite phase (lattice parameters nearly a = 5.725 Å and c = 11.462 Å) and their molecular formulae are $CuIn_{0.76}Ga_{0.24}Se_2$ and $CuIn_{0.74}Ga_{0.26}Se_2$. Optical studies revealed that the thin fundamental absorption edge arises at 0.9 eV (film 1) and 0.98 eV (film 2). The band gaps are due to the direct electronic transition. The reported results give an indication that the deposited layers may find applications in the fabrication of thin film solar cells and photo-detector.

References

[1] K. Bouabid, A. Ihlal, A. Manar, A. Outzourhit, E. L. Ameziane Thin Solid Films **488**, 62 (2005).
[2] T. Wada, Y. Hashimoto, S. Nishiwaki, T. Satoh, S. Hayashi, T. Negami, H. Miyake Solar Energy Materials & Solar Cells **67**, 305 (2001).
[3] M. A. Contreras, B. Eggas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, Prog. Photovoltaics **7** 311 (1999).
[4] M. Venkatachalam, M. D. Kannan, S. Jayakumar, R. Balasundaraprabhu, N. Muthukumarasamy Thin Solid Films **516**, 6848 (2008).
[5] M. A. Contreras, K. Ramanathan, J. AbuShanma, F. Hasoon, D. L. Young, B. Egaas, R. Noufi, Progress in Photovoltaics Research and Applications **13,** 209 (2005).
[6] K. Ramanathan, G. Teeter, J. C. Keane, R. Noufi, Thin Solid Films **480**, 499 (2005).
[7] V. Nadenau, D. Braunger, D. Hariskos, M. Kaiser, Ch. Koble, A. Oberacker, M. Ruckh, U. Ruhle, R. Schaffler, D. Schmid, T. Walter, S. Zweigart, H. W. Schock, Prog. Photovolt. **3**, 363 (1995).
[8] M. A. Contreras, J. R. Tuttle, A. M. Gabor, A. L. Tennant, K. R. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, R. Noufi, Prog. Photovolt. **3**383, (1995).
[9] M. A. Contreras, J. R. Tuttle, A. M. Gabor, A. L. Tennant, K. R. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, R. Noufi, Sol. Energy Mater. Sol. Cells **41/42**, 231 (1996).
[10] M. Wagner, I. Dirstorfer, M. M. Hofmann, M. D. Lampert, f. Karg, B.K Meyer, Phys. Status Solidi, A Appl. Res. **167**, 131 (1998).
[11] SeJin Ahn, KiHyun Kim, Kyung Hoon Yoon Current Applied Physics **8**, 766 (2008).
[12] Grzeta Plenkovic.B et al J. Appl. Crystallogr. **13,** 311 (1980).

*Corresponding author: atvenkatachalam@yahoo.com