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Grain Size and Lattice Parameters of $CuInSe_2$ Films

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Abstract. Thin films CuInSe2 (CIS) cells have been fabricated by the electro chemical method. Some of the physical properties such as lattice parameter, crystal structure and grain size of CuInSe2 (CIS) films with different Cu/In ratios (0.50-1.1) were determined using X-ray diffractornetry. A structural transition from chalcopyrite to sphalerite was observed on the electro deposition $CuInSe_2$ when the composition of the thin films was varied from a quasi stoichiometry to indium rich. The lattice constants calculated from X-ray diffraction spectra of the films were a 5.764 and c = 11.562A. The surface morphology with different Cu/En ratio was studied with SEM. The gain size was in the range 0.36-0.65 nm, with a sharp change when increasing Cu/In from (0.50-1.1).

Keywords: CIS thin films, solar cells, Structural properties.

1. Introduction

The structural properties of the sputtered and the vacuum — evaporated $CuInSe_2$ thin films fabricated by single-source, two-source and three source methods, have been characterized by several groups [1-4]. Thin film polycrystalline $CulnSe_2$ (CIS) is an attractive material for low cost photo voltaic application and related compounds have reached small area conversion efficiencies exceeding 16% (5/6). Several methods have been used to prepare $CuInSe_2$ thin films, single-source evaporation and two sources evaporation of $CuInSe_2$ and In_2Se_3 [7]. Both the band gap and the lattice constants can be adjusted by substituting the other group I, III and VI elements into the structure. Some Characterization of $CuInSe_2$ thin films and bulk crystals has been carried out [7-13]. In the present paper, we report our studies on the preparation and characterization of $CuInSe_2$ (CIS) films with different Cu/In ratios (0.49-1.1). X-ray data have been investigated including the structure and lattice parameters of these materials. Also the surface Morphology with different Cu/In ratios was studied.

2. Experimental Methods

The thin films samples were grown by the electrochemical deposition method and thermal evaporation. Polycrystalline thin films of $CuInSe_2$ (CIS) were deposited on glass substrate coated with 1 um of molybdenum (Mo) as a back contact to the CIS. The film generally had a total thickness of approximately 3 pm. The chemical composition of the sample investigated was measured using wavelength dispersive X-ray spectrometry and the microstructures of the films deposited with different Cu/In ratios, were studied with a scanning electron microscope. X-ray diffractometry was used to determine the lattice and the structure of CIS films. This was done using a SIEMENS D5000 with copper CuKa radiation of average wavelength 1.5406 A°. It was operated with target voltage and current of 30 kV and 20 mA respectively. The diffraction patterns were recorded from 2θ = 20° to 2θ = 95°. The optical absorptions were recorded using a Cary 2300 spectrophotometer at room temperature.

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3. Results and Discussion

3.1. X-ray Diffraction Analysis

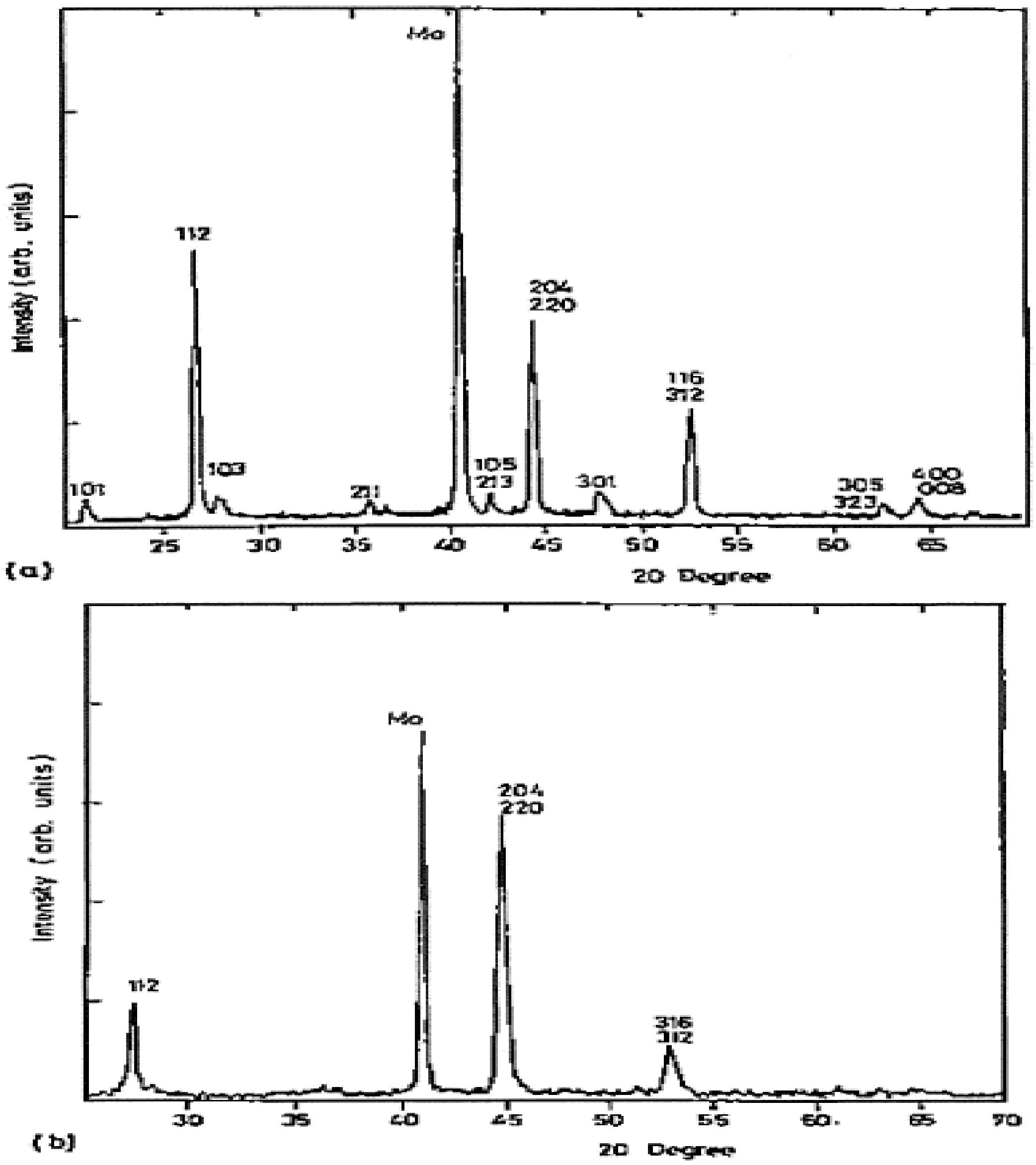

Fig. 1: The XRD spectra of two representative films (a) copper-rich film (Cu/ln=0.84) and (b) Indium-rich film (Cu/ln=0.68)

The XRD spectra of two representative films with different Cu/In ratios: 0.84and 0.68.are shown in fig (1). In the former, all characteristic peaks of the chalcopyrite structure, such as (101), (103), (211), (301), (105, 213), (323, 305) etc. are clearly obtained for the quasti-stoichiometric film (Fig. 1a). In contrast, the indium- rich film clearly does not exhibit any of the characteristic peaks of chalcopyrite (Fig. lb).

a more detailed XRD analysis revealed a totally different structure for the indium rich films, which is a disordered version of chalcopyrite structure are all absent. This is fully in accordance with the systematic structural change from chalcopyrite to sphalerite [3]. The tetragonal chalcopyrite has a c/a ratio 11.562 /5.762 = 2.005. The displacement of (112) peak is observed to be merely 0.475° (2θ).

These results indicate that a structural transition exists for the electrodeposited $CulnSe_2$ from a tetragonal to a cubic structure, as the film composition varies from a quasi- stoichiometry to indium rich [1]. Evidence for this transition is shown by the monitored decrease and eventual disappearance of chalcopyrite (211) peaks at 3 5.623°, as a result of increased Cu/In ratio (see table 1).

Table 1: Crystallographic parameters of CIS with different Cu/In ratios

Cu/In=0.80				**Cu/In=0.68**			
2θ (deg)	**D (A°)**	**I/Io**	**(hkl)**	**2θ (deg)**	**D A°**	**I/Io**	**(hkl)**
20.9	3.362	2.7	(101)	27.21	3.2748	26.18	(112)
26.73	3.3319	50.64	(112)	44.81	2.0211	76.70	(220.204)
27.823	3.2039	2.17	(103)	52.88	1.7300	13.96	(116.312)
35.623	2.518	3.04	(211)				
42.05	2.147	1.84	(105, 213)				
44.292	2.0434	40.61	(204, 220)				
47.934	1.896	1.50	(301)				
52.47	1.7425	23.84	(116, 312)				
62.73	1.479	1.13	(305, 323)				
64.45	1.4445	4.01	(400, 008)				

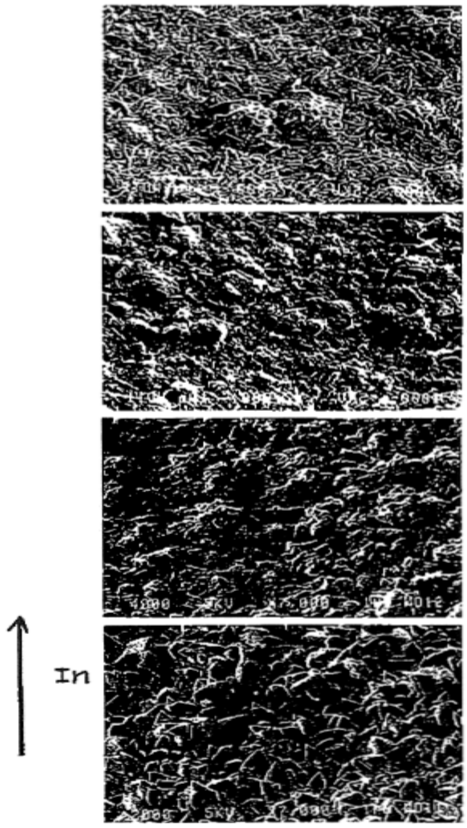

Fig. 2: Surface morphology of CIS films as a function of In content

3.2. Scanning Electron Micrograph Analysis

The SEM micrographs of CuInSe films deposited with different Cu/In ratios indicated very rough surface. Fig. 2 shows the general trend of surface morphology as a function of increasing in content in the CIS material. Table 1 gives the composition measurements of several CIS films with grain sizes determined from the SEM micrographs. The Cu/In ratio tends to decreases as the amount of Se increases.

Similar results for the surface morphology of CIS films as a function of In content have been found by Al – Bassam [14-15], Pal. [16] and Arya et al. [17]. They suggested that the Cu/In ratio tends to decrease as the amount of Se increases. This is consistent with an In-loss mechanism in which In_2Se is the volatile compounds, Pal et al. [16] suggested that the SEM micrograph of CuInSe films with ratios of 0.67, 0.86 and 1.18 had very rough surface which will increase capacity for capturing incident radiation and thus will improve solar cell performance. The surface morphology of CIS shows larger grains for Cu rich material and for Cu deficient material. The grain sizes with Cu/In are shown in Fig.3. It can be observed that a sharp change in grain sizes occurred with the increase in Cu/In from 0.68 to 0.87. This is in good agreement with other results reported by Pal et al. [16] and by Al-Bassam [14-15].

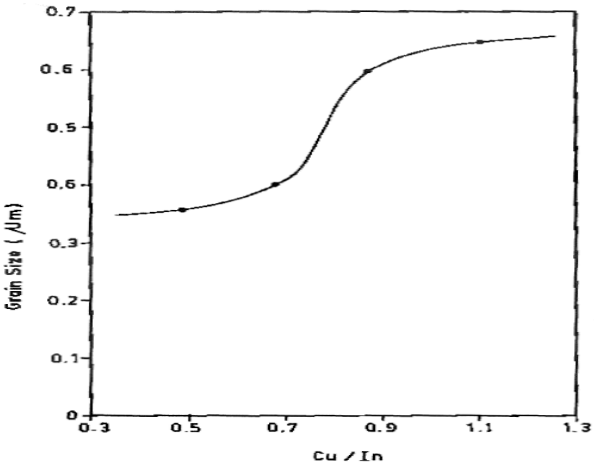

Fig. 3: Variation of grain size with Cu/In ratio for CIS films

They suggested a sharp change in grain sizes occurred with the increase in Cu/In from 0.7 to 0.9. Thus the grain size was found to vary in the range of 0.36-0.65. It was observed that Se/(Cu + In) of the CIS films was between 0.97 and 1.20, (See table 2).

Table 2: Composition and grain size in CIS films

Film No.	**Composition (at %)**			**Cu/In**	**Se (Cu+In)**	**Grain Size (nm)**
	Cu	In	Se			
1	15	30.4	54.6	0.49	1.20	0.36
2	20.1	29.5	50.4	0.68	1.02	0.40
3	22.3	26.5	51.2	0.84	1.05	-
4	23.2	26.6	50.2	0.87	1.01	0.60
5	26.5	24.5	49.3	1.1	0.97	0.65

From table 1 it can be noted that the samples. Closer to the indium source or the copper source were richer in indium or copper respectively. The amount of selenium present is expected to be 50 at % since an excess vapour pressure of selenium was maintained during the deposition.

4. Conclusion

Thin films of Copper Indium Diselemide with different Cu/In ratios (0.49-1.1) have been fabricated by electrochemical deposition method and thermal evaporation. The surface morphology with different Cu/In ratios was studied with SEM. The grain size was in the range 0.49–1.1 micro-m, with a sharp change when increasing Cu/In from 0.68 to 0.87.

5. Acknowledgements

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6. References

[1] F.J. Pem R. Noufi A. Mason, A. Franz. (1991), Thin Solid Films 202 - 299.

[2] E.R. Don, R. Hill, G.J. Russel, Solar Cells (1986) 16 -131.

[3] Isomura, S. Nagamatsu, A. Shinohara, K. Anono, T. (1986) Sol. Cells 16 -143.

[4] Dhere, NG. Lourenco, MC.Dhere, RG. Kamerski, L. L. (1986) Sol. Cells 16 - 369.

[5] Hedstrom,H,. Ohlsemn H,. Bodgard M,. Kylner A, .Stolt L, Hariskos Ruckh M, Shock H.W. (1993), 23rd IEEE US-Pusc, p. 364.

[6] Baumgartner, F.P, M, Regula. E. Bucher, (1994), l2the E. C. Photo vohaic Solar Energy Cong., p 637.

[7] Neelakanth, G., Crhstina, G.M., Kazmersi, L and Here, R.D, solar cells, 13 (198)

[8] Albin, D., Mooney, G., Duda, A., Tuttle, J., Matsin, R and Noufi, (1991), Solar cells, 30 - 47.

[9] Schmid, D., Kessler, J and Schock, H (1994) 12th European –photobolataic energy conference, 653.

[10] Arya, R., Lommasson, T., Wiedeman, S., Russell, L., Skibo, S and Fogleboch, IEEE (1993) 516.

[11] Bulent M., Kapur, V and Halani, A (1991) IEEE - 893

[12] Tuttle, J. Albin, D and Noufi, Rolar Cells, (1991) Thin solid films, (247) 8-14.

[13] Pal, R., ChattopadhYaY, K. K., Chaudhuri, S and Pal, A. K (1991) Thin solid films, (247) 8 - 14.

[14] A. Al-Bassam , J. Physica.B (condensed) B. 266 (1999) P. 192.

[15] A. Al-Bassam, 23rd Eurepean Photo Voltaic Solar Energy conference and Exhibition, August, 2008, Volencia , Spain

[16] Kamerski, L. L., Ayyagari, M.S., Sanborn, GA., White, F.R., Merrill, A.J. (1976) Thin Solid Films 37, 323.

[17] Shih, I., Champriers, C.H., Shadidi, A.V. (1983) Solar Cells 16, 27.

[18] Lipson, H., Steeple, H., (1970, Interpretation of X-ray powder Diffraction Patterns, Mac Millian, London. UK.