THE EFFECT OF pH ADJUSTMENTS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CIAS THIN FILMS

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Abstract

$Cu(In1_{-x}Al_x)Se_2$ (CIAS) thin films were prepared by the economical chemical bath deposition (CBD) technique on well-cleaned glass substrates. Two different thickness films were prepared by varying the pH. The thickness of the films was measured by gravimetric technique. The structure, morphology, composition, and optical transition of the prepared films were determined. X-ray diffraction studies confirmed the polycrystalline nature of the thin films with a chalcopyrite structure. The structural parameter such as lattice constants, axial ratio, tetragonal distortion, crystallite size, dislocation density, and number of crystallites per unit area has also been evaluated. Scanning electron microscopy studies revealed that the morphology of the prepared films was smooth, dense, uniform, and granular. The composition of various constituents such as Cu, In, Al, and Se in the CIAS films has been determined from energy dispersive X-ray (EDX) analysis. The optical properties have been studied in detail from the transmittance spectra in the visible and near infra-red region and the optical transition has been found to be direct and allowed with the band gap of around 1.4 eV Due to the pH adjustment, the changes in the preferential orientation on the structural properties and the band gap variation with respect to thickness on the optical properties have also been discussed.

Keywords: Thin Films, X-ray Diffraction, Crystal structure, CBD (Chemical Bath Deposition), CIAS ($Cu(InAl)Se_2$)

Introduction

Recently CIAS has been considered as one of the viable alternates for higher band gap copper inidium diselenide (CIS) based solar cells, because it requires a smaller relative alloy concentration than gallium (CIGS) or sulphur (CISS) alloys to achieve a comparable band gap (Srinivas *et al.*, 2006). Many researchers have prepared CIAS thin films by evaporation methods (Itoch *et al.*, 1998; Marsillac *et al.*, 2002; Paulson *et al.*, 2002; Halgand *et al.*, 2005). Hence an attempt has been made to prepare CIAS thin films by a low cost CBD technique. The significance of the pH value in the preparation of CBD thin films has
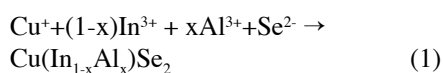
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been presented elsewhere (Dhanam *et al.*, 2002; Dhanam *et al.*, 2005; Prabahar and Dhanam, 2005). After many trials of investigations it has been found that the manner of the pH adjustment of the reaction mixture had a huge influence on the film properties and therefore we report the results of our investigation in this paper.

Experimental Procedure

Two chemical baths (1 and 2) have been prepared by mixing the solutions A, B, and C. Solution A contained 7.5 ml (0.2 M) of $CuSO_4$ and 7.5 ml (0.1 M) of trisodium citrate solution, solution B contained 10 ml of selenium solution (1000 mg/Se), whereas solution C had 0.1 M of $InCl_3$ and 0.1 M of Al_2So_4 dissolved in 12.5 ml of citric acid. In the chemical baths, Cu^+ ions are released from the trisodium citrate complex (solution A), Se^{2-} ions are released from the selenium solution (solution B), and $(In, Al)^{3+}$ ions are released from the citric acid complex of $InCl_3$ and $Al_2(So_4)_3$ (solution C). The common complexing agent citrate was used to avoid binary formation Dhanam *et al.* (2002) The deposition of CIAS thin films is based on the reaction of Cu+, In^{3+}, Se^{2-}, and Al^{3+} ions and formed as per the following reaction:-

$$Cu^+ + (1-x)In^{3+} + xAl^{3+} + Se^{2-} \rightarrow$$
$$Cu(In_{1-x}Al_x)Se_2 \qquad (1)$$

The reaction mechanism differs from the CIS film formation in which some of the x number of In^{3+} lattice points are replaced by x number of Al^{3+}. The value of x was found by EDAX composition analysis. The concentration, volume, and pH of the reaction mixture, the deposition time, and the temperature are maintained as the same for both the chemical baths and the chemical baths differ only in the way in which the pH is adjusted. Both the chemical baths are mixed thoroughly and adjusted to a pH value of 10 by a digital pH meter (Model 101E-Electronic India). In chemical bath 1, the pH of the reaction mixture is adjusted to 10 and then heated to 50˚C for 10 min, whereas in chemical bath 2, the

pH is adjusted to 10 after heating the solution to 50˚C for 10 min. In chemical bath 1, the pH of the solution decreases when the temperature is increased, because at the higher temperature the weak acid, citric acid, is having more of a degree of dissociation and releasing a greater number of H^+ ions. This acid proton decreases the pH. Therefore it is understood that the manner of the pH adjustments varies the pH of the bath. Well-cleaned glass substrates were suspended in the chemical baths for 60 min. The prepared films were taken out from the reaction mixture and dried naturally. The thicknesses of the prepared films were determined by the gravimetric technique.

An XRD-6000 X-ray diffractometer (Shimadzu Corporation, Japan) with a vertical goniometer fitted with a vanadium filter and copper radiation ($\lambda = 1.5406$ Å) was used for the structural analysis of the thin films of different thicknesses. The surface morphology of the CIAS thin films was studied using a scanning electron microscope (JSM6330F, JEOL Ltd., Japan). A V570:UV-VIS NIR (JASCO, Inc., USA) double beam spectro-photometer was used for optical studies in the wavelength range 400-2500 nm. An energy dispersive X-ray analyzer (S44Oi, Leica Microsystems GmbH, Germany) was used to confirm the composition of the constituents in the CIAS thin films.

Results

Structural Properties

The X-ray diffraction profiles of CIAS thin films prepared from 2 chemical baths are presented in Figure 1 which confirm the polycrystalline nature of the thin films. The Bragg condition (Dhanam *et al.*, 2002) has been employed to identify the directions in which the film diffracted the beam of monochromatic X-rays. The absence of broadening of peaks suggests that the films are free from stress and that that may be the reason for the better adhesion of the films.
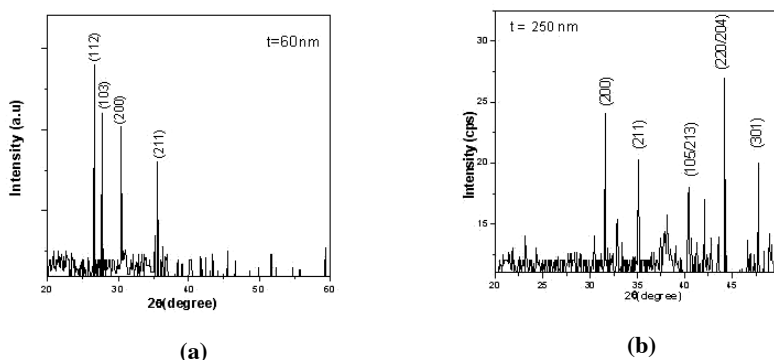
The predicted peaks 112, 103, 200, 211, 105) 204/220, and 116/312 are reported as

identified peaks for CIAS thin films by earlier reports (Shafarman *et al.*, 1996; Marsillac *et al.*, 2002; Paulson *et al.*, 2002; Halgand *et al.*, 2005) and JCPDS file 40-1487. CIS standards have been used by in the present study due to the non-availability of CIAS standards as suggested by Halgand *et al.* (2005). The diffraction patterns enabled us to conclude the structure of the CIAS thin films as chalcopyrite. The intensity of the 112 plane increases significantly faster than the other peaks in the films prepared from chemical bath 1 confirming the preferred orientation as 112. But in chemical bath 2, the preferred orientation is changed to 220/204 from 112 because of the heating of the reaction mixture before the pH adjustments i.e. due to the manner of the pH adjustment. The 220/204 peak has also been reported earlier as prominent and the preferred orientation peak in CIS and CIGS thin films (Kazmerski *et al.*, 1976; Kazmerski *et al.*, 1977; Varela *et al.*, 1985). The peaks corresponding to the 200 plane were due to reflection from the glass substrate (Dhanam *et al.*, 1998). The preferred orientations are again confirmed by comparing the orientation factors of the different planes of the films by the method suggested by Prabahar and Dhanam (2005) and the results are presented in Table 1.

From the observed d-spacing, various structural parameters such as lattice constants (a,c), axial ratio, tetragonal distortion, volume of the unit cell, crystallite size, dislocation density, and number of crystallites per unit area and strain have been estimated using standard expressions (Dhanam *et al.*, 2002) and are presented in Table 2. From X-ray diffraction it can be concluded that the lattice constants agree very well with the American Society for Testing and Materials value for their films prepared from both chemical baths and also that the tetragonal distortion was less for bath 1 films compared with bath 2 films.

The variation of the grain size with the film thickness showed the usual trend. At the lower film thickness of 60 nm, the grain size was low (~8 nm) and increased sharply to a value of 33.5 nm with the increase of film thickness to 250 nm. The observed behavior of the grain size at the lower thickness might be due to the stronger interaction between the substrate and depositing atoms, which restricts the mobility of both the additional atoms and subcritical nuclei. As the film thickness increased, the effect of the substrate could be decreased, as the ions being deposited layer by layer on the substrate, so that an increase in the grain size could be observed. At the higher thickness, the grain size reached a saturation value and the improvement was marginal (Prathap *et al.*, 2008). When the thickness of the films increases (irrespective of chemical baths) the crystallite size increases, but the dislocation density and strain decreases. Since the dislocation density and strain are the manifestation of the dislocation network in the films, the decrease

(a)   (b)

Figure 1.   X-ray diffractogram of CIAS thin films prepared from a) chemical bath 1 and b) chemical bath 2

in the strain and dislocation density indicate the formation of higher quality films (Lalitha *et al*., 2004).

Even though films prepared from bath 1 have 112 as the preferential orientation, the crystalline size, lesser defect, and lower strain were obtained for the films prepared from bath 2. Recently, however, the National Renewable Energy Laboratory group has reported on a new world-efficiency CIGS solar cell with an efficiency of 18.8%, in which the CIGS absorber has a 204-preferred orientation. So the films prepared from bath 2 will be suitable alternate absorbers for fabricating CIAS thin film solar cells.

In and Al Composition from EDX

Figure 2 shows the EDX spectra of the CIAS thin films from chemical baths 1 and 2. The EDX quantitative analysis confirms the atomic percentage of copper, indium, aluminum, and selenium in the prepared films and the compositions of the CIAS thin films are presented in Table 3. The presence of Si and O peaks are due to the glass substrates. The EDX spectra also enabled us to conclude that the stoichiometric CIAS thin films can be obtained from chemical bath 1.
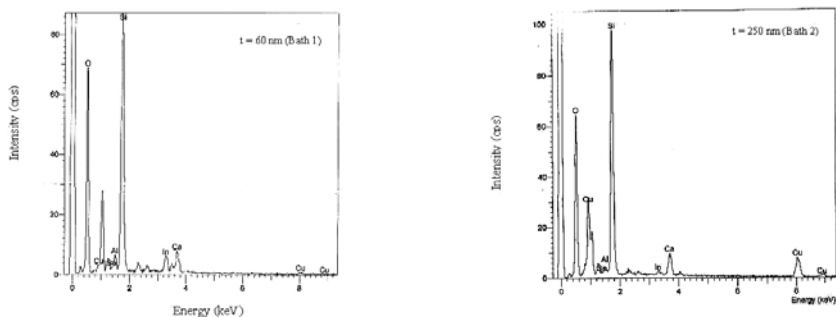

Figure 2. EDAX result of CIAS thin films prepared from bath 1 and 2

Table 1.   Confirmation of preferential orientation

Chemical bath	Film thickness (nm)	Peak	Preferential orientation factor	Preferential orientation
1	**60**	**112**	**0.4122**	**112**
		103	0.3360	
		200	0.3097	
		211	0.2484	
2	**250**	200	0.1956	**220/204**
		220/204	**0.2682**	
		105	0.1820	
		211	0.1701	
		116/312	0.1623	

Because, in chemical bath 1, the pH is adjusted to 10, and then solution is increased to 50°C. So the pH of the solution may be decreased in between 9-10, when the temperature is increased. Because at the higher temperature the weak acid- citric acid is having more degree of dissociation and releasing more number of H$^+$ ions. This acid proton decreases the pH value. So the films obtained with lower thickness from bath 1. The effect of pH on the composition takes place in chemical bath 2. Because in bath 2 the solution is first heated upto 50°C then the pH is adjusted to 10. So before adjusting, due to the presence of heat inside the solution the ions may be released mainly the indium easily be released with out the complexing agent. This appears in the EDX composition the wt% of In is very lower when compared to wt% of Al .

Surface Morphology Studies

Figure 3(a) and 3(b) shows the SEM images of the CIAS thin films prepared from the chemical baths 1 and 2. Figure 3(a) reveals that the deposited film has a distribution with a reasonably low defect density, a good crystalline quality, and the film surface has generally smooth and dense morphologies (Park et al., 1994; Sadigov et al., 1999). Figure 3(b) reveals that the deposit distribution is less porous and indicate that the CIAS films are polycrystalline in nature (Dhanam et al., 2002).

In CBD technique, the deposition parameters such as pH, temperature, time, concentration and volume plays an important role in the formation of thin films.

The effect of pH adjustments on

(i) Structural properties:

- The preferential orientation changes from (112) to (220/204)
- Thickness increases
- Grain size increases
- Volume decreases

(ii) Composition

- Increases the wt% of Al
- Automatically wt% of In decreases
- Grain size increases when Al %

Table 2. Structural parameters of CBD CIAS thin films of different thicknesses.

Chemical Bath	Film Thickness (nm)	Lattice Constants (Å)				axial ratio c/a	tetragonal distortion (2-c/a)	Volume of the unit cell (Å)^3		Crystallite size D_c (nm)	Dislocation density (10^{15} lines/m²)	Number of crystallites per unit area (10^{15} m^{-2})	Strain x 10^{-3}
		a		c									
		Observed	ASTM	Observed	ASTM			Observed	ASTM				
1	60	5.785	5.782	11.616	11.619	2.06	-0.06	388.8	388.4	8	16.43	117	1.273
2	250	5.784		10.77		1.89	0.13	385.4		33	0.92	7	0.504

increases observed in structural properties and also in surface analysis.

(iii) Thickness- Increases

Optical Properties

The optical transmittance spectra of the CIAS thin films prepared from chemical baths 1 and 2 are shown in Figure 4. The transmittance spectra illustrate the growth process. At the onset of the decrease of the transmittance value near the absorption edge (~890 nm) of the thin films prepared from chemical bath 1, a small shift towards a higher wavelength reveals a more significant growth of CIAS than in the case of chemical bath 2. The absorption coefficient, extinction coefficient, and band gap of the CIAS thin films were

calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relations,

$$\alpha = \frac{-\ln(T)}{t} \qquad (2)$$

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

as reported by Dhanam *et al.* (2002) and the evaluated values are tabulated in Table 4.

The plot of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for the CIAS thin films of different thicknesses is shown in Figure 5. The straight line extrapolated to the energy axis has been rotated many times and the band gap has been
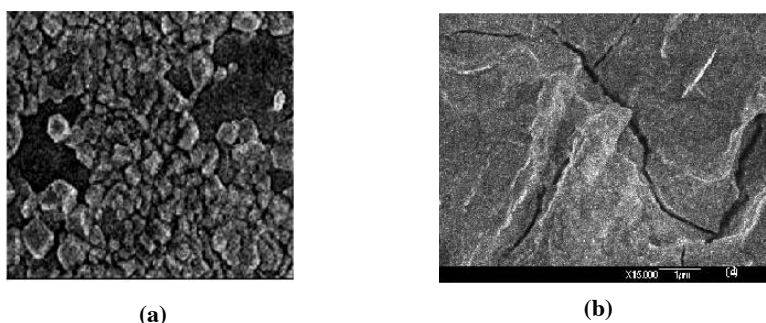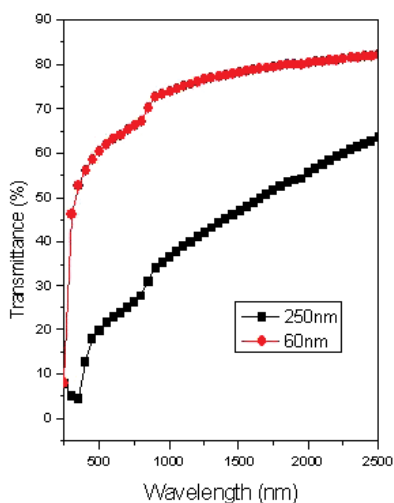
(a)

(b)

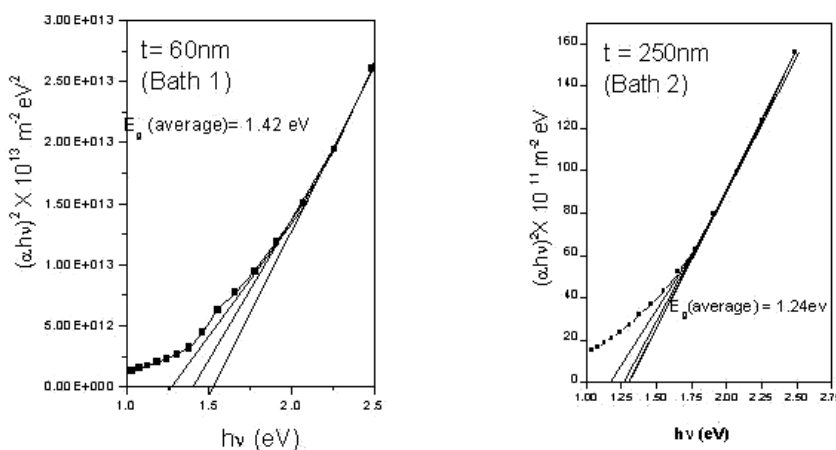**Figure 3. SEM images of CIAS thin films prepared from a) chemical bath 1 and b) chemical bath 2**

Table 3.   EDAX results of CIAS thin films

Chemical bath	Thickness (nm)	Composition	Atomic percentage
1	60	$CuIn_{0.5}Al_{0.5}Se_2$	Cu-23.7%
			In-14.5%
			Al-14.5%
			Se-47.5%
2	250	$CuIn_{0.03}Al_{0.96}Se_2$	Cu-26.06%
			In-0.95%
			Al-25.31%
			Se-47.15%.

Figure 4.   Transmittance spectra of CIAS thin films prepared from chemical bath 1 and 2

estimated each time and the average value of *Eg* has been given in Table 5. The direct allowed band gap of 1.42 eV to 1.24 eV has been obtained for the CIAS films of baths 1 and 2, which reveal the presence of the direct allowed transitions in the CIAS thin films. The observed band gap values are in agreement with earlier reported values (Itoch *et al.*, 1998; Marsillac *et al.*, 2002; Paulson *et al.*, 2002; Halgand *et al.*, 2005). As the film thickness increases from 60 to 250 nm, there is a decrease in the band gap that can be due to the influence of various factors such as grain size, structural parameters, carrier concentration, presence of impurities, deviation from stoichiometry of the film, and lattice strain (Kuhaimi, 1998; Rakhshani *et al.*, 2000). A detailed analysis is needed to bring out the effect of each of these parameters on the value of band-gap energy. However, it was observed that the lattice

Figure 5. Plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ of CIAS thin films prepared from chemical baths 1 and 2

Table 4.   Optical properties of chemical bath deposited CIAS thin films

Chemical bath	Thickness (nm)	Absorption coefficient (α) x 10^6 m^{-1} $(\lambda= 1000$ Å$)$	Extinction coefficient (k) $(\lambda= 1000$ Å$)$	Band gap *Eg* (eV)
1	60	17.17	1.37	1.42
2	250	1.22	0.09	1.24

Table 5.   Determination of (Eg) average of CIAS thin films

Baths	S.No of rotations	Band gap (eV)	Eg (average) (eV)
Bath 1	1	1.23	
	2	1.45	**1.42**
	3	1.54	
Bath 2	1	1.18	
	2	1.26	**1.24**
	3	1.30	

parameters, grain size, and the strain have a direct dependence on the film thickness (Enriquez and Mathew, 2003). Hence, we consider that the observed decrease in Eg with the increasing thickness is due to the decrease in the lattice strain. The plot of (hυ) versus $(\alpha h\upsilon)^{1/2}$, $(\alpha h\upsilon)^{1/3}$, and $(\alpha h\upsilon)^{3/2}$ (not shown) reveal that the CIAS films from both baths did not have lines above hυ>Eg, since extrapolation of it did not touch the zero absorption axis, which confirms the fact that the CIAS phase does not have indirect allowed, direct forbidden, and indirect forbidden transitions. The thin films prepared from chemical bath 1 have a widened band gap compared with that of the films from chemical bath 2.

Conclusions

The effect of the pH adjustment before heating helped to prepare the CIAS thin films with the expected properties such as 112 preferential orientations, composition, crack free surface morphology, better crystallite size, and widened band gap. Hence the structural and optical properties of the CIAS thin films helped to realize the effect of the pH adjustment in the preparation of the thin films.

Acknowledgements

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