Revue des Energies Renouvelables Vol. 13 N°4 (2010) 603 – 612

The effect of pH adjustments on the structural and optical properties of CIAS thin films

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(reçu le 15 Juin 2010 – accepté le 25 Septembre 2010)

Abstract – *CIAS, 'Cu (In Al) Se_2' thin films are prepared on the glass substrates using economical chemical bath deposition 'CBD' technique. The effect of pH adjustments before or after preheating the reaction mixture has been discussed in this paper in a detail. Due to pH adjustment the change in the preferential orientation on the structural properties and the band gap variation with respect to thickness on the optical properties, has also been discussed.*

Résumé - *Les couches minces CIAS, 'Cu (In Al) Se_2' sont préparées sur un substrat de verre en utilisant une technique économique, appelée la déposition en bain chimique, 'CBD'. L'effet de l'ajustement du pH avant ou après le préchauffage du mélange réactionnel est discuté en détail dans ce papier. En raison de l'ajustement de ce pH, le changement dans l'orientation préférentielle sur les propriétés structurales et de la variation de largeur de bande à l'égard de l'épaisseur sur les propriétés optiques, est également discutée.*

Keywords: Thin Films - X-ray Diffraction - Crystal structure - CBD 'Chemical Bath Deposition'.

1. INTRODUCTION

Recently CIAS is considered as one of the viable alternate for higher band gap CIS based solar cells, because it requires smaller relative alloy concentration than gallium (CIGS) or sulphur (CISS) alloys to achieve comparable band gap [1].

Many researchers have prepared CIAS thin films by evaporation methods [2-5]. No researchers have analyzed CIAS thin films prepared by low cost CBD technique.

Hence an attempt has been made to prepare CBD CIAS thin films and a method has also been identified to estimate indium and aluminum composition in CIAS thin films using XRD and transmittance spectra [1].

The significance of pH value in the preparation of CBD thin films has been presented elsewhere [6-8]. After many trials of investigations it has been found that the way of 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.

2. 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 7.5ml (0.1M) of trisodium citrate

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solution, solution B contained 10 ml of selenium solution (1000 mg/Se) where as solution C has 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 selenium solution (solution B) and $(InAl)^{3+}$ ions are released from 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 [6]. 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.

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

The reaction mechanism differ from the CIS film formation [6] 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, deposition time and temperature are maintained as the same for both the chemical baths and the chemical baths differ only in the way of pH adjustments.

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, pH of the reaction mixture is adjusted to 10 and then heated to 50 °C for 10 minutes, whereas in chemical bath 2, pH is adjusted to 10 after heating the solution to 50 °C for 10 minutes. 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 degree of dissociation and releasing more number of H^+ ions.

This acid proton decreases the pH. Therefore it is understood that the way of pH adjustments vary the pH of the bath. Well-cleaned glass substrates were suspended in the chemical baths for 60 minutes. The prepared films were taken out from the reaction mixture and dried naturally. Thicknesses of the prepared films were determined by gravimetric technique.

A Shimadzu XRD-6000 X-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation ($\lambda = 1.5406$ Å) was used for the structural analysis of thin films of different thicknesses. The surface morphology of CIAS thin films was studied using a scanning electron microscope (JEOL JSM 6330F).

A JASCO (V570: UV-VIS-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400-2500 nm. Energy dispersive x-ray analyzer (Leica.S44Oi) was used to confirm the composition of the constituents in CIAS thin films.

3. RESULTS

3.1 Structural properties

X-ray diffraction profiles of CIAS thin films prepared from two chemical baths are presented in Fig. 1 which confirms the polycrystalline nature of thin films.

Bragg condition [6] has been employed to identify the directions in which the film diffracted the beam of monochromatic X-rays.

The absence of broadening of peaks suggest that the films are free from stress and that may be the reason for the better adhesion of films [1].

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 [3-5, 9] and JCPDS file [40-1487]. CIS standards have been used by in the present study due to the due to the non-availability of CIAS standards as suggested by Halgand *et al.* [4].

The diffraction patterns enabled to conclude the structure of CIAS thin films as chalcopyrite.

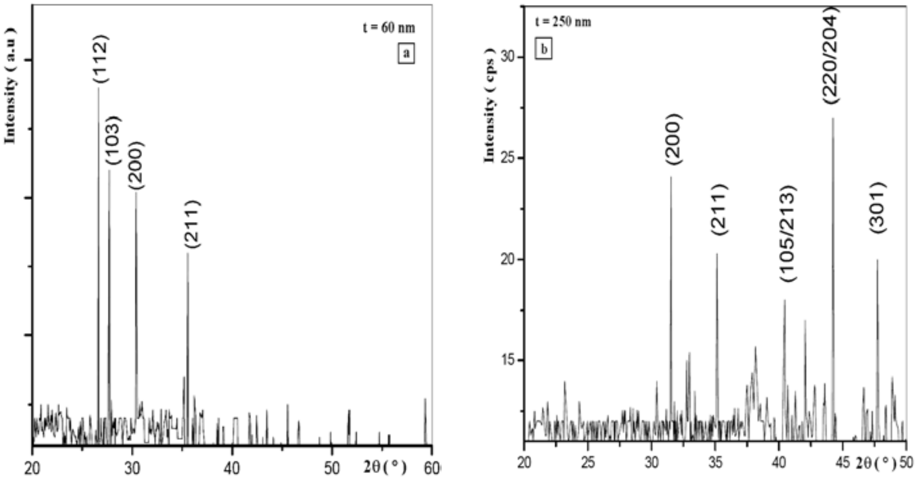

Fig. 1: X-ray diffractogram of CIAS thin film prepared from
a- Chemical bath 1 and b- Chemical bath 2

The intensity of (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 heating the reaction mixture before pH adjustments i.e due to the way of pH adjustment. (220/204) peak is also reported as prominent and preferred orientation peak in CIS and CIGS thin films earlier [10-12].

Table 1: Confirmation of preferential orientation

Chemical bath	Film thickness (nm)	Peak	Preferential orientation factor	Preferential orientation
1	60	112 103 200 211	04122 0.3360 0.3097 0.2484	112
2	250	200 220/204 105 211 116/312	0.1956 0.2682 0.1820 01701 0.1652	220/204

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

Chemical bath	Film Thickness (nm)	Lattice constants (A°)				Axial Ratio	Tetragonal Distorsion	Volume of the Unit cell (A°)^3		Crystallite size D_c (nm)	Dislocation density (10^{15} lines/m^3)	Number of crystallites Per unit area (10^{15} m^{-3})	Strain $\times 10^{-3}$
		a		c		c/a	2-c/a						
		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		1.86	0.13	385.4		33	0.92	7	0.504

The peaks corresponding to (200) plane where due to reflection from the glass substrate [13]. The preferred orientations are again confirmed by comparing the orientation factors of different planes of the films by the method suggested by Prabahar *et al.* [8] 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 [6] are presented in **Table 2**.

From X-ray diffraction it can be concluded that the lattice constants agree very well with ASTM value for their films prepared from both chemical baths and as well as the tetragonal distortion was lesser for bath 1 films compared to bath 2 films.

The variation of grain size with film thickness showed the usual trend. At 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 grain size at lower thickness might be due to the stronger interaction between the substrate and depositing atoms, that restricts the mobility of both the additional atoms and subcritical nuclei.

As the film thickness increased, the effect of substrate could be decreased, as the ions being deposited on the initial layer itself, so that an increase in the grain size could be observed. At higher thickness, the grain size reached a saturation value and the improvement was marginal [14].

When 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 dislocation network in the films, the decrease in the strain and dislocation density indicate the formation of higher quality films [15].

Even though films prepared from bath 1 has (112) preferential orientation, but the crystalline size, lesser defect and lower were obtained for the films prepared from bath 2. Recently, however the NREL 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 a suitable alternate absorber for fabricating CIAS thin film solar cells.

3.2 In and Al composition from EDAX

Figure 2 shows the EDAX spectra of CIAS thin films from chemical bath 1 and 2. EDAX quantitative analysis confirms the atomic percentage of copper, indium, aluminum and selenium in the prepared films and the composition of CIAS thin films were presented in **Table 3**.

The presence of Si and O peaks are due to the glass substrates. EDAX spectra also enabled to conclude that the stoichiometric CIAS thin films can be obtained from chemical bath 1.

3.3 Surface morphology studies

Fig. 3 a- and b- shows the SEM images of CIAS thin films prepared from the chemical baths 1 and 2.

Fig. 3a- reveals that the deposited film has distribution with a reasonable low defect density, a good crystalline quality and the film surface has generally smooth and dense morphologies [16, 17].

Fig. 3b- image reveals that the deposit distribution is less porous and that they indicate CIAS films are polycrystalline in nature [6].

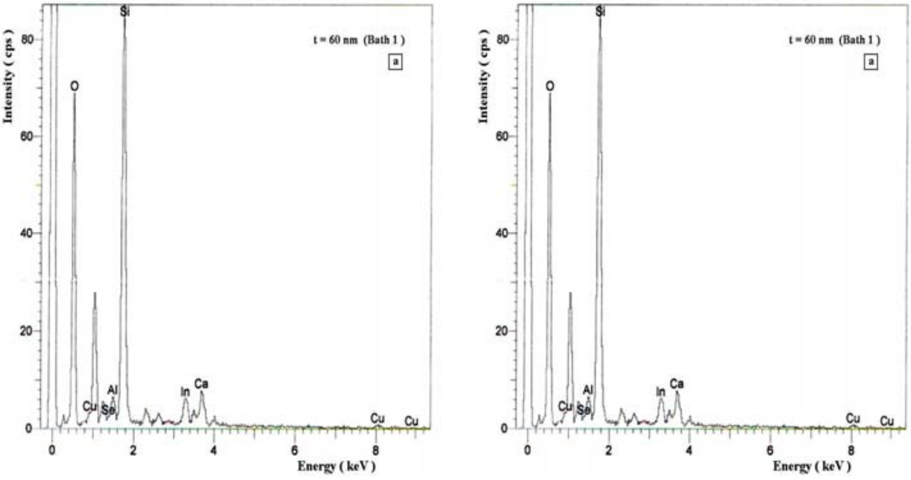

Fig. 2: EDAX result of CIAS thin films prepared from bath 1 and 2

Table 3: EDAX results of CIAS thin film

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 %

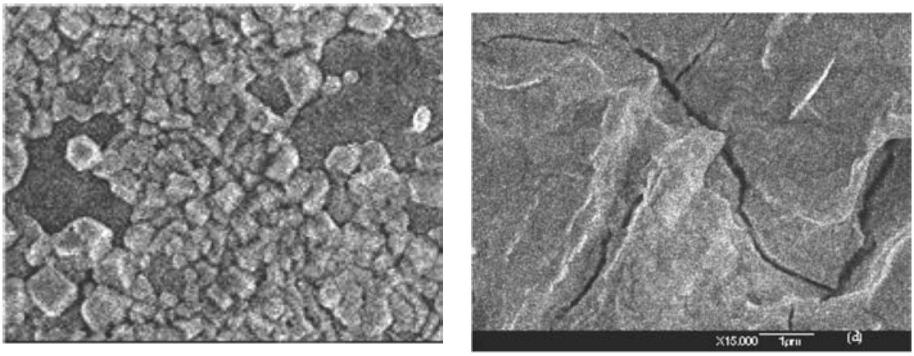

Fig. 3: SEM images of CIAS thin films prepared from
a- Chemical bath 1 and b- Chemical bath 2

3.4 Optical properties

The optical transmittance spectra of CIAS thin films prepared from chemical baths 1 and 2 are shown in Fig 4.

Transmittance spectra illustrate the growth process. On the onset of decrease of transmittance value near the absorption edge (~ 890 nm) of thin films prepared from chemical bath 1and a small shift towards higher wavelength revels the significance growth of CIAS than in the case of chemical bath 2.

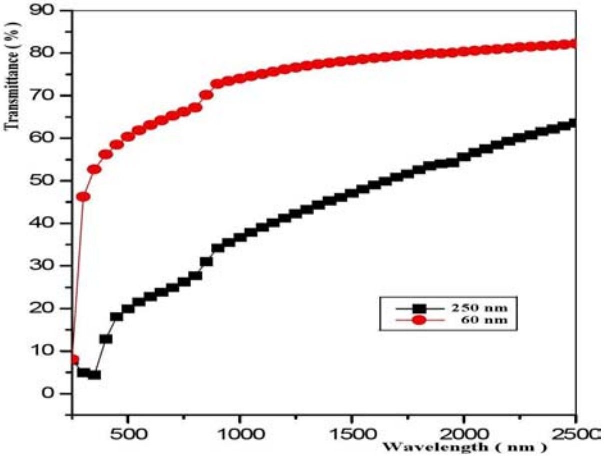

Fig. 4: Transmittance spectra of CIAS thin films prepared from chemical bath 1 and 2

Absorption coefficient, extinction coefficient and band gap of CIAS thin films were calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relations (1) and tabulated in **Table 4**.

Table 4: Optical properties of chemical bath deposited CIAS thin film

Chemical bath	Thickness (nm)	Absorption coefficient $(\alpha)\times10^6$ m^{-1} (λ=1000 A°)	Extinction coefficient (k) (λ=1000 A°)	Band gap E_g (eV)
1	60	17.17	1.37	1.44
2	250	1.22	0.09	1.46

Plot of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for CIAS thin films of different thicknesses is shown in Fig. 5.

The straight line extrapolated to the energy axis has been rotated many times and the band gap has been estimated each time and the average value of E_g has given in **Table 5**.

Direct allowed band gap of 1.42 eV to 1.24 eV has been obtained for CIAS films of bath 1 and 2, which reveal the presence of direct allowed transitions in CIAS thin films. The observed band gap values are in agreement with earlier reported values [2-5, 9, 20].

Table 5: Determination of $(E_g)_{\text{average}}$ of CIAS thin film

Baths	S.N° of rotations	Band gap (eV)	E_g average (eV)
Bath 1	1.	1.37	**1.44**
	2.	1.50	
Bath 2	1.	1.41	**1.46**
	2.	1.52	

As the film thickness increases from 60 to 250 nm, there is a decrease in the band gap 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 [21, 22].

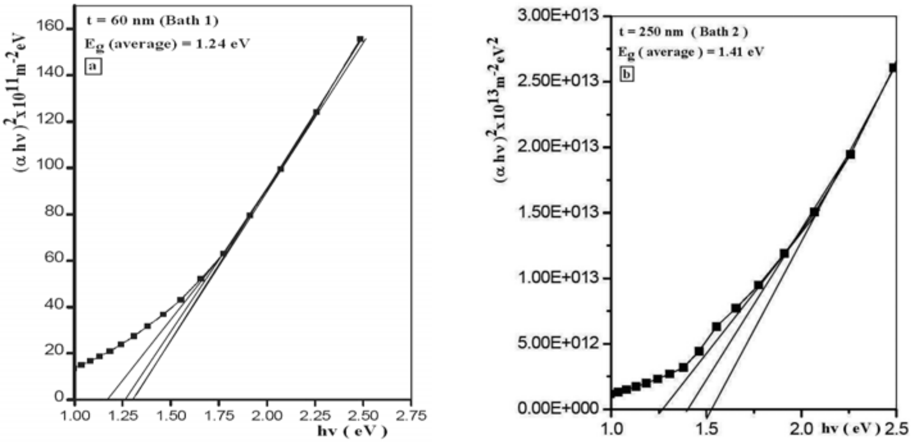

Fig. 5: Plot of $(\alpha h\upsilon)^2$ vs $(h\upsilon)$ of
CIAS thin films prepared from chemical baths 1 and 2

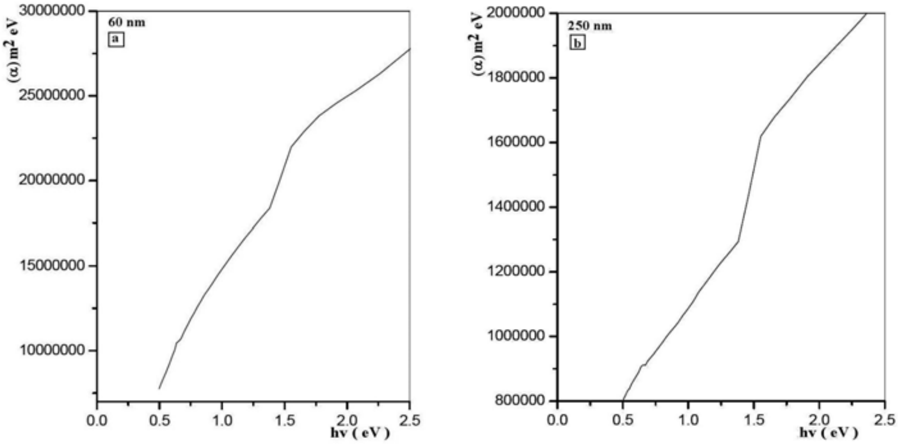

Fig. 6: Plot of (α) vs $((h\upsilon)$ of CIAS
thin films prepared from chemical baths 1 and 2

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 parameters, grain size and the strain have a direct dependence on the film thickness [23].

Hence, we consider that the observed decrease in E_g with increasing thickness is due to the decrease in lattice strain. Plot of $(h\upsilon)$ versus $(\alpha h\upsilon)^{1/2}$, $(\alpha h\upsilon)^{1/3}$, $(\alpha h\upsilon)^{3/2}$ (not shown) reveal that CIAS films from both baths did not have line above $(h\upsilon) > E_g$ since extrapolation of it did not touch the zero absorption axis which confirm the fact that CIAS phase does not have indirect allowed, direct forbidden and indirect forbidden transitions.

Thin films prepared from chemical bath 1 has widened band gap compared to that of the films from chemical bath 2.

4. CONCLUSION

The effect of pH adjustments before heating helped to prepare CIAS thin films with expected properties such as (112) preferential orientation, composition, crack free surface morphology, better crystallite size and widened band gap.

Hence the structural and optical properties of CIAS thin films helped to realize the effect of pH adjustment in the preparation of thin films.

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