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Estimation of lattice constants and type of conductivity of CBD CIAS thin films from EDAX spectra

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ABSTRACT

Near-stoichiometric and stoichiometric CBD CIAS thin films have been prepared onto well-cleaned substrates. EDAX spectra of the prepared thin films enabled to determine the film composition, stoichiometry nature, type of conductivity, lattice constants, volume of the unit cell and density of CIAS thin films. The estimated compositional, structural and electrical parameters are presented and discussed in this paper in detail.

Keywords: CBD; stoichiometric CIAS; near stoichiometric CIAS; EDAX.

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Introduction

Solar cells based on the use of the chalcopyrite compounds such as $CuInSe_2$ (CIS) and $CuInGaSe_2$ (CIGS) are relatively in development trends. Interest was stimulated by the production of a 10% efficient CIS cell by Mickelson and Chen in 1982 [**1**]. Since that time there has been much activity worldwide to develop these solar cells based on the use of CIS and CIGS [**2**]. CIS has a direct band gap of 1.04eV with high absorption coefficient for photons with energies greater than the energy band gap [**3, 4**]. The reason for incorporating Ga in CIS is that it increases the energy band gap towards the optimum value of 1.5eV. It is found that cell performance increases with Ga content up to 1.3eV, partly due to the increase in energy band gap and partly due to Ga inducing improvements in material quality. However it is found that increasing the energy band gap to values greater than 1.3eV results in a rapid decrease in cell performance due to reduction in open circuit voltage and fill factor [**5**]. At present CIGS solar cells can be used to produce 19.9% efficiency in the laboratory [**6**]. Despite the success of this technology there is a concern with the lack of abundance of Ga and In when the technology moves to very large scale production over the next decade. This problem may be minimized by the development of CIS solar cells, replacement of Ga by Al to produce $CuInAlSe_2$ (CIAS) rather than CIGS as Al is more abundant than Ga. Enhancing device efficiency by the development of chalcopyrite tandem solar cells using CIAS as upper cells (CIGS cannot be used to make upper cells because its energy band gap is too narrow).

The properties of CIS based absorber material mainly depends on Cu/In. The strength of the I-VI and III-VI

bonds are different and therefore the ratio c/a is not exactly equal to 2. In the literature c/a is reported as being equal to 2.01 in CIS [**7**]. Cu-In ratio variation leads to high concentration of electrically active native defects and these results in large changes in carrier density. Hence a deviation from a unity value of Cu/In ratio determines whether the conductivity is n or p-type [**8**]. Cu/In ratio in the precursor is an important factor for the absorber layer preparation in CIS based thin film solar cells because their morphology as well as optoelectronic and structural properties have been found to be dependent on it [**9**]. Cu/In ratios higher than 0.95 have been shown result with poor performance due to unwanted Cu-related secondary phases present in the absorber material which leads to significantly lower shunt resistance [**7**]. Moreover, Cu-depleted films produced using an excess supply of Se form p-type material while Cu-rich films selenised in deficient Se supply would lead to form n-type layers because the Se-vacancy (V_{Se}) acts as a dominant donor in n-type chalcopyrite material and the Cu vacancy (V_{Cu}) acts as a dominant acceptor in Cu-poor p-type material [**10**]. However the Cu-rich phase plays an important role during absorber film growth, it leads to yield grain size in excess of 1 micrometer whereas an In-rich composition results in smaller grain structured films [**11**]. This survey motivated to carryout EDAX analysis of CBD near- stoichiometric and stoichiometric CIAS thin films. The composition, structural and electrical parameters evaluated from EDAX spectra have been presented in this paper in detail.

Experimental

Near-stoichiometric and stoichiometric CBD CIAS thin films are prepared from the reaction mixture containing copper sulphate (≥ 99 % purity – Merck), trisodium citrate (≥ 99 % purity – Merck), indium trichloride (≥99.999 % Sigma Aldrich), selenium (≥99.99 % Sigma Aldrich) aluminium sulphate (≥ 99 % purity – Nice) and citric acid (≥ 99 % purity – Merck). All solutions were prepared in double distilled water and the chemical used with different concentration and volume for near stoichiometric and stoichiometric CIAS thin films are presented in **Table 1**. A digital pH meter (model 101 E-Electronic India) has been used to adjust the pH of the reaction mixture. pH meter was standardized using buffer solutions of pH 4 ± 0.05 abd 9.2 ± 0.05. The substrates used for the deposition of films were suspended closer to the inner wall of the deposition beaker for better uniformity and adherence of the film on the substrates and to avoid shaking of the substrates while deposition [**12**].

A constant and very slow stirring is provided while adding the different solutions of the reacting mixture. $CuSO_4$ solution was taken in a 100 ml beaker, TSC solution is then added drop by drop to it and followed by sodium selenosulfite (Solution A). Citric acid is used as a complexing agent for $InCl_3$ and Al_2SO_4 and thus solution is added drop by drop to solution A (reaction mixture). The pH of the reaction mixture was varied from 9 to 10 and optimized as 10 [**13**] and the deposition time range was optimized as 30 to 120 minutes to obtain films of uniform thickness. The depositions were carried out in water bath at two different temperatures (50°C and 60°C) and optimized as 60°C. Near-stoichiometric CIAS thin films has been prepared when the concentration of coppersulphate is varied as 0.5 & 0.2M respectively to obtain Cu-rich and Cu-poor CIAS thin films, whereas the concentration of indium trichloride and aluminium have been changed to obtained In-rich and In-poor thin films without changing the volume of the solution (**Table 1**). The preparation conditions of stoichiometric CIAS thin films have been presented in **Table 2**. After deposition the films were taken out and dried naturally and annealed at 100°C for one hour. Energy dispersive x-ray analysis attachment (Thermo SuperDry II) is used to carry out semi-quantitative elemental analysis of the annealed CBD CIAS thin film samples.

Expressions used to calculate compositional parameters

Shi et al. [**1**] expressed the compositional deviations from their ideal formula by two parameters, the non-stoichiometry and non-molecularity as

Non-molecularity parameter-

$$(\Delta x) = \frac{Cu}{In} - 1$$

Non-stoichiometry parameter-

$$(\Delta y) = \frac{2Se}{Cu + 3In} - 1$$

Table 1. Concentration and volume of the chemicals used for the preparation of near-stoichiometric CBD CIAS thin films.

	Chemicals	Volume (ml)				Concentration (M)			
		Cu-rich	Cu-poor	In-rich	In-poor	Cu-rich	Cu-poor	In-rich	In-poor
Near-Stoichiometric CIAS thin films	Copper sulphate	15	15	7.5	7.5	***0.5***	***0.2***	0.2	0.2
	Trisodium citrate	10	10	7.5	7.5	0.1	0.1	0.1	0.1
	Citric acid	20	20	25	25	0.1	0.1	0.1	0.1
	Indium trichloride	10	10	12.5	12.5	0.1	0.1	***0.2***	***0.1***
	Aluminium sulphate	10	10	12.5	12.5	0.1	0.1	***0.1***	***0.125***
	Sodiumselenosulphite	20	20	40	40	0.1	0.1	0.1	0.1

Table 2. Concentration and volume of the chemicals used for the preparation of stoichiometric CBD CIAS thin films.

	Chemicals	Volume (ml)	Concentration (M)
Stoichiometric CIAS thin films	Copper sulphate	20	0.2
	Trisodium citrate	10	0.1
	Citric acid	20	0.1
	Indium trichloride	10	0.2
	Aluminium sulphate	10	0.15
	Sodiumselenosulphite	40	0.1

Dependences of aluminum concentration (x) on the lattice parameters ‘a’ and ‘c’ will change linearly in accordance with the Vegard’s law and are expressed by [**2**],

$$a = 5.782 - 0.177x$$

$$c = 11.620 - 0.656x$$

The volume of the unit cell was calculated by using the lattice constants estimated from the aluminium (x) composition estimated from EDAX spectra [**2**],

$$V = a^2 c$$

The density of CIAS thin films [**2**] can also be evaluated using unit cell parameters (a,c) and unit cell volume V in the expression,

$$d = \frac{1.65 \times 10^{-24} NM}{V}$$

where N is the number of crystallites in a unit cell (calculated from XRD data), M is the molar mass of the compound (363.246 gm/mole) and V is the unit cell volume respectively.

Results and discussion

Fig. 1 and **2** show the EDAX spectra of near stoichiometric and stoichiometric CIAS thin films prepared by CBD technique and the spectra show the presence of the chemical constituents (Cu, In, Al and Se) of CIAS thin films. EDAX quantitative results confirm the atomic percentage of constituents in the prepared films as well as the composition of near-stoichiometric and stoichiometric CBD CIAS thin films (**Table 3**).

Table 3. EDAX quantitative results of CBD CIAS thin films.

Near-Stoichiometric CBD CIAS Films	Atomic percentage (%)				Film composition
	Cu	In	Al	Se	
Slightly Cu-rich (t = 800 nm)	27	11.32	11.20	50.49	$Cu_{1.1}(In_{0.45}Al_{0.55})Se_2$
Slightly Cu-poor (t = 750 nm)	23	13.19	12.11	51.36	$Cu_{0.92}(In_{0.52}Al_{0.48})Se_2$
Slightly In-rich/Al-poor (t = 450 nm)	23.64	14.41	11.10	50. 94	$Cu_1(In_{0.6}Al_{0.4})Se_2$
Slightly In-poor/Al-rich (t = 600 nm)	25.17	10.48	12.87	50.54	$Cu_1(In_{0.4}Al_{0.6})Se_2$
Stoichiometric CBD CIAS films	Cu	In	Al	Se	Film composition
(t = 500 nm)	25.02	12.50	12.51	50.8	$CuIn_{0.5}Al_{0.5}Se_2$
(t = 625 nm)	25.13	12.49	12.51	51.0	$CuIn_{0.49}Al_{0.50}Se_2$
(t = 710 nm)	25.40	12.51	12.48	50.7	$CuIn_{0.5}Al_{0.49}Se_2$

The non-molecularity parameter (Δx) estimated by substituting the composition of copper and indium obtained from EDAX spectra in the expression [**14, 15**] helped to confirm the nature of thin film as Cu-rich/In-rich. As reported earlier the identified Cu-rich and In-rich films have positive (Δx > 0) and negative (Δx < 0) non-molecularity parameter respectively. CIAS thin films of thicknesses 450nm, 600nm and 750nm have slightly In-rich/Al-rich compositions which have been confirmed by negative non-molecularity parameter (**Table 3**).

In a similar manner 800nm thick CBD CIAS thin film having positive non-molecularity factor suggested its Cu-rich composition. The non-molecularity parameter suggests only the composition of Cu & In and not the composition of aluminum and selenium. Zero value of non-molecularity parameter confirms the stoichiometric nature of CBD CIAS thin films (**Table 4)** and therefore the non-molecularity parameter is an excellent tool to confirm the near-stoichiometry/stoichiometry of CIAS thin films.

Table 4. Sturactural parameters estimated from EDAX spectra of CBD CIAS thin films.

	Film composition	Thickness (nm)	Non-molecularity parameter (Δx)	Non-Stoichiometric parameter (Δy)	Type of Conductivity	Lattice Constants (Å) a (ASTM: 5.78)		c (ASTM: 11.61)		Volume of the CIAS thin films (Å)³ (ASTM: 388)		Density of the CIAS thin films (Kg/m³) (ASTM: 5.27)	
						From EDAX	From XRD	From EDAX	From XRD	From EDAX	From XRD	From EDAX	From XRD
Near-Stoichiometric	$Cu_1(In_{0.6}Al_{0.4})Se_2$ (Slightly In-rich/Al-poor)	450	-0.07	0.01	P	5.69	**5.74**	11.27	11.60	365	**382**	5.65	**5.35**
	$Cu_1(In_{0.4}Al_{0.6})Se_2$ (Slightly In-poor/ Al-rich)	600	0.07	0.06	P	5.68	**5.69**	11.33	**11.50**	366	**372**	5.50	**4.85**
	$Cu_{0.92}(In_{0.52}Al_{0.48})Se_2$(Slightly Cu-poor/In-rich)	750	-0.09	0.03	P	5.69	**5.78**	11.30	**11.30**	366	**377**	5.54	**5.26**
	$Cu_{1.1}(In_{0.45}Al_{0.55})Se_2$ (Slightly Cu-rich/In-poor)	800	0.19	0.06	P	5.68	**5.75**	11.30	**11.30**	365	**373**	5.15	**4.99**
Stoichiometric	$Cu_1In_{0.5}Al_{0.5}Se_2$	500	0	0.014	P	5.71	**5.75**	11.37	**11.17**	371	**369**	5.74	**5.30**
	$Cu_1In_{0.5}Al_{0.5}Se_2$	625	0	0.02	P	5.68	**5.76**	11.30	**11.18**	365	**370**	5.65	**5.20**
	$Cu_1In_{0.5}Al_{0.5}Se_2$	710	0	0.01	P	5.68	**5.74**	11.30	**11.23**	365	**370**	5.60	**5.28**

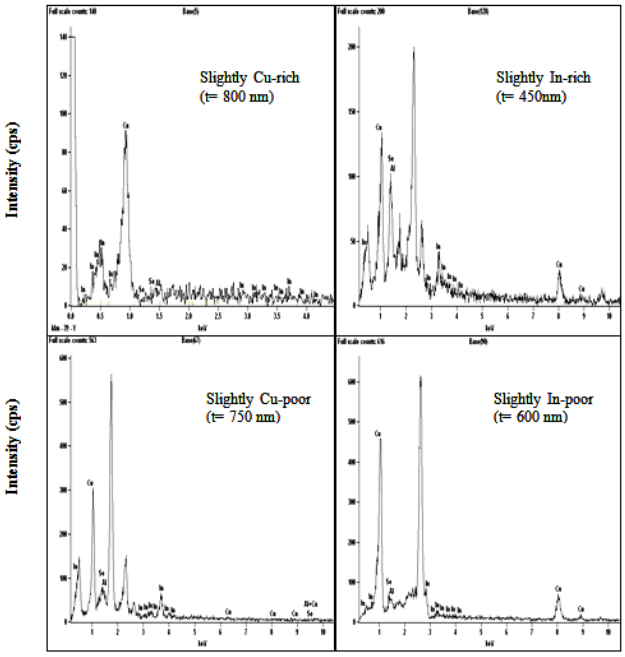

Fig. 1. EDAX spectra of near-stoichiometric CIAS thin films.

Copper and indium vacancies (V_{Cu} and V_{In}), substitutional copper in indium sites (Cu_{In}) and the defect pairs such as ($2V_{Cu}^{-} + In_{Cu}^{2+}$) and ($CuIn_2^{-} + InCu_2^{+}$) can introduce shallow acceptor levels. Such defects and defect pairs which have particularly low formation energies in grain boundaries may produce gap-states near the band edge **[13, 16]**. It is reasonable to assume that Cu_{In} and V_{In}

increase with the increase of [Cu]/[In] ratios, so that the material should be p-type degenerate [**15**]. Shi et al. [**15**] expressed the compositional deviations from their ideal chemical formula by non-stoichiometry (Δy). Δy has been determined from the composition of constituents estimated from the EDAX spectra and are also presented in the Table 4. The parameter Δy is related to the electronic defects [**17**]. Shi et al. [**15**] reported that the films with Δy>0 would behave as p-type materials while Δy<0 would show n-type conductivity. From EDAX analysis, it has been confirmed that CBD CIAS films have Δy>0 and therefore it has been confirmed that the prepared films have p-type conductivity. Thus Cu and In composition helped to understand the stoichiometry/near-stoichiometry nature as well as conductivity type of CBD CIAS thin films. The composition of aluminium (x) substituted in Vegard's law [**18**] helped to determine the lattice constants and in turn unit cell volume and density of CIAS thin films. The estimated structural parameters and ASTM values are presented in **Table 4**. The lattice constants estimated from EDAX spectra are lesser compared to ASTM, earlier reports [**19-23**] and those estimated from XRD spectra (**Table 4**). This may be due to the estimation method of lattice constants which uses only Al concentration without considering Cu, In and Se concentrations.

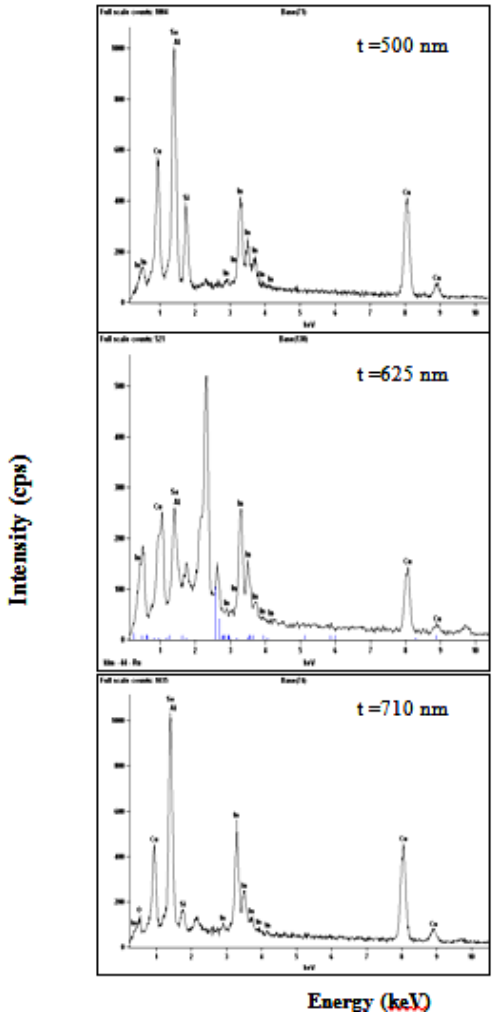

Fig. 2. EDAX spectra of stoichiometric CBD CIAS thin films.

Conclusion

EDAX spectra have been employed as a tool to determine the composition of thin films. In addition EDAX spectra have been used to identify the p-type conductivity of CBD thin films. The lattice constants were also estimated from the aluminium composition and in turn other parameters, volume and density of CIAS thin films are determined.

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