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Determination of Optimum Film Thickness and Composition of $Cu(InAl)Se_2$ Thin Films as an Absorber for Solar Cell Applications

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Abstract

$Cu(InAl)Se_2$ [CIAS] thin films have been prepared by chemical bath deposition [CBD] technique. X-ray diffraction [XRD] and Energy dispersive X-ray analysis [EDAX] spectra have been employed to confirm the structure and composition of the prepared films. The structural parameters have been estimated from XRD and EDAX spectra and their variation with film thickness and composition has been discussed in this paper in detail. From the discussion we enabled to find the optimum film thickness and composition of CIAS thin films for solar cell applications.

Keywords: CBD, XRD, EDAX, CIAS Thin Films

1. Introduction

Solar cells based on thin film materials have been given much attention for their high efficiency, low material consumption and the ability to be implemented on large area substrates. $CuInSe_2$ (CIS) thin films and their quaternary compounds have been considered as one of the most promising material classes for absorber layers for solar cells mainly due to their high optical absorption coefficient and stability, approaching 20% laboratory efficiencies on $Cu(InGa)Se_2$ [CIGS] [1]. CIS has a 1.04 eV band gap which is rather low for optimum conversion efficiency and this can be mproved by modification of the chemical composition as has been done by either replacing In with gallium [Ga] or aluminium [Al] and selenium [Se] or with sulphur [S] [2].

Chalcopyrite $Cu(InGa)(S,Se)_2$ alloys are used as the light-absorbing medium of high conversion efficiency, low cost, light-weight and radiation resistant solar cells. For example, co-evaporation method provides full flexibility for device optimization and high efficiency of 19.9% has been demonstrated using a small-area CIGS absorber [3]. The band gap energy of CIGS with 1.4 eV should be ideal for use in solar cells. However, growing single phase CIGS alloys or CGS solid solutions of high $CuGaSe_2$ (CGS) molar fraction is difficult because of unwanted compositional separation into CIS and CGS, or compositional graduation due to the difference in reaction rates of the two-end point compounds [4]. In addition, the open-circuit voltage and conversion efficiency of CIGS solar cells do not increase proportionally with the bandgap, because of insufficient grain size and crystal quality of GIGS films [5]. Furthermore, there is also a need to reduce the manufacturing cost of solar cells by employing low cost technology and materials [6].

Due to the above reason, $Cu(InAl)Se_2$ (CIAS) has been considered as promising alternative, since it requires less aluminum concentration than gallium to achieve a similar band gap. CIAS have been prepared by several techniques such as co-evaporation [7-11], and sequential deposition methods [12-14]. In the present work CIAS thin films have been grown by chemical bath deposition [CBD] technique in which the deposition occurs when the substrate is maintained in contact with dilute chemical bath containing reaction mixture. The film formation on substrate takes place when ionic product (IP) exceeds solubility product (SP). Of the various techniques CBD, a non-vacuum electroless technique has many advantages such as simplicity, no requirement for sophisticated instruments, minimum material wastes, economical way of large area deposition, no need of handling poisonous gases like H_2Se or Se vapour and possibility of room temperature deposition. In view of these advantages, CBD technique has been selected for the preparation of

CIAS thin films and moreover thorough literature survey revealed that no researchers in the world have studied the structural properties of CBD CIAS thin films in detail. Hence it has been planned to carry out a systematic XRD and EDAX analysis of CBD CIAS thin films.

This paper presents the preparation, structural, and compositional characterization of CIAS thin films. We also discussed briefly about the comparison of structural and compositional parameters to find out the optimum film thickness and composition of CIAS thin films for solar cell applications.

2. Experimental Details

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 and 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 [15]. 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 this 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 [16] 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 & 0.2 M respectively to obtain Cu-rich and Cu-poor CIAS thin films, whereas the concentration of indium trichloride and aluminium have been changed to obtain 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.

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
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)
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

Characterization

The thickness of the prepared CIAS films was determined by the gravimetric technique and the films were annealed at 100˚C for one hour and used for the analysis. Structural characterization of these films was carried out by using Shimadzhu (Lab X-6000) X-ray diffractometer with Cu Kα (λ = 1.5406 A) line in 2θ range from 20 to 80 degrees. Energy dispersive X-ray analysis attachment (Thermo Super Dry II) is used to carry out semi-quantitative elemental analysis of the annealed CBD CIAS thin film samples.

3. Results and Discussion

3.1. XRD Analysis

A representative X-ray diffraction pattern of CBD CIAS thin film of thickness 625 nm [stoichiometric] is presented in **Figure 1(a)**. The prepared films were found to be polycrystalline in nature exhibiting chalcopyrite structure. From the diffraction profiles the diffraction angles and the intensity of lines are measured with greater accuracy. Possible directions in which the films diffracted the beam of monochromatic X-rays are determined by Bragg's expression [3]. The crystallites are found to have main peak orientations along (112), (200), (204/220) (116/312), (301) and (325/413) directions. Since no Joint Committee on Powder Diffraction Standards (JCPDS) file is available for CIAS, $CuInSe_2$ (JCPDS No. 40-1487) and $CuAlSe_2$ (JCPDS No. 44-1269) standards were used and the results were compared with earlier reports [2,7-14]. The extra-protruding background in the 2θ range originates from the diffraction of glass substrates [17]. Due to change in the Cu/(Al + In) ratio, 2θ values for the predicted peaks slightly varies from ASTM data and the variation was also observed by earlier reporters in CIAS thin films for different Al ratio [18] and in CIS thin films by Shi etal [17] for differ Cu/In. Itoch *et al*. [12] also reported that as Al ratio increases, automatically In ratio decreases and there is a shift in the 2θ value for the preferential orientation. From the (hkl) planes the lattice constants [16], the structural parameters such as tetragonal distortion, volume of unit cell, density of CIAS, [19,20] have been estimated (**Table 4**) and are in good agreement with ASTM.

3.2. EDAX Analysis

Figure 1(b) shows the EDAX spectrum of CBD CIAS thin films and it shows 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**). The composition of aluminium (x) obtained from EDAX spectrum is substituted in Vegard's law [19] helped to determine the lattice constants and in turn unit cell volume and density of CIAS thin films. The estimated structural parameters estimated from EDAX spectra and ASTM values are presented in **Table 4**.

3.3. Structural Parameters Estimated from XRD and EDAX Spectra

Lattice parameters "a" and "c" and in turn tetragonal distortion, volume of the unit cell and density of CIAS thin films were estimated from both XRD and EDAX spectra (**Figures 2** and **3**) vary non-linearly with respect to Cu/(In + Al) ratio, thickness and atomic % of Al [12,21,22] (**Table 4**). The reported lattice constants of single crystal and bulk showed linear variation [23,24]. The lattice con-

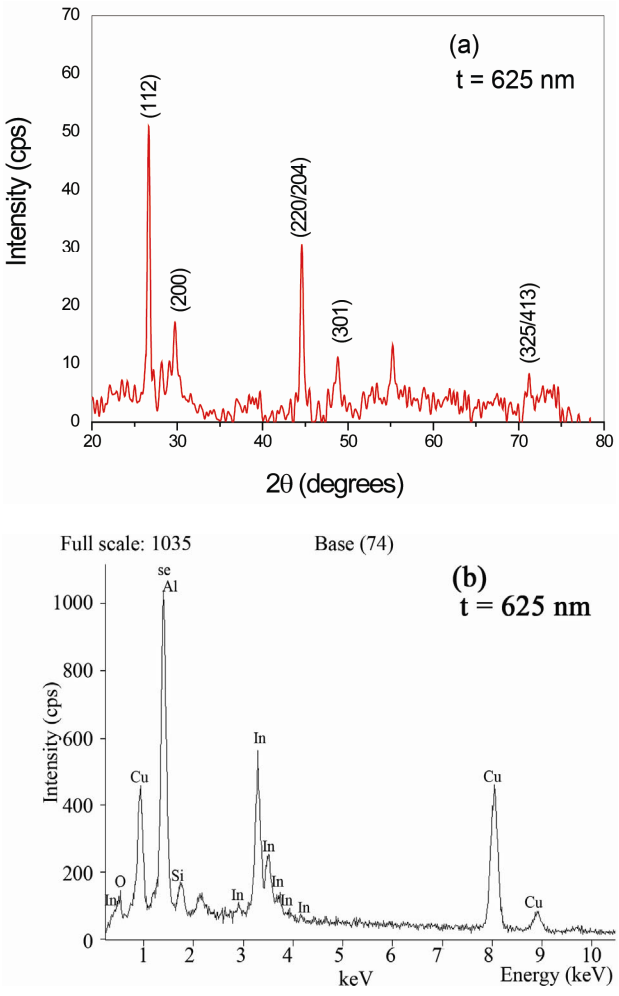

Figure 1. Representative (a) XRD spectra; (b) EDAX spectra of CBD CIAS thin films.

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

Near-Stoichiometric CIAS films	Atomic percentage (%)				Film composition
	Cu	In	Al	Se	
Slightly Cu-rich (800 nm)	27	11.32	11.20	50.49	$Cu_{1.1}(In_{0.5}Al_{0.5})Se_2$
Slightly Cu-poor (750 nm)	23	13.19	12.11	51.36	$Cu_{0.9}(In_{0.5}Al_{0.5})Se_2$
Slightly In-rich/Al-poor (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 (600 nm)	25.17	10.48	12.87	50.54	$Cu_1(In_{0.4}Al_{0.6})Se_2$
Stoichiometric CIAS films	Cu	In	Al	Se	Film composition
500 nm	25.02	12.50	12.51	50.8	$Cu_1In_{0.499}Al_{0.50}Se_2$
625 nm	25.13	12.49	12.51	51.02	$Cu_1In_{0.5}Al_{0.50}Se_2$
710 nm	25.40	12.51	12.48	50.7	$Cu_1In_{0.5}Al_{0.49}Se_2$

Table 4. Parameters estimated from XRD and EDAX spectra of CBD CIAS thin films.

$\left(\frac{Cu}{In+Al}\right)$	Film Thickness (nm)	Wt% of Aluminum (x = 12.5%)	Lattice Constants (Å)				Tetragonal distortion (2-c/a)		Volume (V) $(Å)^3$ (ASTM = 388.51)		Density (D) (Kg/m^3) (Average = 5.27)	
			a (ASTM = 5.78)		c (ASTM = 11.61)							
			XRD	EDAX	XRD	EDAX	XRD	EDAX	XRD	EDAX	XRD	EDAX
0.92	450	11.10	5.74	5.69	11.55	11.27	–0.012	0.019	385	365	5.35	5.65
1.07	600	12.87	5.75	5.68	11.55	11.33	–0.008	0.005	386	366	4.85	5.50
0.9	750	12.11	5.72	5.69	11.58	11.30	–0.024	0.014	381	366	5.26	5.54
1.1	800	11.20	5.73	5.68	11.59	11.30	–0.022	0.011	384	365	4.99	5.15
1	500	12.502	5.75	5.71	11.52	11.37	–0.003	0.008	388	365	5.30	5.74
1.02	625	12.510	5.74	5.68	11.50	11.30	–0.003	0.011	386	366	5.20	5.65
1.01	710	12.495	5.75	5.68	11.51	11.30	–0.001	0.011	387	366	5.28	5.60

stants estimated from EDAX spectra are lesser compared to those estimated from XRD spectra, ASTM and earlier reports [2,7,9-14]. This may be due to the estimation method of lattice constants which uses only Al concentration without considering Cu, In and Se concentrations. And therefore XRD analysis has been used in the present study to determine the optimum film thickness, Cu/(In + Al) and At % of aluminium to get the tetragonal structure with minimum distortion.

The lattice constants show a maximum when Cu/(In + Al) is 1 and this indicates the existence of significant defects in the crystallites when the films are far from stoichiometry [25]. The plots (**Figures 2** and **3**) suggest that the optimum the film thickness range as 475 nm - 710 nm and Al% is 12.5 to obtain the reported lattice constant values [JCPDS 40-1487]. Non-linear variation of lattice constants with atomic percentage of aluminium may be due to the variation in the average ionic radii r_{III}^{3+} as reported earlier [12,22].

Tetragonal distortion is an important parameter in chalcopyrite compounds, which results in a crystal field that lifts the degeneracy of the top most valance band [22]. The strength of I-IV and III-VI bonds are different and therefore the ratio c/a is not equal to 2 as reported [20]. This may be due to the reason for the non-zero values of tetragonal distortion estimated from both XRD and EDAX spectra in CBD CIAS thin films. It is found that the tetragonal distortion is minimum when the Cu/(In + Al) ratio is 1, atomic % of Al is 12.5 and the film thickness is about 500nm (**Figure 4**).

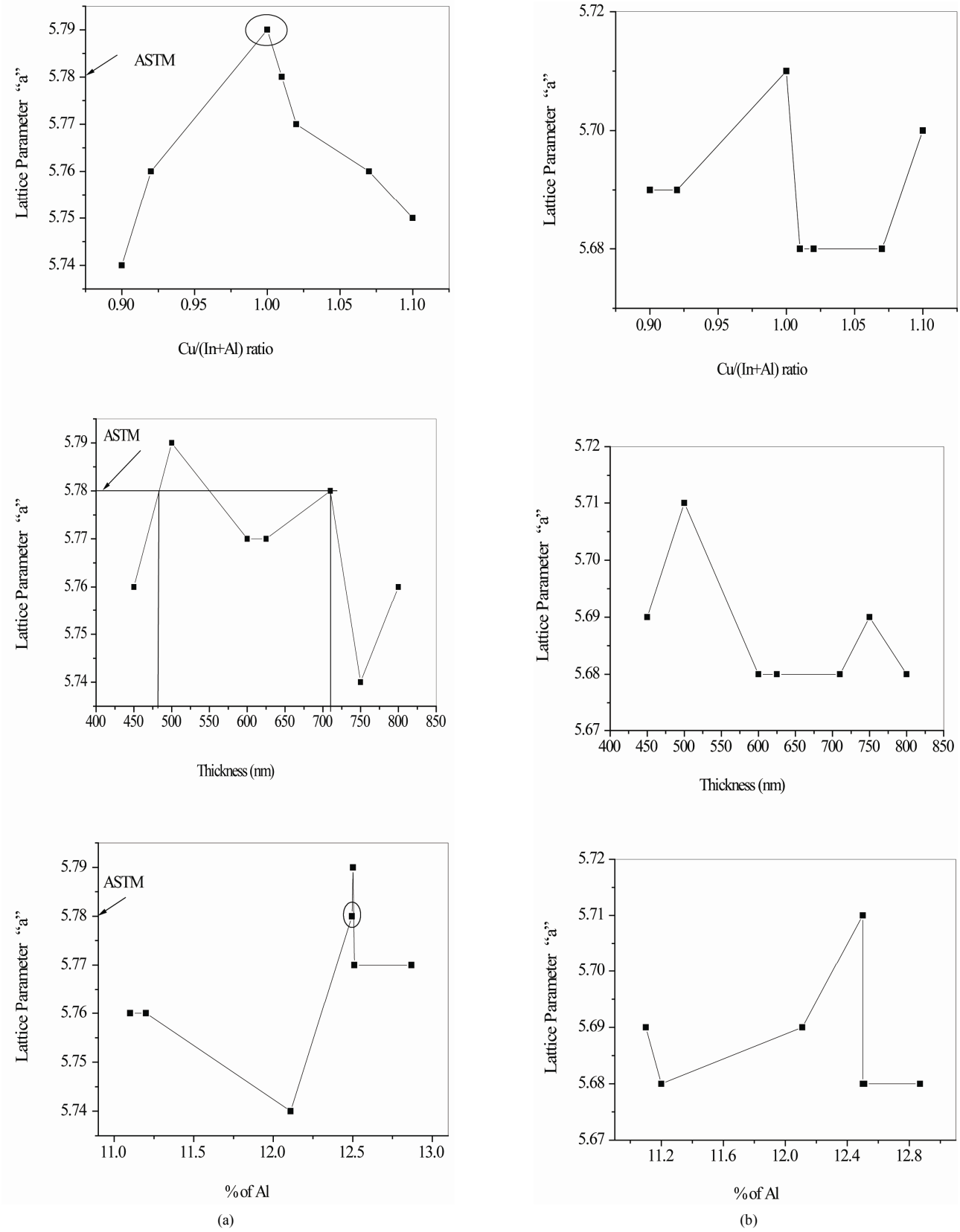

Figure 2. Variation of f lattice parameter "a" [estimated from (a) XRD spectra; (b) EDAX spectra] with film parameters.

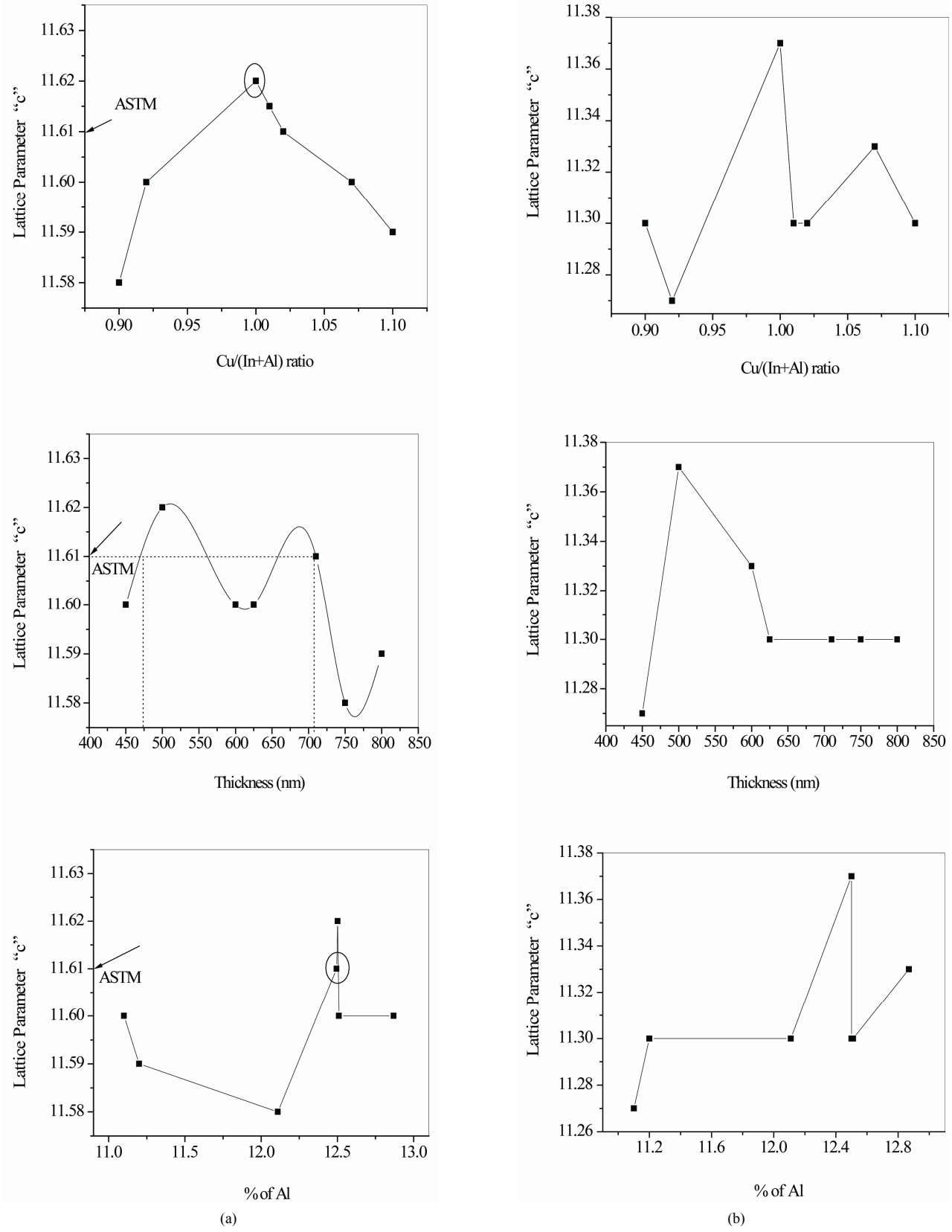

Figure 3. Variation of f lattice parameter "c" [estimated from (a) XRD spectra; (b) EDAX spectra] with film parameters.

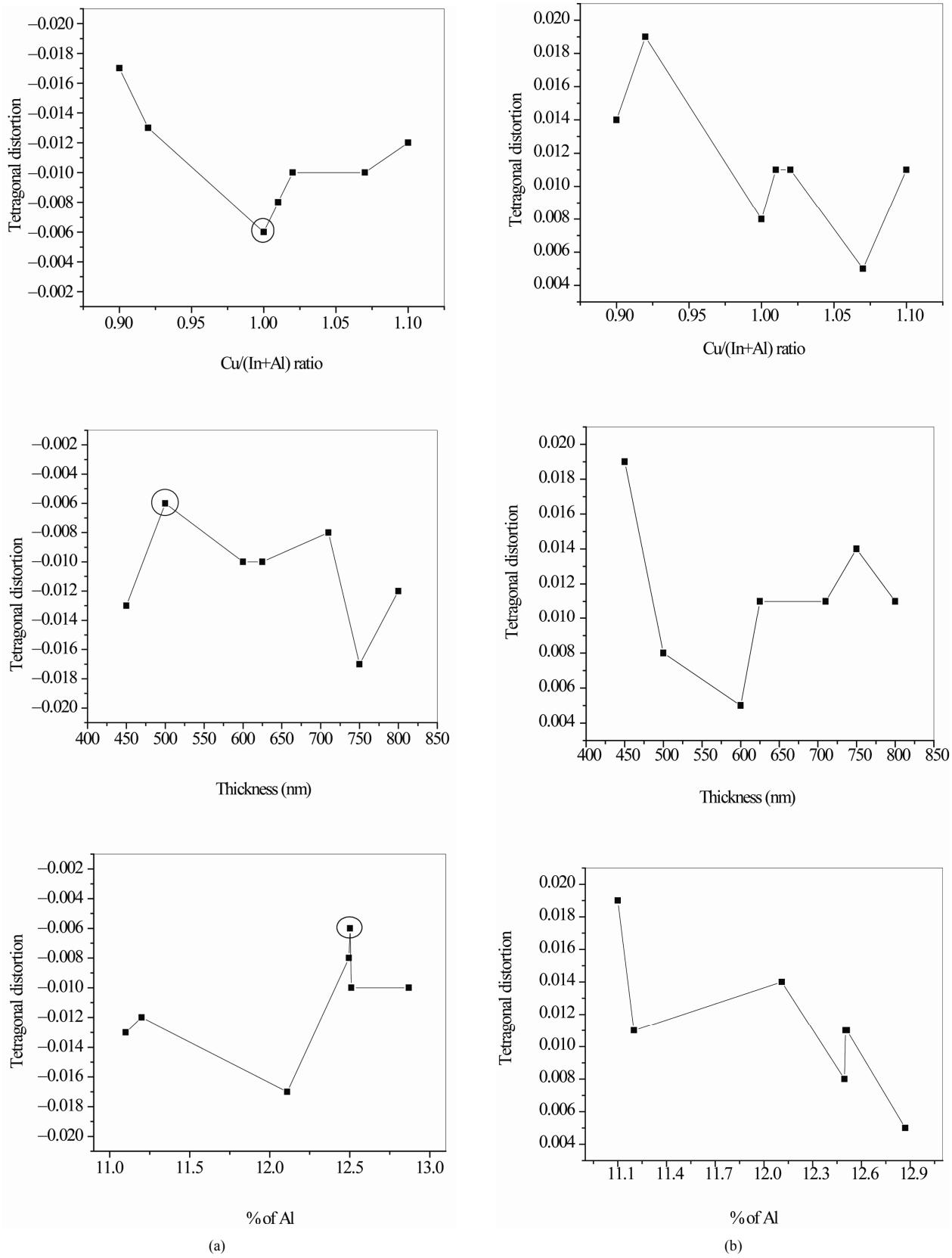

Figure 4. Variation of tetragonal distortion [estimated from (a) XRD spectra; (b) EDAX spectra] with film parameters.

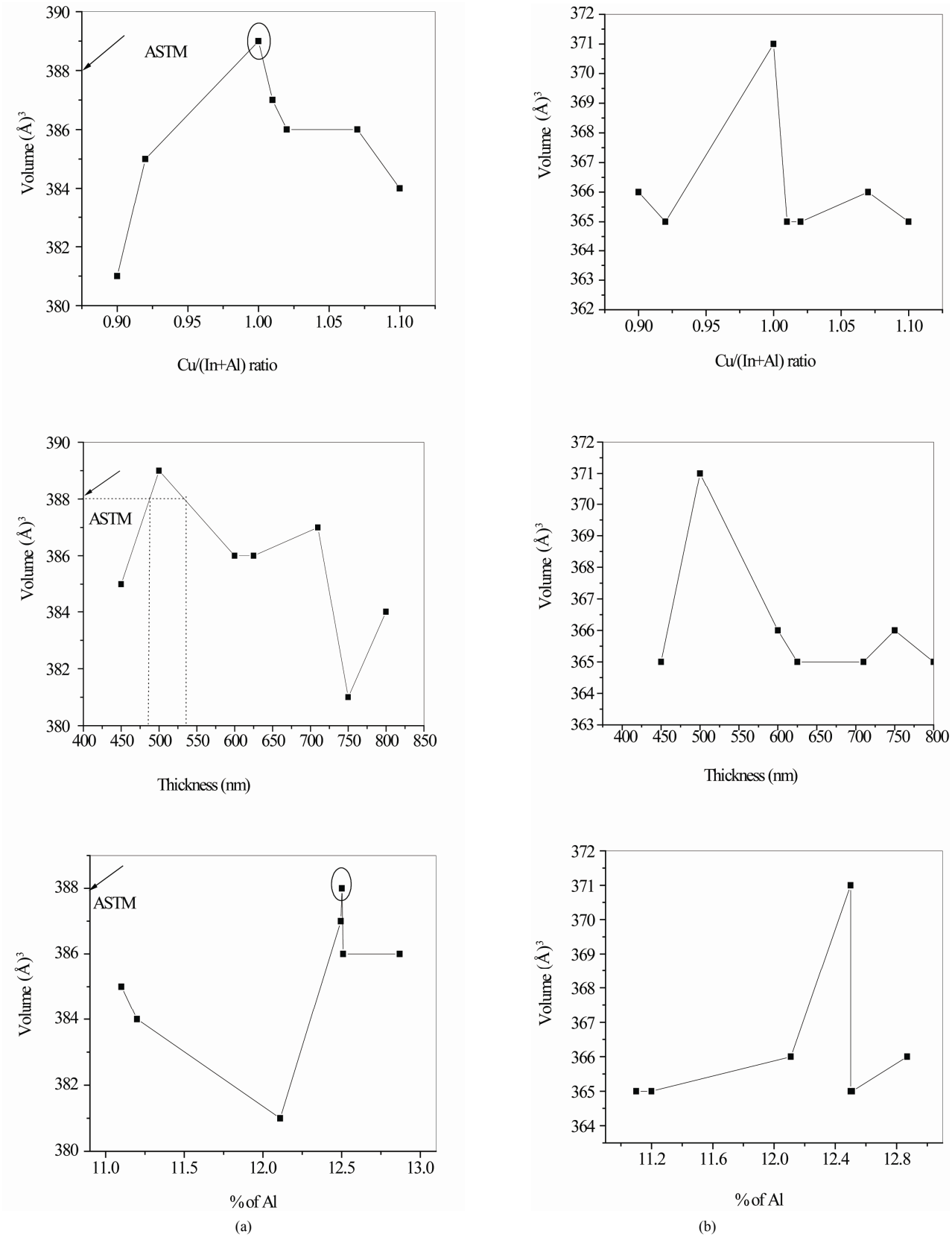

Figure 5. Variation of volume [estimated from (a) XRD; spectra (b) EDAX spectra] with film parameters.

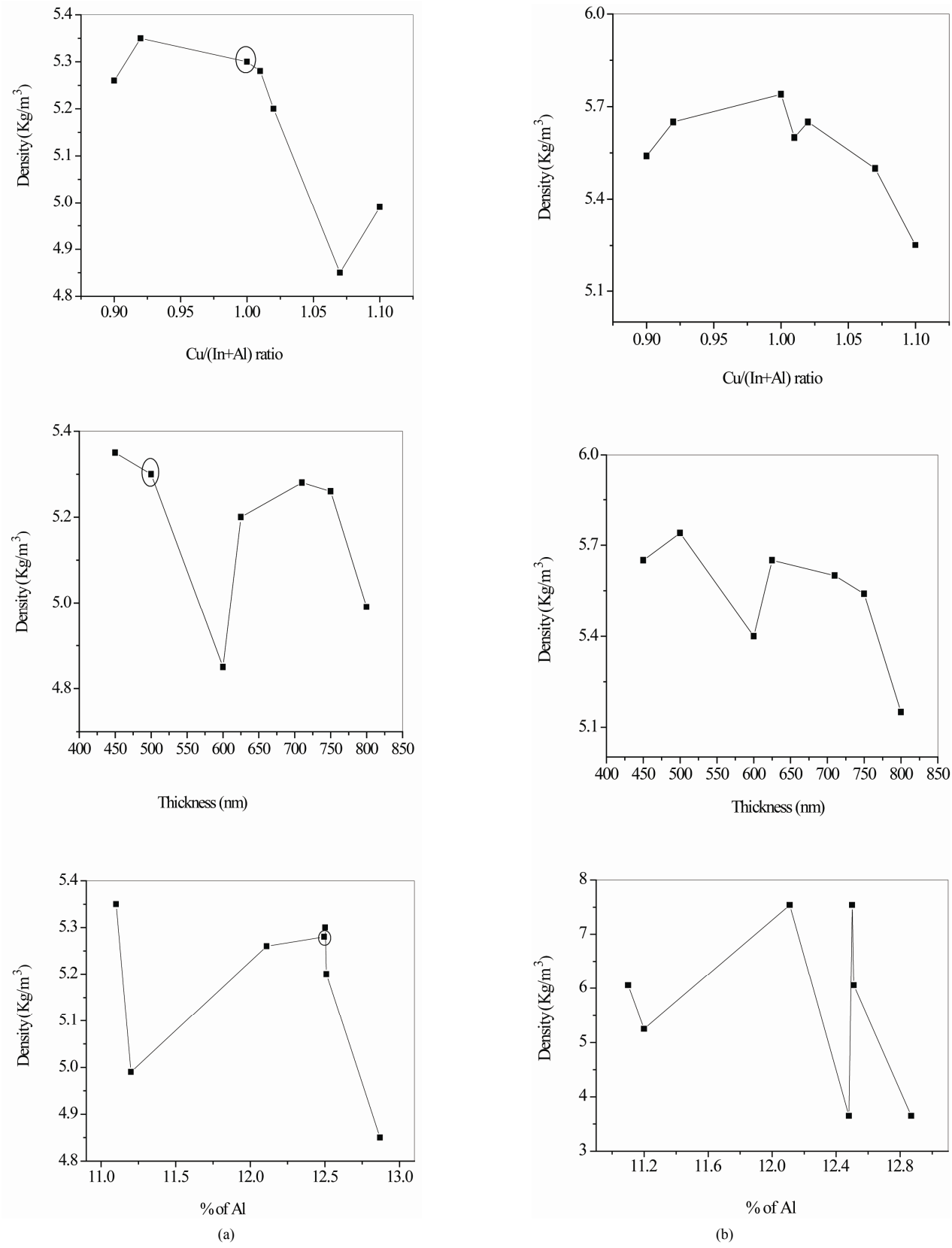

Figure 6. Variation of density [estimated from (a) XRD spectra; (b) EDAX spectra] with film parameters.

The volume of the unit cell has been found maximum when Cu/(In + Al) ratio is 1 and the atomic % of Al is about 12.5. The volume of the unit cell varies non-linearly with film thickness and approaches ASTM value when film thickness is around 480 nm to 530 nm in CBD CIAS thin films (**Figure 5**). The estimated density of CBD CIAS thin films lies in between the density of CIS [5.77 Kg/m^3] and CAS [4.77 Kg/m^3]. The average density 5.27 Kg/m^3 may be considered as the density of CIAS thin films and this value is found when the Cu/(In + Al) is unity, film thickness is 500 nm and the atomic % of Al is 12.5 (**Figure 6**).

It has been found that the lattice constants, tetragonal distortion, volume of the unit cell and density of CIAS are in agreement with ASTM values when the film is stoichiometric in nature (Cu/(In + Al) is 1, Al% is 12.5) with film thickness in the range 500 - 710 nm.

4. Conclusions

CIAS thin films have been prepared by CBD technique. XRD and EDAX spectra have been employed to confirm the structure and composition of the prepared films. The structural parameters have been estimated from XRD and EDAX spectra. From the estimated values suitable Cu/(In + Al), % of Al and film thickness has been identified for solar cell applications.

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