An investigation on silars Cu(In$_{1-x}$Al$_x$)Se$_2$ thin films

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**Abstract**

Cu(In$_{1-x}$Al$_x$)Se$_2$ [CIAS] thin films were prepared for the first time by successive ionic layer adsorption and reaction [SILAR] method with two different dipping cycles. The thickness of the films was measured by gravimetric technique. The structural, morphological, compositional, optical transition and electrical investigation of SILAR CIAS thin films with respect to two different dipping cycles have been discussed in this paper.

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1. Introduction

Ternary I–III–VI chalcopyrite semiconductors are quite promising materials for photovoltaic application. CuInSe$_2$ [CIS] with band gap of 1.04 eV has proved to be a leading candidate for the development of high-efficiency and low cost thin film solar cells [1,2] owing to high absorption coefficient of 10$^6$ cm$^{-1}$. The chalcopyrite CIS is a very interesting material used as a absorber layer in thin film solar cells. Moreover, CIS can tolerate wide range of anion-to-cation off-stoichiometric, which makes it act as n-type and p-type layers for either homojunction or heterojunction solar cells [3]. In order to increase the CIS band gap for an optimal match with solar radiation spectrum and to improve the module performance CIS is alloyed with gallium [Ga] or sulphur [S]. However Ga is a scarce and expensive material and therefore it can be replaced by inexpensive abundant aluminium [Al]. Cu(In$_{1-x}$Al$_x$)Se$_2$ [CIAS] has been considered as promising alternative, since it requires less aluminium concentration than gallium to achieve a similar band gap [4]. CIAS thin films have been prepared by several techniques including co-evaporation [5,6], one step RF magnetron sputtering [7] and sequential deposition methods [8–10].

In the present work, CIAS thin films have been grown by successive ionic layer adsorption and reaction [SILAR] method which is often termed as modified chemical bath deposition. In previous work we have investigated CIAS thin films prepared by chemical bath deposition [CBD] [11]. In CBD, deposition of thin films occurs due to substrate maintained in contact with dilute chemical bath. The film formation on substrate takes place when ionic product (IP) exceeds solubility product (SP). Actually SILAR process involves immersion of substrates into separately placed cationic and anionic precursors for reaction at chosen temperatures. Between every immersion it is rinsed in distilled water or deionised water and the rinsing time is important for ionic layer formation. SILAR technique involves adsorption of a layer of complex ion on the substrate followed by reaction of the adsorbed ion layer [12]. So, the immersion programs which can alter the chemical distribution of the deposit layer by layer provides an opportunity to tailor CIAS precursor deposits with homogenous element distribution for easy phase synthesis in the subsequent processing [13]. Through literature survey revealed that no researchers have studied chemically deposited CIAS thin films. Hence it has been planned to carry out a systematic study on SILAR CIAS thin films.

2. Experimental details

In SILAR technique, the depositions of CIAS thin films were carried out from solutions containing two cationic precursors and one anionic precursor. The cationic precursors were (i) 0.03 M of copper sulphate [CuSO$_4$] and triethanolamine [TEA] [pH 8] (ii) 0.03 M of indiumtrichloride [InCl$_3$], 0.03 M of citric acid and 0.03 ml of aluminium sulphate [Al$_2$SO$_4$] [pH 9]. The anionic precursor contained 60 ml of sodium selenosulphate [Na$_2$SeSO$_3$] [pH 10]. The deposition process is as follows:

- Well-cleaned substrates was immersed into the cationic precursor 1 for 30 s and then rinsed with deionised water for 30 s to
Table 1: Structural parameters of CIAS thin films.

<table>
<thead>
<tr>
<th>Dipping cycle</th>
<th>Film thickness (nm)</th>
<th>Growth rate (nm/no of dipping cycles)</th>
<th>Lattice constants (Å) A</th>
<th>Axial ratio (c/a)</th>
<th>Tetragonal distortion (2-c/a)</th>
<th>Crystallite size, Dc (nm)</th>
<th>Dislocation density (×10^15 lines/m^2)</th>
<th>Number of crystallites per unit area (×10^16 m^-2)</th>
<th>Strain (×10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>410</td>
<td>164</td>
<td>5.785</td>
<td>11.56</td>
<td>1.99</td>
<td>0.01</td>
<td>18</td>
<td>3.03</td>
<td>1.95</td>
</tr>
<tr>
<td>50</td>
<td>520</td>
<td>104</td>
<td>5.786</td>
<td>11.54</td>
<td>1.99</td>
<td>0.01</td>
<td>23</td>
<td>1.96</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Fig. 1 shows variation of CIAS thin film thickness with dipping cycles.

Schematic diagram of SILAR technique. C1: cationic precursor 1; C2: cationic precursor 2; A: anionic precursor; W: water.

As the dipping cycle increased above 50, the cationic and anionic precursors are found to decrease in volume significantly. Moreover indium and aluminium concentrations are found to be decreased in the films above dipping cycle 50. Therefore dipping cycles are optimized as 25 and 50. Many researchers annealed the films at higher temperature (500 °C) for minimum time duration (5–10 min). In the present work the films were dried and annealed at low temperature (100 °C) for 1 h to make the annealing temperature will most probably lower than the temperature of discontinuity of the film and thereby avoiding the material loss or a complete break in the film and moreover this is the convenient way of stabilization of the film [14].
more free ions [15]. The thickness of the films was measured by gravimetric technique. The error of the thickness measurement is ±0.0001 nm. However, this error does not affect the comparative data of measured film thickness [12]. All the properties investigated in this work strongly depended on the number of dipping cycles (thickness) because thickness plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the thickness and deposition parameters are kept constant [14].

2.1. Characterization

In the present study the structural characterization of the prepared (CIAS) thin films has been carried out using Shimadzu (Lab X-6000) X-ray diffractometer with Cu Kα (λ = 1.5406 Å) line in 2θ range from 20 to 60°. The composition of the chemical constituent in the deposited CIAS thin films has been confirmed by energy dispersive X-ray analyzer (LEICA.S440i) and scanning electron microscopy used in the present investigation was JEOL-JSM-100. JASCO-UV/VIS/NIR (JASCO V-570) double beam spectrophotometer has been used for optical transmittance measurements in the wavelength range of 200–2500 nm.

3. Results and discussion

3.1. Structural analysis

Fig. 2(a) and (b) shows the XRD profiles of CIAS thin films, film 1 (25 dipping cycle) and film 2 (50 dipping cycle), respectively. The predicted peaks of the films (1 1 2) (2 0 0) (2 0 4/2 2 0) (3 0 1), (2 0 0) and (3 2 5/4 1 3) are reported as the identifying peaks and the normalized diffraction peaks enable to quickly understand the preferential orientation as (1 1 2). Since no JCPDS file is available for CIAS, CIS standard (JCPDS no. 40-1487) was used and reported earlier [16–19]. From the observed d-spacing and (h k l) planes the lattice constants ‘a’ and ‘c’ and other structural parameters such as crystalline size, number of crystallite per unit area, dislocation density and strain were calculated and are presented in Table 1.

The crystallite size was calculated by the X-ray line broadening method using the Scherrer formula [20]

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

(1)

where \( \lambda \) is the wavelength of radiation used (Cu Kα in this case), \( k \) is the Scherrer constant, \( \beta \) is the full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size is to be calculated, \( \theta \) is the diffraction angle of the concerned diffraction peak and \( D \) is the crystallite dimension (or particle size). While calculating the particle size, the instrumental broadening and strain broadening was not taken into account. In Scherrer equation, \( \beta \) represents the broadening due to particle size alone. In general the experimentally observed broadening \( (\beta_o) \) is the total contribution from particle size broadening \( (\beta_p) \), instrumental broadening \( (\beta_i) \) and strain broadening \( (\beta_s) \) and is represented as

\[ \beta_o = \beta_p + \beta_i + \beta_s \]  

(2)

In the present study, \( \beta \) has been considered as \( \beta_o \) (without considering \( \beta_i \) and \( \beta_s \)). Thus the measured particle sizes are always differ slightly from the actual particle size. The composition variation may lead to a variation in lattice parameters of the ultra fine particles and in turn XRD line profile broadening which will cause an inconsistency between the mean particle size measured by TEM and that calculated by Scherrer equation, because the line profile broadening due to the variation in the lattice parameter caused by composition distribution is not considered in Scherrer equation [21,22–25]. As per the earlier reports [22,23,26] dislocation density has been determined by

\[ \delta = \frac{1}{D^2} \]  

(3)

It was observed that the crystalline size increases but the strain and dislocation density decreases with increase of film thicknesses (number of dipping cycles) and this is because as the film thickness increases, the effect of substrate could be decreased due to the ions being deposited on the initial layer, so that there may be increase in the grain size [27]. As 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 [22]. It was observed that the lattice parameters, grain size and the strain have a direct dependence on the film thickness [28].

3.2. Composition from EDAX

Fig. 3 shows the EDAX spectra of CIAS thin films. EDAX quantitative analysis helped to confirm the atomic percentage of copper, indium, aluminum and selenium in the prepared films. Table 2 shows the elemental composition of the films estimated from EDAX spectra. As the dipping cycle increased above 50, the cationic
and anionic precursors are found to decrease in volume significantly. Moreover indium and aluminium concentrations (Table 2) are found to be decreased in the films above the dipping cycle 50. Therefore dipping cycles are optimized as 25 and 50. Fig. 4(a) shows that Cu/(In + Al) ratio decreases with increase in the number of dipping cycles. Increasing the grain size with increasing Cu/(In + Al) ratio, shows that the growth of crystallite is dominant in Cu-rich thin films (Fig. 4(a)) [29,30]. Fig. 4(c) Cu/(In + Al) ratio lies in the range of unity, whereas it decreases markedly when the films show either Cu-rich or Cu-deficient.

Dividing the measured overall film thickness by number of reaction cycles, growth rate can be determined. This gives a numerical value for growth rate under the given conditions. Since the measured growth rate exceeds the lattice constant of the material in the present study (Table 1) a homogenous precipitation in the solution could have taken place (Table 1) [31]. This may be the reason for the variation in the film thickness with number of dipping cycles.

3.3. Surface morphology studies

Fig. 5(a) and (b) shows the representative SEM images of CIAS thin films. Scanning electron micrographs showed a good adhesion to the glass substrates [32]. There is not much significant structural difference between the micrographs. The crystallites have a similar shape but the grain size evaluated for films 1 and 2 is about 1 μm and 5 μm, respectively. Comparative the grain size of the film 1 decreases slightly which may be due to decrease in Al content and this implies that when Al content increases the grain size increases, similar behavior is observed in structural studies. Fig. 5 confirmed the densely packed, columnar nano-grains and a good homogeneity of CIAS thin films. The increase in grain size is very important because it is reported that the efficiency in polycrystalline solar cells increases with increase in grain size for the absorbing materials [33].

Table 2
Elemental composition of CIAS films estimated from EDAX spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film thickness (nm)</th>
<th>Dipping cycle</th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Al (at%)</th>
<th>Se (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film 1</td>
<td>410</td>
<td>25</td>
<td>25.03</td>
<td>14.12</td>
<td>11.21</td>
<td>49.29</td>
</tr>
<tr>
<td>Film 2</td>
<td>520</td>
<td>50</td>
<td>26.03</td>
<td>13.47</td>
<td>12.72</td>
<td>49.13</td>
</tr>
</tbody>
</table>
3.4. Optical properties

Fig. 6 shows the absorbance spectra of CIAS thin films. The shift in the absorbance edge and in turn the change in the band gap energy may be due to incorporation of more aluminum atoms in the film.

Absorption coefficient was calculated using the transmittance ($T$) value measured for a particular wavelength and the film thickness ($t$) using the relation,

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

In the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ (Fig. 7) of CIAS thin films the straight-line portion is extrapolated to cut the energy axis to estimate the band gap. The estimated bandgaps as well as other estimated optical parameters are presented in Table 3 and it is observed that the band gap decreases with increase of film thick-
ness which may be due to the influence of various factors such as grain size, structural parameters, carrier concentration, presence of impurities, composition of the film and lattice strain \[34,35\]. The calculated band gap values are in good agreement with the earlier investigations \[36–39\]. It can also be seen that both the films have relatively high absorption coefficient than \((10^6 \text{ m}^{-1})\). Plot of \((h \nu/\text{ETB})^{1/2}\), \((h \nu/\text{ETB})^{1/3}\) and \((h \nu/\text{ETB})^{3/2}\) (not shown) reveal that CIAS films did not have line above \(h \nu > \text{E}_g\) which confirm the fact that CIAS phase do not have indirect allowed, direct forbidden and indirect forbidden transitions.

### 3.5. Electrical studies

DC electrical resistivity of CIAS thin films was measured as a function of temperature in the range of 300–423 K. The resistivity decreases with increase in temperature (Fig. 8) indicating the semiconducting behavior of CIAS thin films \[40\]. The variation in the resistivity of thin films 1 and 2 may be due to change in aluminum content of thin films \[41\].

For example, copper and indium vacancies (\(V_{\text{Cu}}\) and \(V_{\text{In}}\)), substitutional copper in indium sites (\(\text{Cu}_{\text{In}}\)) and the defect pairs such as (\(2\text{VCu}^- + \text{InCu}^2^+\)) and (\(\text{CuIn}_2^- + \text{InCu}^2^+\)) 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 \[42\]. It is reasonable to assume that \(\text{Cu}_{\text{In}}\) and \(V_{\text{In}}\) increase with the increase of \([\text{Cu}]/[\text{In}]\) ratios, so that the material should be p-type degenerate \[43\]. Shi et al. \[40\] expressed the compositional deviations from their ideal chemical formula by

\[
\Delta y = \frac{2\text{Se}}{\text{Cu} + 3\text{In}}
\]

The parameter \(\Delta y\) is related to the electronic defects. Shi et al reported that the films with \(\Delta y > 0\) would behave as p-type materials while \(\Delta y < 0\) would show n-type conductivity. From EDAX analysis, it has been confirmed that SILAR CIAS films have \(\Delta y > 0\) and therefore it confirms that the prepared films have p-type conductivity.

The activation energy (\(E_a\)) of the films has been calculated using the relation

\[
\sigma = \sigma_0 e^{-E_a/kT}
\]

where \(E_a\) is the activation energy and \(\sigma_0\) the conductivity at infinite temperature \[39\]. The activation energies of the prepared CIAS films are found to be 0.66 eV and 0.62 eV, respectively (Table 4). The activation energy values are found approximately equal to the half of semiconductor energy gap (\(E_g/2\)) as reported earlier \[38\].

### Table 3

Optical parameters of CIAS thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dipping cycle</th>
<th>Film thickness (nm)</th>
<th>Absorption coefficient, (\alpha (\times 10^6 \text{ m}^{-1}))</th>
<th>Extinction coefficient, (k)</th>
<th>Band gap, (E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>410</td>
<td>4.86</td>
<td>0.38</td>
<td>1.38</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>520</td>
<td>5.35</td>
<td>0.42</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Fig. 7. Plot of \((a \nu)\) vs. \((h \nu)\) of CIAS thin films.

Fig. 8. Variation of resistivity with temperature of CIAS thin films.
4. Conclusion

CIAS thin films have been prepared by first time by SILAR technique. The results of XRD, EDAX spectra, scanning electron micrographs, compositional and electrical analysis of CIAS thin films prepared at two different dipping cycles were presented in this paper in detail.

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