ESTIMATION OF STRUCTURAL AND OPTICAL PARAMETERS FROM EDAX SPECTRA

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Abstract

$CuInS_2$ thin films have been grown onto glass substrates by novel SILAR deposition technique. The composition of the prepared films has been confirmed by EDAX spectra. From the EDAX data, the non - stoichiometry, non - molecularity, lattice constants, band gap and type of conduction has been estimated. SEM and optical transmittance spectra are employed to confirm the results of EDAX spectra. Therefore this paper is a new attempt to employ EDAX spectra to estimate the structure, optical band gap and electrical conductivity of $CuInS_2$ thin films.

Keywords: $CuInS_2$, SILAR, EDAX, Lattice constants, Band gap

Introduction

Among the I-III-IV chalcopyrite, $CuInS_2$ (CIS) is a promising absorber in photovoltaic device because it has direct band gap of about 1.5eV (Guha *et al*., 2003; Guillen *et al*., 2005; Shi *et al*., 2006; Chen *et al*., 2007; Zribi *et al*., 2008; Ben Rabeh *et al*., 2009) which is closely matched to the visible part of the solar spectrum and a high absorption coefficient ($>10^5$ cm^{-1}) (Shi *et al*., 2006). In comparison with $CuInSe_2$, this material has the advantage that it does not contain toxic constituent selenium and therefore the use of non-toxic sulphur instead of toxic selenium is attractive. Moreover this material can be prepared as both n - and p - type enabling the fabrication of both homojuction and heterojunction structures. It is reported that n-$CuInS_2$ can be obtained on heat treatment in an excess indium environment and p-$CuInS_2$ can be obtained on heat treatment in an excess sulphur environment (Bini *et al*., 2000). Theoretical predicted solar conversion efficiency is between 27 and 32% for $CuInS_2$ based homojunctions (Bini *et al*., 2000). Variety of methods employed for the deposition of CIS thin films are three source molecular beam epitaxy, RF sputtering, sulphurisation, co-evaporation from elemental source, single source evaporation, diffusion of Cu and S into In_xS precursor, electrodeposition, spray pyrolysis, chemical bath deposition (CBD) etc. (Pathan and Lokhande, 2004). Among them one of the newest solution method for the deposition of thin films is successive ionic layer adsorption and reaction (SILAR) method which is also known as modified

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version of chemical bath deposition. In this method basic building blocks are ions instead of atoms, the preparative parameters are easily controllable and better orientation as well as improved grain structure can be obtained in the films (Pathan *et al.*, 2002; Pathan and Lokhande, 2004).

The main emphasis and purpose of the present work is to deposit good quality SILAR CIS thin films. SILAR is an attractive method because large area thin films with good uniformity can be prepared at low cost. Different processing parameters are optimized to prepare uniform, pin-hole free and adherent CIS thin films. The composition of the films has been confirmed by EDAX spectra. From the EDAX data the lattice constants, band gap energy and type of conductivity have been estimated. SEM and transmission analysis have been carried out to support the EDAX analysis results.

Experimental Procedure

Solution Preparation

Blue star glass microslides of dimensions 78 mm × 22 mm × 1 mm were used as substrates. Since substrate cleaning plays an important role in the deposition of thin films, the substrates were ultrasonically cleaned with detergent solution, acetone and purified deionized water.

Chemicals used for the preparation of CIS thin films are copper sulphate ($CuSO_4$), indium chloride ($InCl_3$) and thiourea (NH_2-CS-NH_2) which are the source materials of Cu^+, In^{+++} and $^{S--}$ ions. All chemicals used in the present investigation were of analytical grade. The required amount of chemicals were weighted accurately and dissolved in double distilled water. All solutions of appropriate concentrations were prepared prior to the deposition. The pH of the cationic precursor solution (copper and indium ions) was maintained at 5 by adding the mixture of 2N hydrazine hydrate (HH) and 2N triethanolamine (TEA) in 1:1 proportion. The pH of anionic solution (sulphur) was maintained at 12 with the addition of ammonia (NH_3).

Preparation of $CuInS_2$ Thin Films

Triethanolamine and hydrazine hydrate were added as complexing agents which avoids immediate precipitation by the controlled release of Cu^+ and In^{++} and therefore ion by ion deposition helps to achieve uniform thin films (Pathan and Lokhande, 2004). $CuSo_4$ (25 ml, 0.12 M) and $InCl_3$ (25 ml, 0.08 M) are taken and mixed in 100 ml beaker and pH of solution was adjusted to 5 with triethanolamine (TEA) and hydrazine hydrate (HH) (Figure 1). The reaction mixture was stirred well so that a clear homogeneous cationic solution was formed. Thiourea (NH_2-CS-NH_2) (50 ml, 0.05 M) is taken in another beaker and the pH of this anionic solution was adjusted to 12 by addition of NH_3. The substrates were immersed in cationic precursor solution (copper and indium ions) at 40°C for 30 sec and thereby copper and indium ions were adsorbed on the surface of the substrates. Then the substrates were rinsed with double distilled water (30 sec) to remove loosely bounded copper and indium ions. When the glass substrates were immersed in an anionic precursor (thiourea) at 40°C for 30 sec, sulphur ions get reacted with pre-adsorbed copper and indium ions on the substrate to form CIS. This was followed by rinsing the substrate in double distilled water (30 sec) to remove the unreacted sulphur ion or powdery CIS. Such deposition cycles were repeated 75 times to get good quality CIS thin films with maximum thickness.

Chemical Path to $CuInS_2$ Thin Films

$CuInS_2$ thin films can be obtained from aqueous bath containing $CuSO_4$, $InCl_3$ and NH_2-CS-NH_2 which are the source materials for Cu^+, In^{+++} and S^{--} . The adsorption of Cu and In ions and their reactions with sulphur ions was carried out to form CIS as per the reaction (Pathan and Lokhande, 2004),

$$Cu^+ + In^{3+} + 2S^{2-} \rightarrow CuInS_2 \qquad (1)$$

Characterization of CIS Films

Scanning electron microscope (JEOL JSM 5300) was used to observe surface morphology and compositional analysis has been carried out by energy dispersive x-ray analyzer (LEICA. S440i). Optical properties were estimated from transmittance spectra recorded using JASCO-UV/VIS/NIR(JASCO V-570) spectrophotometer.

Results and Discussion

Estimation of Lattice Constants and E_g from the EDAX Spectra

Figure 2 shows the energy dispersive X-ray spectra of $CuInS_2$ thin film of thickness 1010 nm. EADX analysis confirmed the presence of copper, indium and sulphur and their atomic percentages are found as [Cu : 70.635%, In : 3.63 % and S : 25.735%] in the deposited film with the non-stoichiometric film composition $Cu_{2.8}In_{0.2}S_1$. The peak at 1.75 keV shows the presence of silicon which is attributed due to the glass substrate. The absence of the other peaks in EDAX spectra indicated that the prepared CIS thin films are pure in nature without impurities (Aldrin *et al*., 2004; Shi *et al*., 2006). EDAX analysis of CIS thin films have been carried out and reported by many earlier researchers (Krunks *et al*., 2005; Krunks *et al*., 2006). whereas in the present work the film composition estimated from EDAX analysis has been employed to determine the lattice constants (in turn structure), band gap and the type of conductivity of CIS

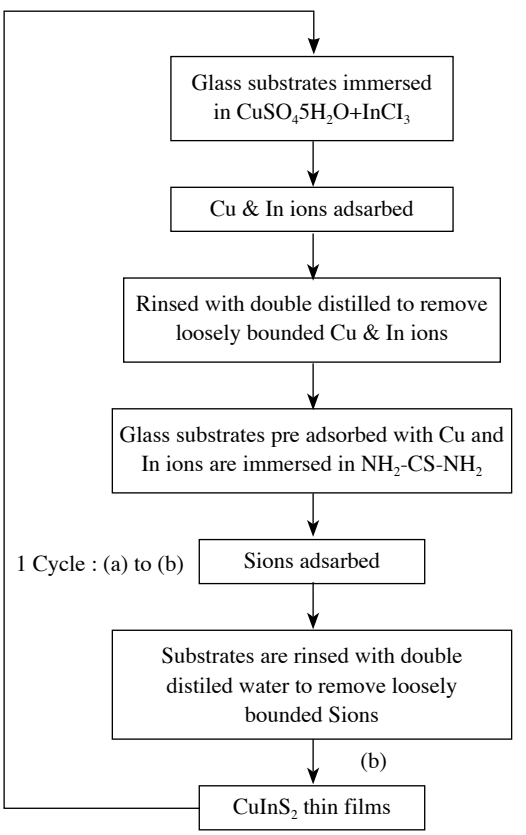

Figure 1. Scheme of the steps of the SILAR

thin films. The novelty in the present study is the estimation of some of the structural, optical and electrical parameters from the single compositional analysis.

It is interesting to note that the lattice constants can be estimated by substituting the composition of sulphur (x) in the equation: a = 5.769 - 0.253x and c = 11.726 - 0.669x (Zeaiter *et al.*, 2000). The lattice constants evaluated from the EDAX analysis are a = 5.516Å and c = 11.057Å and these are in well agreement with JCPDS values (a = 5.523 Å, c = 11.140Å) [JCPDS No.27-0159].

It has been known that the electrical properties of the semiconductor are determined by the compositional deviations from the ideal chemical formula of the $CuInS_2$ compound, which can be described conveniently by two parameters, non-molecularity (Δx) and non-stoichiometry (Δy) and are expressed as

$$\Delta x = \frac{Cu}{In} - 1 \qquad (2)$$

$$\Delta y = \left[\frac{2S}{Cu + 3In}\right] - 1 \qquad (3)$$

EDAX results proved that the prepared film consists of Cu, In and S with the compostion of $Cu_{2.8}In_{0.2}S_1$ and free from other elements. The lattice constants (cell parameters) estiamted from EDAX spectra enebled to conclude the presnece of single phase (chalcopyrite phase with tetragonal structure) of $CuInS_2$ film. Therefore the ideal chemical formulae (Equations 2 and 3) of $CuInS_2$ compound have been used. The variation of Δx would lead to the formation of equal numbers of donor and acceptor. The estimated Δx value is 13 which in turn results in a compensated crystal. The parameter Δy is related to the electronic defects and could determine the type of the majority charge carrier. Films with $\Delta y > 0$ would behave as p-type material while $\Delta y < 0$ would show n-type conductivity. The prepared film is found to have Δy = -0.41176 which is < 0 and therefore n-type conduction mechanism occurs in $CuInS_2$ thin films (Aldrin *et al.*, 2004; Qiu *et a*l., 2005; Shi *et al.*, 2006). Shi (Shi *et al.*, 2006) reported that p-type conductivity is expected due to excess sulphur whereas EDAX results showed the deficient sulphur in the prepared CIS films which may lead to the n-type conductivity. Bihri (Bihri *et al.*,1999) reported that the control of conductivity type can also be related to an energy shift of the center of gravity of sulphur 3p band. They also reported that the conduction type may depend on the intrinsic defects such as cation (indium in the present study) vacancies and anti-site defects. Hence the reasons for n-type may be due to the deficient sulphur or energy shift of the centre of gravity

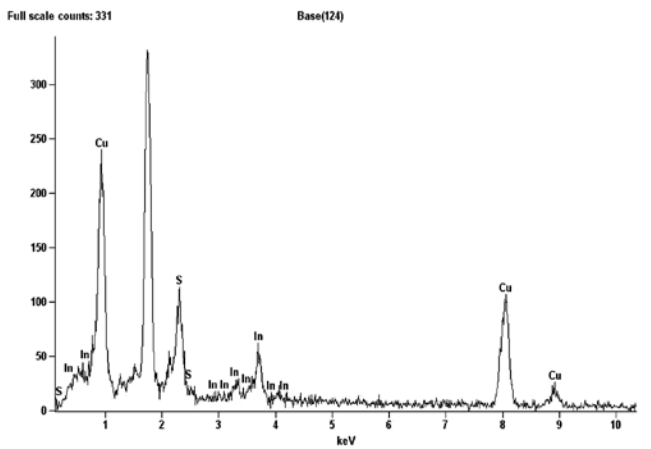

Figure 2. EDAX spectra of CIS thin film of thickness 1010 nm

of sulphur 3p band or the intrinsic defects of cation vacancies and anti-site defects. Shi (Shi *et al*., 2006) reported that $CuInS_2$ thin films having non - stoichiometric parameter values 0.02 and 0.36 have the band gap energy values of 1.45 and 1.30eV respectively (Table 1). Therefore reported change in Δy of 0.34 corresponds to a change of 0.15eV band gap energy. In the present work Δy of a representative $CuInS_2$ thin film has been found as -0.41. The difference in Δy with reference to the earlier work (-0.41 and 0.02) is 0.43 which corresponds to a change in band gap energy of 0.189eV from 1.45eV. The band gap energy of $CuInS_2$ thin film estimated from Δy obtained from EDAX spectra has been identified as 1.64eV which is in good agreement with E_g obtained from transmittance spectra Figure 5. Therefore this approach of E_g estimation from EDAX spectra can be considered as valid technique.

Confirmation of Non - Stoichiometry and Cu - Rich Nature from SEM Images

Figure 3 shows the surface morphology of $CuInS_2$ thin film of thickness 1010 nm.

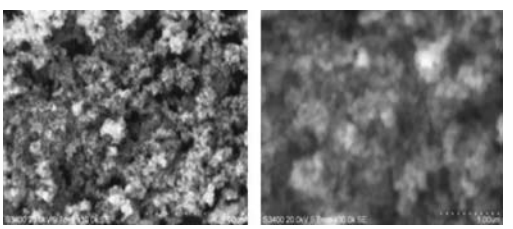

Figure 3. Scanning electron micrographs of CIS thin film of thickness 1010 nm with different magnifications

SEM images show the uniform and continuous morphology of the grown films containing the accumulation of grains. From the scanning electron micrographs it is seen that the substrate surface is well covered and moreover the absence of fine grains confirmed the non-stoichiometry of $CuInS_2$ thin films as reported (Pathan and Lokhande, 2004). The morphology of the prepared CIS thin films looks as that of copper rich films (Krunks *et al*., 2001) and hence the non - stoichiometry in particular copper rich nature of the prepared CIS thin film has been confirmed by SEM analysis. Roughness of the film increase with the increase of relative amount of copper in mixed precursor (Shi *et al*., 2006). Cu-rich films are rough due to the formation of bigger grains. SEM analysis of CIS thin films have been carried out and reported by the earlier researchers (Aldrin *et al*., 2004; Pathan and Lokhande, 2004).

Confirmation of Eg from Transmittance Spectra

Figure 4 shows the transmittance spectra of CIS thin films of thickness 1010 nm. Similar type of transmission spectra has been reported earlier (Bihri and Abd-Lefdil, 1999; Bereznev *et al*., 2007). The absorption coefficients of $CuInS_2$ thin films was calculated using the percentage of transmission obtained from the transmission spectra and are found to be very high and are in the range 10^6 cm^{-1} (Dhanam *et al*., 2002). This relatively high absorption coefficient is very important because the spectral dependence of α can

Table 1. Determination of Eg from EDAX data

	Non Stoichiometry Parameter (Δy)	Eg estimated from Transmission spectra $E_g(o)$ (eV)	Change in Δy	Change in $E_g(o)$ (eV)	E_g estimated from EDAXspectra $E_g(E)$ (eV)
Reported	**0.02**	**1.45**	-----	-----	-----
values	0.36	1.30	0.34	0.15	-----
Present Work	-0.41	1.64	0.43	0.189	1.64

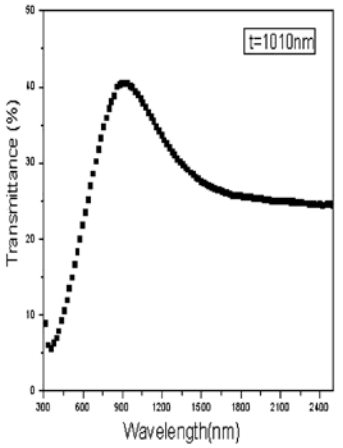

Figure 4. Optical transmittance of CIS thin film

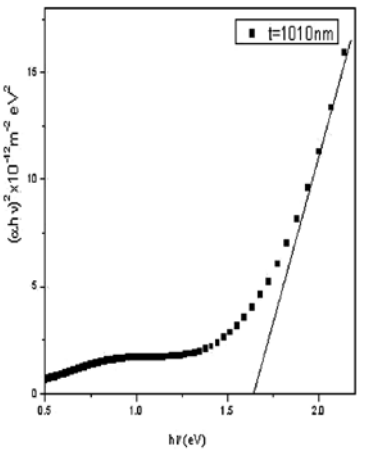

Figure 5. Plot of $(\alpha h\nu)^2$ versus hν of CIS thin film

drastically affect the solar conversion efficiency.

For the direct band gap materials, the absorption coefficient is related to the energy gap Eg according to the equation,

$$\alpha = \frac{A\,(h\nu - Eg)^{1/2}}{h\nu} \qquad (4)$$

where A is the parameter which depends on the transition probability (Aldrin *et al*., 2004) and h is Planck constant. E_g can be obtained from the graph of $(\alpha h\nu)^2$ versus hν, which is illustrated in Figure 5. The linear nature of the plot at the absorption edge confirms that $CuInS_2$ thin films of thickness 1010 nm has direct band gap with $E_g(o)$ values 1.64 eV and is in good agreement with the reported values (Liang *et al*., 2008) and the values estimated from the EDAX spectra $E_g(E)$ (1.64 eV).The higher value of band gap (1.64eV) compared to the reported value (1.5eV) may be to the deviation in stoichiometry that gives rise to defects states and thus induce smearing of absorption edge as reported earlier (Askay *et al*., 2007).

Conclusions

$CuInS_2$ thin films have been prepared by SILAR technique. EDAX spectra has been employed to identify the composition, lattice constants, non-molecularity, type of conductivity and band gap energy. It is interesting to conclude that the simple composition analysis has been used to calculate some of the important structural, optical and electrical parameters of CIS thin films.

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