Effect of stirring on the properties of SILAR Cu-rich CuInS$_2$films

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Abstract−CuInS$_2$ (CIS) thin films are prepared by the successive ionic layer adsorption and reaction method (SILAR) by single cationic route under two different conditions (without stirring and with stirring). The effect of stirring on the structural, optical, compositional and morphological properties of the prepared Cu-rich CuInS$_2$ thin films has been studied and reported in this paper.

Large scale introduction of solar energy requires a drastic price reduction. That is why the efforts in the field of thin films particularly in the cost-effective deposition techniques and new design of solar cells are continuously in progress [1]. Of all the alternatives of conventional energy, solar energy has been receiving considerable attention [2]. CuInS$_2$ is a promising absorber material for thin film solar cells having a high absorption coefficient and a band gap of 1.5eV being close to the optimum range for photovoltaic conversion [3-4]. In addition there is no high toxic component included [5]. Some researches reported that the efficiency of a CuInS$_2$ solar cell is limited by its open circuit voltage, which is far below the theoretical value calculated for an ideal solar cell with a band gap of 1.5eV. The difference between the theoretical efficiency (27-32%) and the measured efficiency is mainly attributed to the qualities of CuInS$_2$ films. The efficiencies are expected to improve if the qualities of this material reach optimum [6]. Therefore different techniques such as spray pyrolysis [1, 7], chemical deposition [8] ionic layer gas reaction (ILGAR) [4], sputtering [7], liquid-liquid interface reaction technique (LLIRT) [9], thermal evaporation [10] and successive ionic layer adsorption and reaction (SILAR) are focused on preparing device quality CIS thin films.

For the present study the SILAR method has been selected for the preparation of CIS thin films because it is simple, attractive, less expensive and less time consuming. Copper sulphate (CuSo$_4$), indium chloride (InCl$_3$) and thiourea (CH$_4$N$_2$S) are used as source materials for Cu$^+$, In^{3+} and S^{2-} ions and their solutions are prepared in deionized water. 2N triethanolamine (TEA) and 2N hydrazine hydrate (HH) are added as complexing agents. Both cationic precursors, CuSo$_4$ (12.5 ml, 0.1M) and InCl$_3$ (12.5ml, 0.2M) are taken and mixed in a 100ml beaker and the pH of the solution is adjusted to 5 with

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TEA+HH. The reaction mixture is stirred well so that a clear homogeneous solution is formed (single cationic solution). CH$_4$N$_2$S (25ml, 0.5M) is taken in another beaker (anionic solution) and its pH is adjusted to 12 by the addition of ammonia. A digital pH meter (ELICO LI - 120) has been used to adjust the pH of the reaction mixture. The pH meter is standardized using buffer solutions of pH 4+0.05 and 9.2+0.05. The deposition is carried out by SILAR coating unit HO-TH-03A at a deposition temperature of 45^0. Cu-rich films are prepared without stirring (trial 1) and with stirring (trial 2) and the prepared films are analyzed after annealing at 100^{0}C for 60 min. The atomic composition is determined by an energy dispersive x-ray analyzer (EDAX) with a INCA penta FET X3 7582. The surface morphology of the CuInS$_2$ thin film is observed by scanning electron microscopy (SEM) with a JEOL-6390 scanning electron microscope, using an accelerating voltage of 20kV.The optical transmission spectra of the prepared thin films are taken using a JASCO-UV/VIS/NIR(JASCOV-570) optical spectrometer in the wavelength range 200-2500nm.

The deposition process involves four steps. In the first step the substrate is immersed in the mixed cationic precursor for 30 sec so that Cu and In ions (diffusion, reaction and adsorption) are adsorbed on the substrate surface. In the second step the substrate is rinsed with ion exchange water for 30 sec to remove loosely bounded particles (convection, diffusion and desorption). In the third step, the substrate with pre-adsorbed Cu and In ions reacted with newly adsorbed sulphur from the anionic solution to form CuInS$_2$. In the fourth step, the substrate is rinsed with ion exchange water for 30 sec to remove loosely bounded particles (convection, diffusion and desorption). The deposition process has been repeated for 100 deposition cycles without stirring (trial 1) and with stirring (trial 2) and their thickness are found as 180 and 110nm respectively (the thickness of the films has been determined by a gravimetric technique).

The films prepared without stirring are found to have higher thickness compared to the films prepared with stirring. Fig.1 shows the EDAX spectra of Cu-rich CIS films which confirmed that the films prepared without and with stirring are found to have almost the same Cu-rich composition, Cu$_{2.26}$In$_{0.135}$S$_{1.59}$ and Cu$_{1.9}$In$_{0.14}$S$_{1.93}$

respectively [11]. In^{3+} sites have been occupied by a larger number of copper atoms in the films prepared without stirring where as In^{3+} sites of CIS films have been occupied with a larger number of sulphur ions in the films prepared with stirring. The lattice constants have been estimated by substituting the composition of sulphur (x) in the equation: a = 5.769 - 0.2253 x and c = 11.726 - 0.669 x [12]. The estimated values of trial 1 and 2 films are a = 5.410Å; c =10.662Å and a= 5.334Å; c = 10.434Å, respectively. The estimated values are in agreement with JCPDS values [27-0159]. The estimated lattice constants confirm that the films prepared from both trials have a tetragonal structure.

The compositional deviations of Cu-rich CIS can be expressed by non-stoichiometric parameter [Δy = (2S/Cu+3In)−1] which is related to the electronic defects and would determine the type of majority charge carriers. Films with $\Delta y > 0$ will behave as p-type material while $\Delta y < 0$ will show n-type conductivity [13]. Since the estimated values of Δy of the films, 0.19 (trial 1) and 0.66 (trial 2) are > 0 it can be concluded that the prepared films from both trials are of the p-type in nature [13]. The p-type nature may be attributed to Cu_{In} because the formation energy of V_{In} is larger compared to Cu_{In} [14].
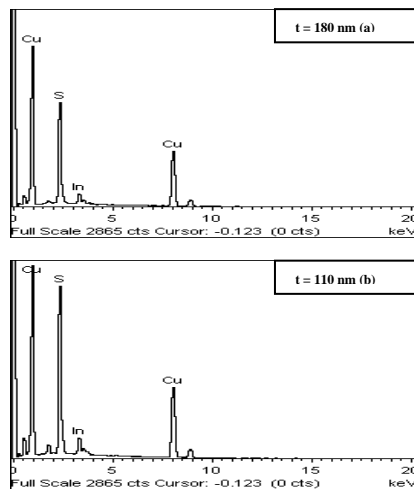

Fig.1. EDAX spectra of Cu - rich CIS thin films prepared with (a) without stirring (b) with stirring.

From the scanning electron micrographs (Fig.2) it has been found that the films prepared without stirring are covered with more voids than the film prepared with stirring. Surface morphological change is common in thin films and strongly depends upon the preparation method [15]. Stirring affects SILAR films by preventing the deposition of loosely adhering, large aggregates.

The loose deposits block the substrate and prevent normal adherent film growth when the films are prepared without stirring and this may be the reason for more voids in the films (Fig. 2a). The loose deposits are readily

removed by stirring action and enhanced normal adherent film growth was confirmed by the dense morphology of $CuInS_2$ films prepared with stirring (Fig. 2b) [16].
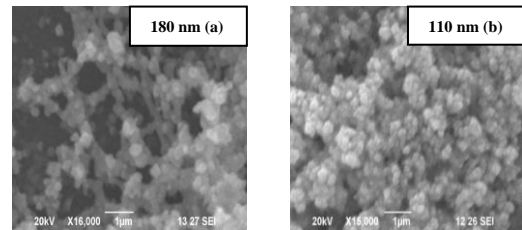

Fig.2. SEM micrographs of Cu-rich CIS thin film prepared (a) without stirring and (b) with stirring.
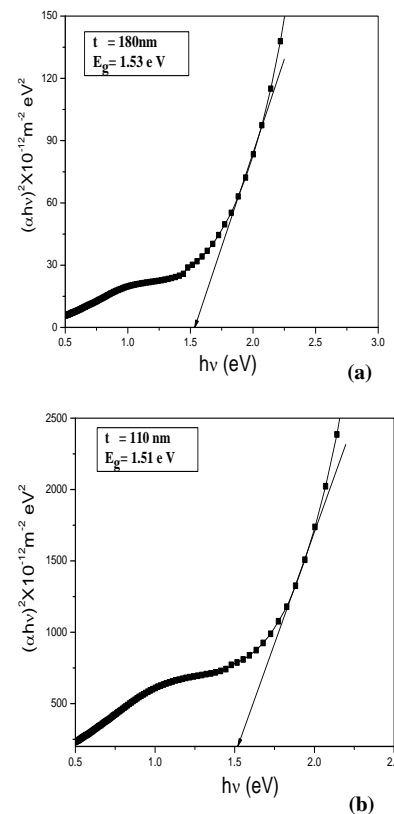

Fig. 3. $(\alpha h\nu)^2$ vs. hν plot of Cu-rich $CuInS_2$ thin film prepared (a) without stirring and (b) with stirring.

Figure 3 shows the plot $(\alpha h\nu)^2$ versus (hν) of Cu-rich CIS films prepared without and with stirring. It is well established that $CuInS_2$ is a direct band gap semiconductor with the band extrema located at the centre of Brillouin [10]. Both trial 1 and trial 2 films are found to have direct allowed transition with band gaps of about 1.53 and 1.51eV, respectively, which agree very well with earlier reports [10,17-19]. Trial 2 (with stirring) is found to have a comparatively closer bandgap of single crystal

(1.5eV) [18]. It can also be seen that the film prepared without stirring has a relatively higher absorption coefficient ($3.8 \times 10^6 m^{-1}$) than the film prepared with stirring ($2.1 \times 10^6 m^{-1}$) He *et al.* [20] pointed out that due to the high absorption coefficient ($> 10^4 cm^{-1}$), the ternary compound $CuInS_2$ (CIS) has been regarded as a promising absorber for thin film photovoltaic applications [20]. Plots of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$ and $(\alpha h\nu)^{3/2}$ versus $(h\nu)$ (not shown) reveal that Cu rich CIS films prepared from both trials do not have the line above $h\nu > Eg$, which confirms the fact that the CIS phase does not have indirectly allowed, directly forbidden and indirectly forbidden transitions.
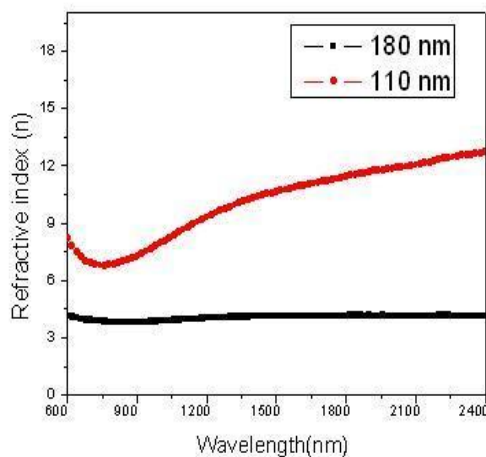

Fig. 4. Refractive index spectra of CIS films.

Figure 4 shows the spectra of the refractive index of CIS films of trial 1 and 2. It has been understood that the films prepared without stirring are found to have a closer reported refractive index (3) [21]. As the refractive index is a measure of transparency to incident spectral radiation, the lower refractive index of films prepared without stirring corresponds to comparatively lower transparency and in turn higher absorption than in the case of the films prepared with stirring [22].

In conclusion, Cu-rich CIS thin films prepared without stirring and with stirring have the same tetragonal structure, p type nature, and directly allowed transition. The film prepared with stirring is uniform in nature having voids less dense morphology and bandgap (1.51eV) closer to that of a single crystal (1.5eV) whereas the film prepared without stirring has a slightly higher absorption coefficient and a lower refractive index. Therefore this study enables us to realize the influence of stirring on the properties of Cu rich CIS thin films.

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