Indian Journal of Engineering & Materials Sciences
Vol. 8, October 2001, pp. 271-274

Preparation of $CdIn_2S_4$ thin films by chemical method

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Received 3 January 2001; accepted 22 May 2001

Semiconducting $CdIn_2S_4$ thin films have been deposited on amorphous glass substrates using a chemical method, successive ionic layer adsorption and reaction (SILAR). The influence of preparative parameters on the properties of the films has been studied. The thickness of the film is found to be 0.44 μm. The films have been characterized for structural, optical and electrical transport properties by means of X-ray diffraction, optical absorption, electrical resistivity and thermoelectric power measurements techniques. The films are found to be nanocrystalline with optical bandgap 2.12 eV. The electrical resistivity was of the order of 10^4 Ω-cm.

In recent years, binary and ternary semiconductors have been attracting much more interest in photovoltaics[1-3]. A number of ternary semiconductors have been investigated and studied for their photoelectrochemical behaviour[4,5]. Photoelectrochemical (PEC) studies of spinel crystal in various electrolytes reported by Epps and Becker[6]. The low resistivity of photoelectrode is required to minimise the series resistance of the PEC cell.

Cadmium indium sulphide ($CdIn_2S_4$) is a photoactive compound semiconductor having spinel cubic structure of the type $A^{II}B^{III}C^{VI}$ that has received very little attention as a prospective material for solid state and photoelectrochemical solar cells. The optical absorption and photoelectric properties of $CdIn_2S_4$ have been reported by several authors[7-11].

The deposition of $CdIn_2S_4$ thin film has been carried out using a chemical method known as successive ionic layer adsorption and reaction (SILAR). The preparative parameters have been optimized in order to obtain $CdIn_2S_4$ thin films. The $CdIn_2S_4$ film characterization including structural optical and electrical properties has been presented.

Experimental Procedure

The depositions were carried out onto commercially available glass substrates of the size $(7.5\times2.5\times0.1)$ cm^3. Chemicals used were cadmium sulphate ($CdSO_4$), indium trichloride ($InCl_3$) and sodium sulphide (Na_2S). Thin $CdIn_2S_4$ films were deposited from an aqueous solution adopting the following procedure.

The cationic precursors for $CdIn_2S_4$ were 0.1 $mol.dm^{-3}$ cadmium sulphate with pH 8 and 0.04 $mol.dm^{-3}$ indium trichloride with pH 5. The source for sulphur ion was 0.05 $mol.dm^{-3}$ sodium sulphide with pH 12. For the deposition of $CdIn_2S_4$ thin films, cleaned glass substrate was immersed in the solution of cadmium sulphate for 15 s where cadmium ions were adsorbed on the surface of the substrate. This substrate was rinsed in deionised water for 10 s to remove loosely bound or excess cadmium ions. The conductivity of the rinsing water was under $1\mu\Omega^{-1}cm^{-1}$. The substrate was then immersed in anionic precursor (Na_2S) solution for 15 s where the sulphur ion reacted with adsorbed cadmium ion on the substrate to form CdS film. After that substrate is dipped in indium trichloride and sodium sulphide using same procedure. Thus layers of CdS and In_2S_3 thin films were formed alternately to result into $CdIn_2S_4$ thin films. The optimized deposition conditions for $CdIn_2S_4$ as tabulated in Table 1. Films prepared using optimized parameters are used for the further characterization.

Results and Discussion

Thickness measurement

Thickness of the as prepared films were determined by weight difference method given by

$$t = m/A\rho \qquad \text{... (1)}$$

where m is the mass of the film, A is the area of the film and ρ is the density of material (ρ $CdIn_2S_4$ = 4.7175 g/cm^3).

Fig. 1 shows the variation of $CdIn_2S_4$ film thickness with total deposition time. For increase in total

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deposition time, film thickness increases linearly in the initial stage and then shows a decline for the further increase in total deposition time, this is because the films becomes powdery and peel off from substrate[12].

Structural studies

X-ray diffraction (XRD) pattern of $CdIn_2S_4$ films were recorded by using a Philips model PW-1716 in the range of scanning angle 10-100°(2θ) with CuK_α radiations using the wavelength 1.5406Å.

The XRD pattern of as deposited $CdIn_2S_4$ film on the glass substrate is as shown in Fig. 2a. The films are nanocrystalline with spinel cubic structure. The broad hump in XRD pattern is due to amorphous glass substrate. In order to improve the crystallinity the film was annealed at 573 K for 15 min. It was found that the crystnallinity was improved significantly as shown in Fig. 2b. The comparison of observed 'd' values with standard JCPDS data[13] *d* values was made from Table 2, matching of observed '*d*' values with standard JCPDS data confirms that the deposited films are of $CdIn_2S_4$ having spinel cubic structure.

Optical absorption studies

Optical absorption of the $CdIn_2S_4$ thin film deposited on glass substrate was carried out by using Spectrophotometer (Hitachi Model 330) in the wavelength range 350 to 850 nm at room temperature. For allowed direct band gap transition, absorption coefficient , α is given by

$$\alpha = \frac{A\,(h\nu - E_g)^{\frac{1}{2}}}{h\nu} \qquad \ldots (2)$$

where *A* is constant, *h* is Planks constant, ν is the frequency of the incident radiation and E_g is the band gap energy of the semiconductor. The plot of $(\alpha h\nu)^2$ versus $h\nu$ (Fig.3) is linear indicating that the nature of optical transition in semiconducting $CdIn_2S_4$ is direct. The intercept on the energy axis at $\alpha = 0$ yields $E_g \sim$ 2.12 eV which is very near to (2.15 eV) bandgap value of $CdIn_2S_4$ deposited by spray pyrolysis technique [14].

Electrical resistivity measurement

Dark electrical resistivity of the $CdIn_2S_4$ thin film, was measured at room temperature by using d.c. two point probe method. The area of the film (0.25 cm^2)

Table 1 — Deposition conditions for $CdIn_2S_4$ thin films by SILAR method

Precursor	$CdSO_4$	Na_2S	$InCl_3$	Na_2S
Concentration (mol. dm^{-3})	0.1	0.05	0.04	0.1
*p*H~	8	12	5	12
Immersion time (s)	15	15	15	15
Number of immersions	35	35	35	35
Deposition temperature (K)	353	353	353	353

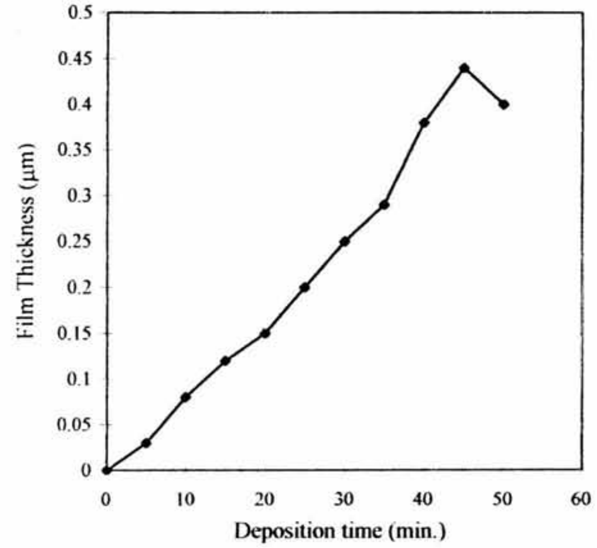

Fig. 1 — Variation of film thickness with deposition time for $CdIn_2S_4$ thin films.

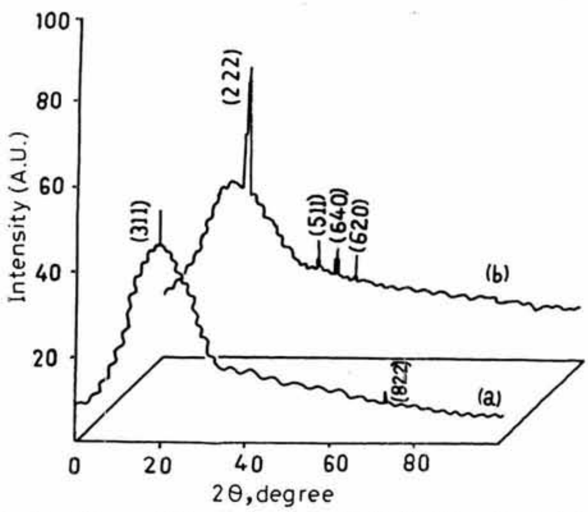

Fig. 2 — X-ray diffractograms of $CdIn_2S_4$ thin films (a) as deposited and (b) annealed at 573 K for 15 min.

was defined and silver paste was applied to ensure good ohmic contact to $CdIn_2S_4$ film. Chromel-alumel thermocouple was used to measure the temperature difference. The dark electrical resistivity at room temperature is found the order of 10^{4} Ω-cm. The variation of log ρ versus (1000/*T*) for the film is shown in Fig. 4, which shows that the electrical resistivity obeys the relation

$$\rho - \rho_0 \exp\left(\frac{E_a}{kT}\right) \qquad \ldots (3)$$

where, E_a is the activation energy and k is the Boltzman constant. It is well known that the temperature dependence of resistivity is related to variation of the carrier concentration and mobility with temperature. In a semiconductor, carrier concentration is a rapidly increasing function of temperature. This increase is due to the thermal excitation of electrons either from imperfections or across the band gap. It is clear from the Fig. 4 that the resistivity of the film decreases on the increase in temperature, showing semiconducting behavior of $CdIn_2S_4$ thin films.

Table 2—Composition of XRD data of $CdIn_2S_4$ thin films deposited by SILAR method with standard JCPDS data

Condition	Observed *d* values (Å)	Standard *d* values (Å)	Plane (hkl)
As deposited	3.2610	3.26	311
	1.2735	1.27	822
Annealed at 573 K	3.1690	3.131	222
for 15 min	2.0733	2.087	511
	1.9013	1.916	440
	1.7627	1.715	620

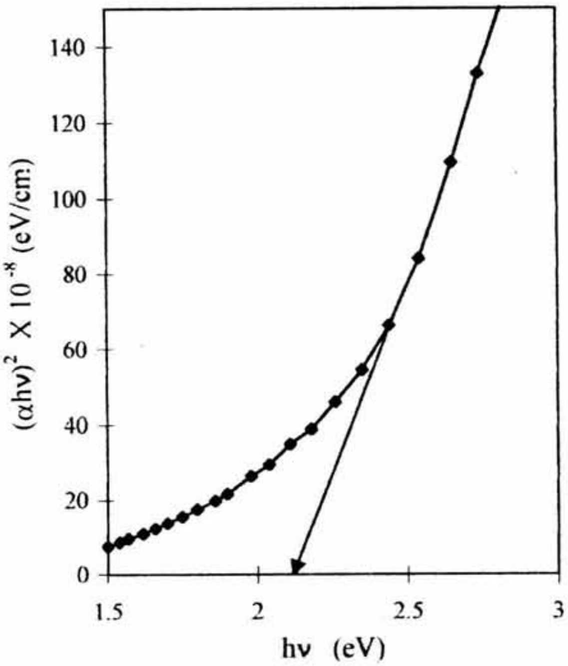

Fig. 3—Plot of $(\alpha h\nu)^2$ versus hν for $CdIn_2S_4$ thin film.

Thermo-emf measurement studies

The type of conductivity exhibited by $CdIn_2S_4$ thin film was determined from thermo-emf measurements. The polarity of thermally generated voltage at the hot end was positive indicating that the $CdIn_2S_4$ films are

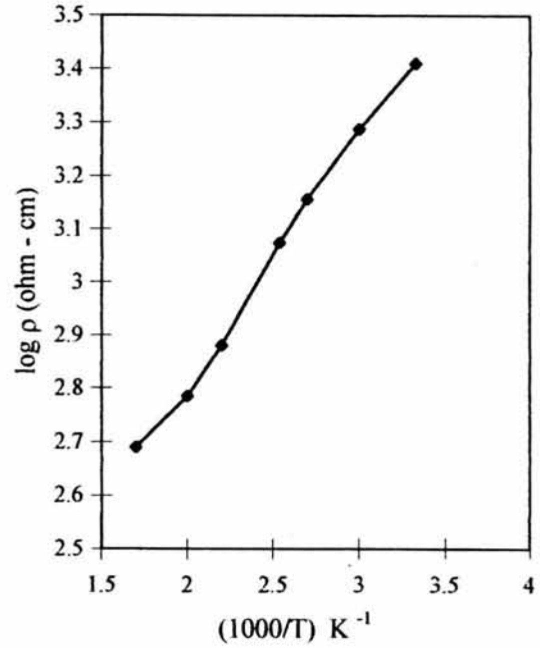

Fig. 4—Plot of log ρ versus (1000/*T*) for $CdIn_2S_4$ thin film.

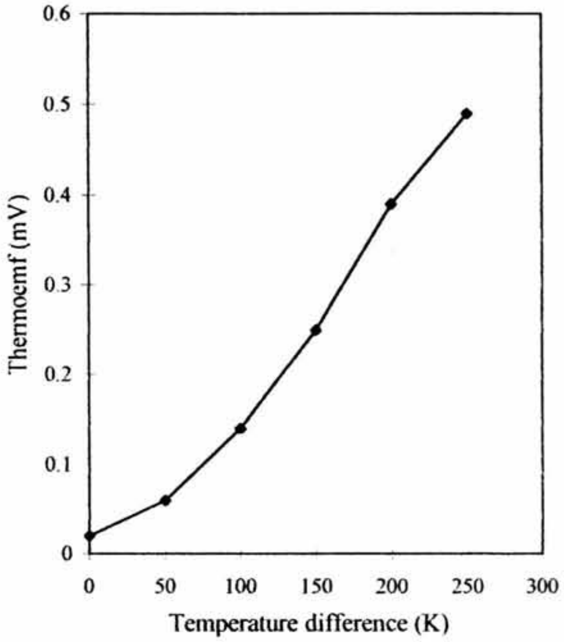

Fig. 5—Variation of thermo-emf with temperature difference for $CdIn_2S_4$ thin .

of *n*-type which is same as reported earlier[7]. Fig. 5 shows the variation of thermo-emf with temperature difference for the $CdIn_2S_4$ thin films. It is seen from Fig. 5 that the thermo-emf varies exponentially with temperature difference.

Conclusion

The growth of $CdIn_2S_4$ thin films onto glass substrates is feasible by SILAR method. The $CdIn_2S_4$ thin films are nanocrystalline with spinel cubic structure. The film shows semiconducting behaviour. The optical band gap of $CdIn_2S_4$ is found to be 2.12 eV. The films are of *n*-type electrical conductivity.

Acknowledgement

Authors are thankful to University Grants Commission, New Delhi for financial support through UGC-DRS (SAP:1999-2004) to Department of Physics, Shivaji University, Kolhapur.

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