Structural and opto-electrical properties of nanocrystalline Cadmium Indium Selenide thin films and to study their effect of annealing

[1] S.G. Gaikwad, [2] V. N. Kadam, [3] M.V. Gaikwad, [4*] M.R. Asabe

[1][2][3] Department of Chemistry, Baburao Patil College of Arts and Science, Angar
[4] Department of Chemistry, Walchand College of Arts and Science (Autonomous), Solapur

Abstract: Nanocrystalline Cadmium Indium Selenide thin film have been prepared for the first time by using a relatively simple chemical bath deposition technique at room temperature using Cadmium sulphate, Indium chloride, Tartaric acid, Hydrazine hydrate and Sodium selenosulphate in an aqueous alkaline medium. Various preparative conditions of thin film deposition are outlined. The films deposited at optimum preparative parameters are annealed at different temperatures. The as-deposited films those annealed at 100^{o} C and have been characterized by X-ray diffraction (XRD), Optical absorption and scanning electron microscopy (SEM). The as grown films were found to be transparent, uniform, well adherent and red in color. The XRD analysis of the as- deposited and annealed films shows the presence of polycrystalline nature in tetragonal crystal structure. Optical absorption study shows the presence of band gap for direct transition at 1.95 and 1.80 eV respectively, for the as-deposited and annealed films. SEM study indicated the presence of uniformly distributed grains over the surface of substrate for the as-deposited as well as annealed film.
Keywords: *Chemical synthesis, Electrical measurements, Scanning electron microscopy, Nanocrystalline $CdIn_2Se_4$ thin films, Semiconductor*

1. Introduction

The compound belonging to semiconductors family exhibit chemical composition dependent optical, electrical and structural properties. The engineering of properties makes these materials quite useful in solar energy conversion [1, 2], Optoelectronic devices [3], and nonlinear optics [4]. So far, a number of methods like vacuum evaporation, slurry pasting, spray pyrolysis, electrodeposition [5-8] etc. have been utilized to deposit $CdIn_2Se_4$ material in thin film form. However, no attempts have been made prepare it using chemical bath deposition method. Recently chemical bath deposition has emerged as an excellent, low cost simple method. The method gives flexibility and choice in selecting precursors so that optimization of depositional parameters could evoke good film [9-11].

In this paper we report, for the first time the preparation of Nanocrystalline $CdIn_2Se_4$ thin films using Chemical Bath Deposition and Investigation on some of its properties.

2 Experimental

2.1 Substrate cleaning

The substrates were cleaned by boiling them in chromic acid for 1 hour, followed by washing successively with detergent and alcohol. They were finally stored in double distilled water before use.

2.2 Reagents and preparation of solutions

The chemicals used for preparation of thin films were AR grade cadmium sulphate, indium trichloride, tartaric acid, hydrazine hydrate, sodium sulphite and selenium. The solutions were prepared in double distilled water. The solution of sodium selenosulphate (0.02M) was used as a source of Se^{-2} ion.

2.3 Synthesis of Nanocrystalline $CdIn_2Se_4$ thin films

The deposition of $CdIn_2Se_4$ thin film have been carried out from a reactive solution obtained by mixing 5 mL (0.02M) Cadmium sulphate, 10 mL (0.02M) Indium trichloride, 2.5 mL (1M) Tartaric acid, 10 mL (10%) hydrazine hydrate and 20 mL (0.02 M) sodium selenosulphate. The total volume of the reactive mixture was made up to 100mL by adding double distilled water. The beaker containing the reactive solution was transferred to an ice bath at 278 K temperature. The pH of the resulting solution was found to be 11.80±0.05. To obtain the film, four glass substrates were positioned vertically on a specially designed substrate holder and rotated in a reactive solution with a speed of 55±2 rpm. The temperature of the solution was then allowed to rise slowly to 293K. After 2 hour of deposition the substrates were subsequently removed from the beaker. The films obtained were washed with distilled water, dried in air and kept in a desiccator.

2.4 Characterization of Nanocrystalline $CdIn_2Se_4$ thin films

The X-ray diffraction study of $CdIn_2Se_4$ film was carried out in 10^0-80^0 the range of the diffraction angle with Cu K□$_1$ radiation using Philips PW-1710 diffractometer □ □ □ 1.54056Å). The electrical conductivity of $CdIn_2Se_4$ thin film was measured using a 'dc' two-probe method. A quick drying silver paste was applied atthe ends of the film for good ohmic contacts. For the measurements of conductivity, a constant voltage was applied across the sample and the current passing through the film was noted at different temperature. A calibrated thermocouple (chromel- alumel, 24 gauge) with a digital indicator was used to sense the working temperature. The optical absorption measurements were made in the wavelength range 400-900 nm by using a Hitachi-330 (Japan) UV-VIS-NIR double beam spectrophotometer at room temperature. An identical, uncoated glass substrate in the reference beam made a substrate absorption correction. The analysis of the spectrum was carried out by computing the values of absorption at every step of 2 nm. A JEOL-JSM 6360 scanning electron microscope (SEM) was used for the microscopicobservations.

3. Results and Discussions

3.1 Growth Mechanism

In the reaction bath, In^{+3} and Cd^{+2} is complexed with tartaric acid in the form of water soluble tartarate complex and thus control metal ion concentration. The dissociation of sodium selenosulphate as well as tartarate complex in alkaline medium takes place. At 278 K, it forms clear solution and no film or precipitate is observed when solution was kept for long time. The metal ions are in stable complex state. As temperature increases slowly selenosulphate and metal complex take place in alkaline medium, favors the formation of $CdIn_2Se_4$ thin film. The deposition process is based on slow release of In^{+3}, Cd^{+2} and Se^{-2} ions in the solution by ion-by-ion basis on the glass substrate. The kinetics growth of film can be understood from the following reaction

$$Cd^{+2} + nA^{-2} \leftrightarrow [Cd\,(A)\,n] \text{ ---------- } 1.1$$
$$In^{+3} + nA^{-2} \leftrightarrow [In(A)n] \text{ ---------- } 1.2$$
$$Na_2SeO_3 + OH^- \rightarrow Na_2SO_4 + HSe \text{ ---------- } 1.3$$
$$HSe^- + OH^- \rightarrow H_2O + Se^{-2} \text{ ---------- } 1.4$$
$$[Cd(A)n] + [In(A)n] + Se^{-2} \rightarrow CdIn_2Se_4 + nA \text{ ---------- } 1.5$$

Hydrazine hydrate acts as complementary complexant, which improve compactness and adherence of the film. Speed of rotation was 55□ 2 rpm was selected to deposit $CdIn_2Se_4$ thin films. Above higher speed very thin film was deposited. At lower speed, thick non-adherent films deposited. The films obtained are uniform, well adherent, red and transparent.

The thickness was measured at the step of 30 min and is plotted against time (Fig. 1). The thickness was found to vary linearly with time up to 120 min thereafter saturates. The saturation can be related to insufficient quantity of reactive species after the time of 120 min. The thickness was also measured as a function of temperature and the variation is shown in Fig.2. The thickness increases linearly with temperature up to 298 K and then decreases sharply. This might happen due to faster release of In^{+3} and Se^{-2} ions forming precipitate instead of film formation. Theterminal thickness was found to be 0.60µm.

3.2 Structural and Morphological Investigation

Structural investigation of as deposited and annealed $CdIn_2Se_4$ thin film is carried out using Cu K□$_□$ radiation in Two theta range 10^0-80^0 Semiconducting $CdIn_2Se_4$ is known to exist in imperfect Zinc blend structure

(Tetragonal pseudo cubic, Space group P42m) a = 5.815 Å . The bulk form of $CdIn_2Se_4$ is tetragonal with at least one vacant cation site per unit cell with respect to perfect zinc blend structure. This periodic vacancy corresponds to opening of a 0.5 eV wide gap just below the top of (Ev) [12, 13] making the material quite useful for diversified applications. The diffractionpattern depict that the films is fairly polycrystalline in nature with a diffraction peaks at values of two theta 26.35, 34.15, 45.8, 46.6, 52 which can be conveniently indexed as reflections originating from 111, 201, 202, 212, and 311 plans of tetragonal $CdIn_2Se_4$ resp. (JCPDS data card No. 08-0267) The annealing of film in air at 100^0 C for 3 hours crystallizes film as observed from the increase in intensity of different peaks without any chemical alterations (Fig.1b). In both the films, the intensity of (111) plan is higher. The deposition of $CdIn_2Se_4$ films using methods other than CBD has been known to accompany with formation of minor phases of CdSe, In_2Se_3 also [14, 15] However in our investigation we do not observe the peaks at d values 3.72, 3.51, 3.56, 3.01 which corresponds to intense peaks of CdSe (Hexagonal), CdSe (Cubic), In_2Se_3 (Hexagonal), In2Se3 (Rhombohedral) phases respectively indicating that these phases are not formed in our film. The lattice constant obtained for thin film is 5.84 which agree well with the literature reported data [15]. The average crystallite size of the as deposited $CdIn_2Se_4$thin film was found to be 200 Å.

The surface morphology of as deposited and annealed $CdIn_2Se_4$ thin film were analyzed by using SEM and are shown in Fig. 3. It is observed that the surface of CdIn2Se4 thin film is homogenous, without cracks or pinholes. The film is composed of minute grains, uniformly distributed over a smooth homogenous background of smaller crystallites. The presence of fine background is an indication of one step growth by multiple nucleation's. The average grain size of sample is reported in Table 1.

3.3 Optical properties

The optical absorption spectra of $CdIn_2Se_4$ film deposited onto glass substratewere taken at in the wavelength range of 400-900 nm. Fig.4 shows variation of optical absorption with wavelength. The optical study shows that the films are highly absorptive (α x 10^4 cm^{-1}). $CdIn_2Se_4$ film is a direct band gap semiconductor. For an allowed direct band gap transition the absorption coefficient α can be related to the photon energy hν by

$(\alpha h\nu)^2 = A\,(h\nu - E_g)$-- 1.6

where A is a constant and E_g is the direct energy band gap. For a direct band gap semiconductor, the $(\alpha h\nu)^2$ versus hν characteristic is predicted to be a straight line with a photoenergy axis intercept indicative for the band gap. This is illustrated in Fig.5, where a band gap of 1.85eV can be obtained.

3.4 Electrical properties

The dark electrical conductivity of $CdIn_2Se_4$ film on non-conducting glass slide was determined by using a 'dc' two probe method, in the temperature range 300-525K. At room temperature the specific conductance was found to be of the order of 10^{-2} $(\Omega\ cm)^{-1}$. The values of specific conductance at 300 and 525 K are reported in Table 2. It is observed that the conductivity on the film increases with increasing in temperature which indicates the semiconducting nature of the thin film. The electrical conductivity with temperature during heating and cooling cycles was found to be slightly different and this shows that the 'as deposited' films undergo crystallization due to annealing that also removes non-equilibrium defects during first heating. A plot of log σ (conductivity) vs. inverse absolute temperature for the cooling cycle is shown in the Fig. 6. The plot shows that electrical conductivity has two linear regions, an intrinsic region setting at low temperature, characterized by small slope (300-350 K). High temperature region is associated with extrinsic conduction due to the presence donor states. The activation energy is calculated using the Arrhenius equation-

$\sigma = \sigma_0 \exp(-Ea/kT)$ --1.7

where, the terms have usual meaning. The activation energies are 0.021 eV and 0.143 eV for low and high temperature regions, respectively.

4. Conclusion:

Homogenous and uniform films of $CdIn_2Se_4$ have been successfully deposited using chemical bath deposition technique. The film formation takes place by ion-by-ion growth mechanism. Crystallographic and micrographic studies revealed the polycrystalline nature in tetragonal crystal system.Optical studies show that,

$CdIn_2Se_4$ films have high optical absorption coefficient and direct band-to-band type optical transition. Temperature dependence of electrical conductivity showed the semiconducting nature of the film.

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Table Captions:

Figure Captions:

Table 1: Structural and morphological data of $CdIn_2Se_4$ thin film

Film	d-values(A^0)			Planes hkl	Grain Size (A^0)
	ASTM	Observed As deposited	Annealed		SEM
$CdIn_2Se_4$	3.47 2.61 2.06 1.75	3.3805 2.6230 2.0650 1.7175	3.4457 2.6687 2.1296 1.8513	111 201 202 311	210

Table 2: Data on optical and electrical properties of $CdIn_2Se_4$ thin film

Film	Band gap (eV)	Activationenergy (eV)		Specific Conductance (□cm)$^{-1}$	
		HT	LT	300 K	525 K
$CdIn_2Se_4$ as deposited	1.98	0.153	0.028	7.67x 10^{-3}	1.02x 10^{-2}
$CdIn_2Se_4$ annealedat 100 ^oC	1.85	0.132	0.021	5.58 x 10^{-2}	5.98 x 10^{-1}

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Table 3: Compositional study of $CdIn_2Se_4$ thin film

Element	Weight %	Atomic %
Cd	11.4	14.3
In	31.3	28.6
Se	54.3	57.2
Total	97.0%	100%

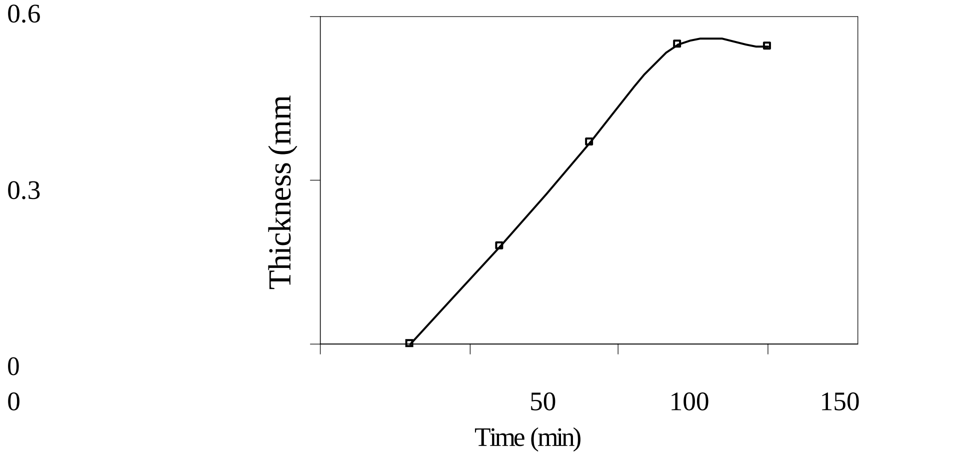

Fig 1:

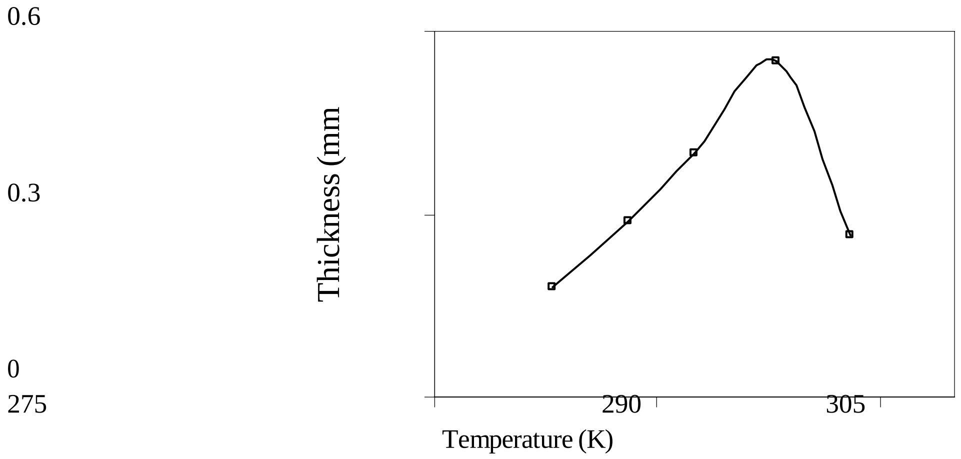

Fig 2:

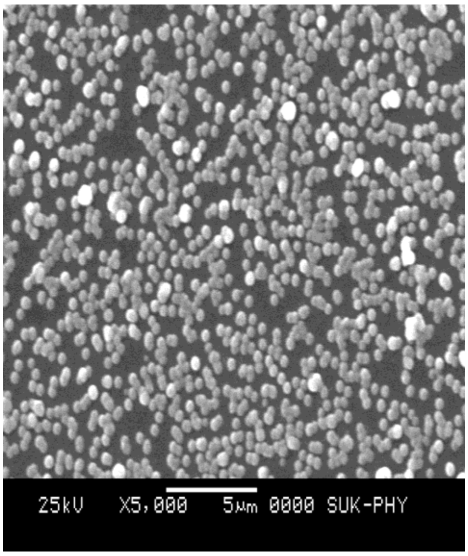
25kV X5,000 5µm 0000 SUK-PHY

Fig. 3:

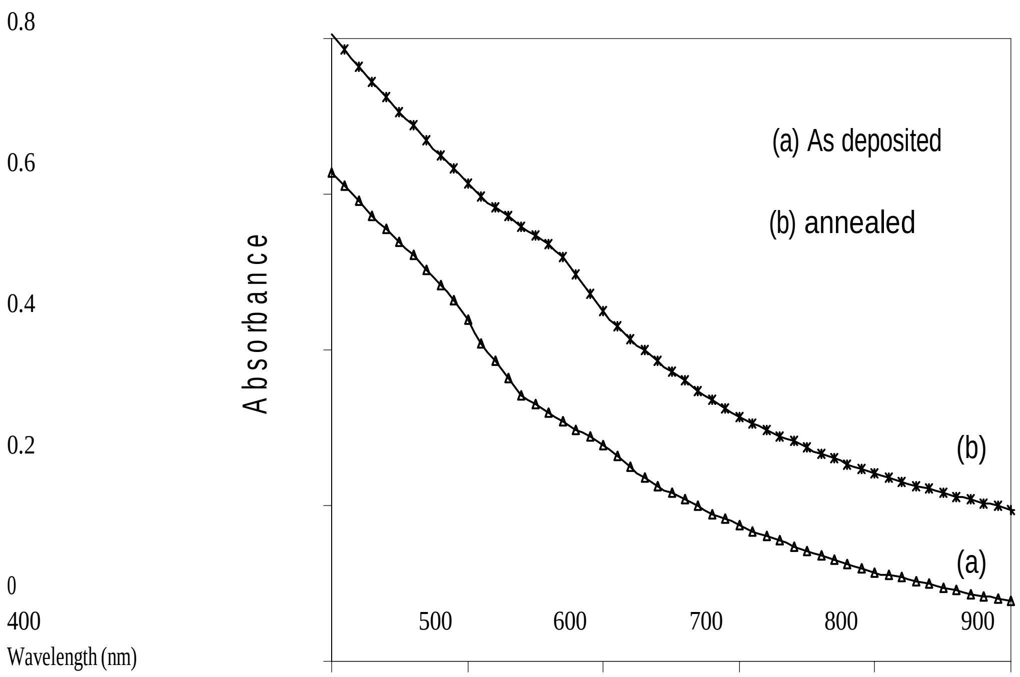
0.8
0.6
0.4
0.2
0
400
500
600
700
800
900
Wavelength (nm)
Absorbance
(a) As deposited
(b) annealed
(b)
(a)

Fig 4:

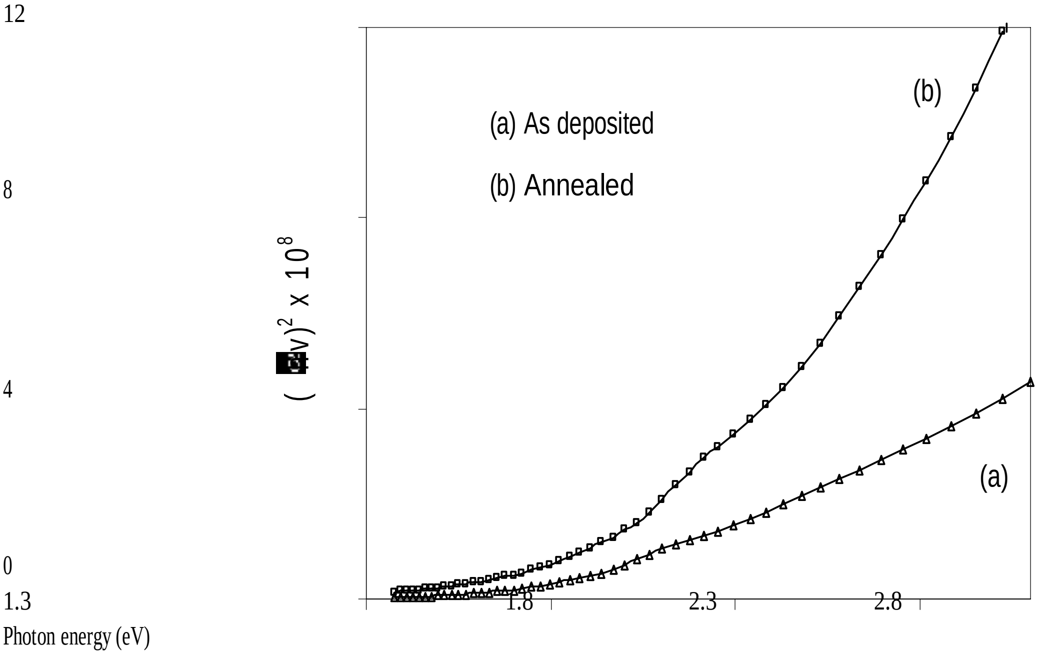
12
8
4
0
1.3
Photon energy (eV)
(a) As deposited
(b) Annealed
(b)
(a)
1.8
2.3
2.8

Fig 5:

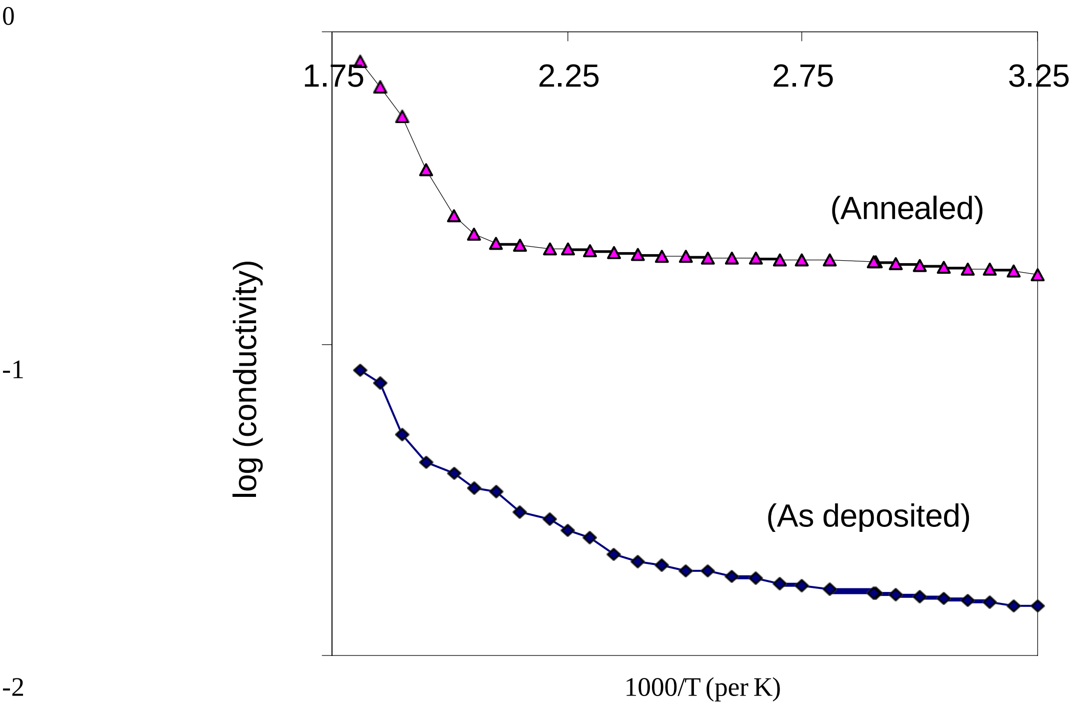
0
-1
-2
1.75
2.25
2.75
3.25
(Annealed)
(As deposited)
log (conductivity)
1000/T (per K)

Fig 6: