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Effect of silver doping on Nanocrystalline $CdIn_2Se_4$ thin films

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ABSTRACT: *$CdIn_2Se_4$: Ag thin films with a variable composition (0–1.0 mol% indium) have been grown on a non-conducting glass substrate by chemical bath deposition method. The effect of doping has been investigated. The color of a film was found to be darkening with increase in the concentration of indium. X-ray diffraction, optical absorption and morphological techniques were used to characterize the films. The X-ray diffraction study indicates the crystalline nature in single cubic phase over whole range of composition. Analysis of absorption spectra gave direct type of band gap, the magnitude of which varies non-linearly as the silver content in the film increases. The promising features observed are the enchantment in crystallinity, grain size, and decrease in band gap, up to 0.1 mol%.*

KEYWORDS: *Thin films; Doping; Chemical bath deposition; XRD and SEM*

I. INTRODUCTION

Cadmium indium selenide ($CdIn_2Se_4$) is the semiconducting chalcogenide of the types $A^{III}B^{III}X_4$ where A =Cd, Zn, Cr, Hg, B= Ga and In and X= S, Se or Te. The interest in the ternary chalcogenide has been increased greatly in the last decade due to their interesting tailored properties and potential applications in solar energy conversion, nonlinear optics and optoelectronics devices [1-8]. Thin film of $CdIn_2Se_4$ has been prepared vacuum evaporation, electrodeposition and slurry pasting techniques [9, 10]. Chemical bath deposition method is an alternative, low cost method which can operate low processing temperature and give large deposition area [11]. The electrical and optical properties of semiconductor are strongly influence by doping process, which provides the basis for tailoring the desired carrier concentration and consequently, the absorption, emission and transport properties as well as when the density of n-type or p-type doping become sufficiently high, the impurity merge with conduction and valance band cause the formation of band tail and band gap shrinkage [12-14].

In this paper deals with successful room temperature deposition of $CdIn_2Se_4$: Ag thin films by chemical bath deposition method. The structural, morphological and optical properties are studied respect to doping concentration.

II. EXPERIMENTAL

2.1 Synthesis of Nanocrystalline $CdIn_2Se_4$: Ag thin films

The deposition of $CdIn_2Se_4$:Ag thin films was made in a reactive solution obtained by mixing of, 5 ml cadmium sulphate octahydrate (0.02M), 3 ml tartaric acid (1M), 5ml hydrazine hydrate (2%) and 10 ml indium trichloride (0.02M), 20ml sodium selenosulphate (0.02M). The varying concentration of silver from 0. 01 to 1.0 mol % was used. The source of silver used was silver nitrate. To obtain Ag-doped $CdIn_2Se_4$ thin films, the calculated volume of $AgNO_3$ solution was directly added to the reaction bath. Sodium selenosulphate was prepared by the following the method reported earlier. All the chemicals used were of AR grade. The total volume of the reaction mixture was made to 150 ml by adding double distilled water. The beaker containing reactive solution was transferred to ice bath of 278 K. The pH was found to be 11.80± 0.05. Four-glass substrate were kept vertically in a reaction mixture and rotated with a speed of 55±2 rpm. The temperature of the solution was allowed to rise slowly to room temperatures. After the deposition, for 240 min. the substrates were taken out of the bath, rinsed with distilled water, dried in air and kept in desiccator.

2.2 Characterization of Nanocrystalline $CdIn_2Se_4$: Ag thin films

X-ray diffraction study of $CdIn_2Se_4$: Ag film was carried out in the range of the diffraction angle 10-80^0 with Cu $K\alpha_1$ radiation using Philips PW-1710 diffractometer (λ=1.54056Å). The current was noted at different temperatures. Maintaining a temperature gradient along the length of a film performed thermoelectric power measurements and the potential difference between the points separated by a 1cm was recorded with a digital microvoltmeter. A calibrated thermocouple probe (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 400-1100 nm by using a Hitachi-330 (Japan) UV-VIS-NIR double beam spectrophotometer at room

temperature. Placing 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 model was used for the scanning electron microscope (SEM).

III. RESULT AND DISCUSSION

3.1 Structural Investigation

X-ray diffraction (XRD) spectra of annealed $CdIn_2Se_4$: Ag thin films deposited on glass substrate are shown in Fig.1. The spectrum for $CdIn_2Se_4$ (JCPDS data card No. 08-0267) was used for identification purpose. The XRD pattern shows a large number of peaks indicating that the films are polycrystalline in nature. The analysis of spectrum indicated that the films are having tetragonal structure. The most intense reflection observed for all the thin films were originating from (111) plane. Along with (111) plane, (102) (202) (113) planes are also observed. The peak intensity and crystallinity of the films were found to increase upto 0.1 mol % of silver. The average crystallite size was calculated by resolving the highest intensity peak (111). The average crystallite size was determined by using Scherrer's formula. Upto 0.1 mol% Ag, the particle size increases from 203 to 248 Å, thereafter decreases upto 193Å for 1.0 mol% Ag concentration as shown in Table No.1.

3.2 Optical properties

The optical properties of as deposited samples have been studied in the wavelength range from 400 to 1000 nm without considering losses due to reflection and scattering at room temperature. The absorption spectra are used to calculate absorption coefficient, optical band gap and type of transition. The absorption spectra of representative silver doped films are shown in Fig.2 for all the compositions, the value of absorption coefficient is high (α x 10^4 cm^{-1}). The value of absorption coefficient is depends upon radiation energy as well as composition of the film. The data were systematically studied in the vicinity of the absorption edge on the basis of three-dimensional model. The interpretation of the results can be easily done with the help of formula derived for three-dimensional crystal. The simplest form of equations obeyed near and above absorption edge is; [15]

$$\alpha h\upsilon = A(h\upsilon - Eg)^n \qquad \text{-------3.1}$$

Where the symbols have their usual meaning. Upto 0.1 mole % Ag, the absorption is edge shifted towards higher wavelength. This is due to filling of low lying energy level by conduction electron and segregation of the impurity along the grain boundary [16]. A plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ should be a straight line whose intercept to the x-axis gives the optical band gap. It is observed that the band gap decreases from 1.98 eV to 1.61 eV as the Silver concentration increases upto 0.1 mol %. Above 0.1 mol % the band gap increases from 1.72 to 1.83 eV.

3.3 Morphological Properties

The SEM micrographs of $CdIn_2Se_4$: Ag samples are shown in Fig.3 at 10000X magnification. $CdIn_2Se_4$: Ag thin films are seen to be homogenous, without cracks or pinhole and well cover the glass substrate. The presence of fine background is an indication of one-step growth by multiple nucleations. Upto 0.1 mol% Ag, the grain size increases from 210 to 253 Å, thereafter decreases upto 201Å for 1.0 mol% Ag concentration. The grain size calculated from SEM was found to tally with those obtained using the XRD.

IV. CONCLUSION

Silver doped $CdIn_2Se_4$ thin films have been deposited using chemical bath deposition method using tartarate bath at 298 K. The silver donor atoms were found to dissolve substitutionally in the lattice of $CdIn_2Se_4$ upto a certain range of doping concentration. The films grow highly oriented in the Tetragonal phase. The crystallinity and particle size were found to increases with silver concentration upto 0.1 mol % whereas for higher values of silver, the material shows decreased crystallinity. The grain size calculated by SEM tallies with the particle size calculated by XRD. The absorption study shows presence of direct band gap transition. The band gap decreases from 1.98 to 1.61 eV as the doping concentration increases from 0.0 to 0.1 mol % whereas for higher values of silver, the band gap increases.

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Table Captions:

Table 1: Crystallographic parameters of $CdIn_2Se_4$: Ag thin films

Figure Captions:

Fig. 1: XRD pattern of $CdIn_2Se_4$: Ag thin film
Fig. 2: SEM micrographs of $CdIn_2Se_4$: Ag thin film
Fig. 3: Absorption spectrum of $CdIn_2Se_4$: Ag thin film

Table 1: Crystallographic parameters of $CdIn_2Se_4$: Ag thin films

Mole % of Ag in $CdIn_2Se_4$	Observed 'd' values (Å)	Std. 'd' values(Å) $CdIn_2Se_4$	hkl	Grain Size(Å)	
				XRD	***SEM***
0.0	3.4405 2.6230 2.0650 1.7115	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	203	210
0.01	3.5428 2.9420 2.6425 2.1008	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	207	215
0.05	3.4768 2.9761 2.6347 2.1115	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	217	217
0.1	3.5024 2.9340 2.6295 2.1426	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	248	253
0.5	3.4875 2.9297 2.6315 2.1380	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	201	207
1.0	3.4650 2.9315 2.6310 2.1310	3.3700 2.9200 2.6100 2.0600 1.3340	111 102 202 113	193	201

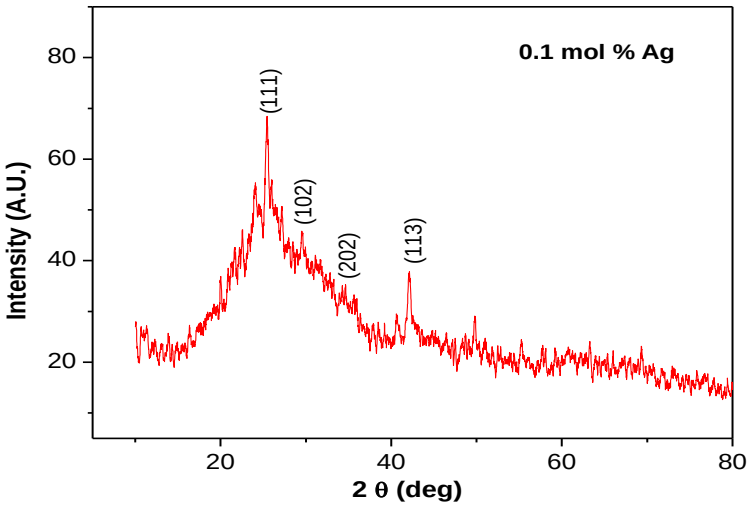

Fig. 1

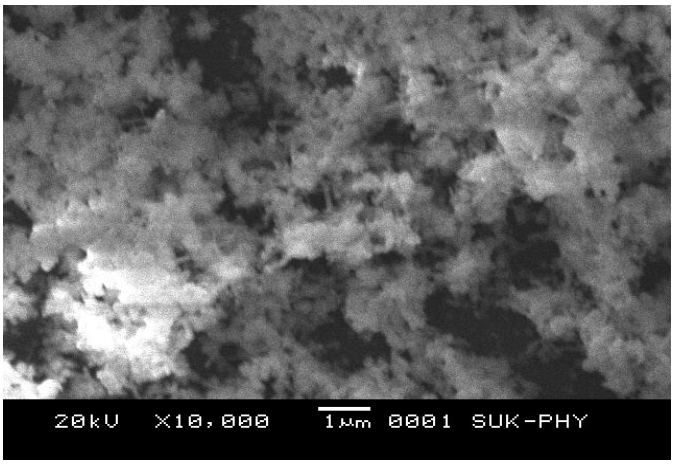

Fig. 2

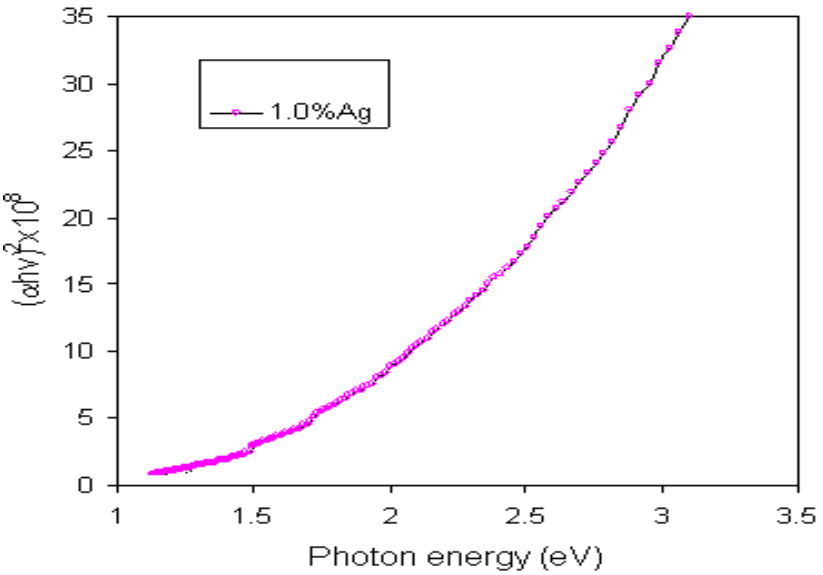

Fig.3