

Synthesis, Growth and Characterization of Rare Earth Doped (CdZnS) Thin Films

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ABSTRACT: Cadmium Zinc Sulphide (CdZnS) thin film grown, with and without doping on commercial glass substrate using chemical bath deposition technique. The bath temperature was kept at 70°C. The pH of the solution was maintained around 11. Two different dopant viz. SmO₃ and EuO₃ were used for doping. The thin films so obtained were characterized using XRD, UV-Spectrophotometer and Two probe methods. The XRD pattern shows nano crystalline phase with cubic and hexagonal structure. Doped film shows the broadening peaks in XRD spectra. Scherrer formula gives particle size around 9.3nm. particle size decreasing on doping. For undoped CdZnS thin film, Optical band gap of comes out to be 2.5 eV, whereas band gap for rare earth doped CdZnS thin film was 2.4 eV, and 2.42 eV, respectively. Thus doping decreases the band gap. Photocurrent show linear increase with applied voltage. Moreover photocurrent is larger than the dark current for the same voltage.

KEYWORDS: Thin films, Photocurrent, CBD, XRD.

I. INTRODUCTION

Energy band gap of CdZnS is larger than CdS. It has been widely used as a wide band gap window material in hetero-junction photovoltaic solar cells and photoconductive devices. Various methods, such as spray pyrolysis, sputtering, Electro deposition, Vacuum evaporation, Chemical vapour deposition (CVD) and Chemical bath deposition (CBD) are frequently used for preparing thin films of II-VI group compounds. In the present study, Cd_{1-x}Zn_xS thin films by varying Zn content was prepared using modified CBD technique. The effects of doping on structural, optical and photo conducting properties were investigated. Europium and Samarium Oxide were used as dopant. The dopant was mixed in starting solutions prepared for growing thin films of CdZnS.

II. EXPERIMENTAL DETAILS

For preparing thin films of CdZnS commercial quality microscopic glass slides having dimension 24X75 mm were used as substrates. Complex chemical bath was prepared by mixing 25 ml of 1M Cadmium acetate solution with TEA in a beaker. Desired volume of 1M solution of Zinc acetate was added to this solution. The volume of zinc acetate to be added was different for different doping concentrations. Simultaneously 30% aqueous ammonia and 7ml of Thiourea (1M) was added drop by drop to this solution. The quantity of ammonia to be added was monitored by measuring the pH of resulting solution. The PH of solution was maintained around 11. The deposition was made by holding the cleaned glass substrates vertically against the wall of beaker containing the mixture solution. The deposition was made at temperature 70°C in a constant temperature water bath. The whole apparatus is left undisturbed for 1 hour till the deposition completed. To carry out sensitization definite volumes of 0.01M solutions of Europium oxide, and Samarium oxide respectively, were added to original mixture separately and then depositions were made. After the depositions was completed on the substrates the films were cleaned with double distilled water and dried in open atmosphere at room temperature.

III. RESULTS AND DISCUSSION

A. X-Rays Diffraction

XRDs were recorded using diffractometer available at RRCAT Indore. Cu -K_α radiation of wavelength 1.54Å⁰ was used to record XRD. XRD results show the presence of cubic and hexagonal phase in CdZnS thin films. The data were

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recorded by scanning 2θ from 0° to 60° . The peaks are detected at $2\theta = 24.86, 26.72, 28.56$ and 30.83 , respectively. They were ascribed due to (100), (002), (101) plane of hexagonal CdS structure, and (200) plane of cubic structure. A comparison between observed and standard d-value for the CdZnS thin films are shown in table-1. The particle sizes of the films were determined using Debye-Scherrer formula,

$$D_{hkl} = K\lambda / \beta \cos \theta$$

Where k is a constant and taken to be 0.94, β is the full width half maxima (FWHM) of the XRD peaks at 2θ . XRD was recorded with an incident wavelength $\lambda (=1.54\text{\AA})$. Peaks are having width indicates poly-crystalline nature of these films. Again broadening of the peaks indicates the increase in full width half maxim and decrease in particle size. The reduction of the grain size is an indication of change in crystal structure from hexagonal to cubic.

TABLE I
XRD DATA FOR CdZnS THIN FILMS USING Cu-K α

S.N.	Standard d-value	Observed d-value	hkl plane	2θ
1	3.380	3.585	100	24.86
2	3.341	3.343	002	26.72
3	3.131	3.132	101	28.56
4	2.907	2.906	200	30.83

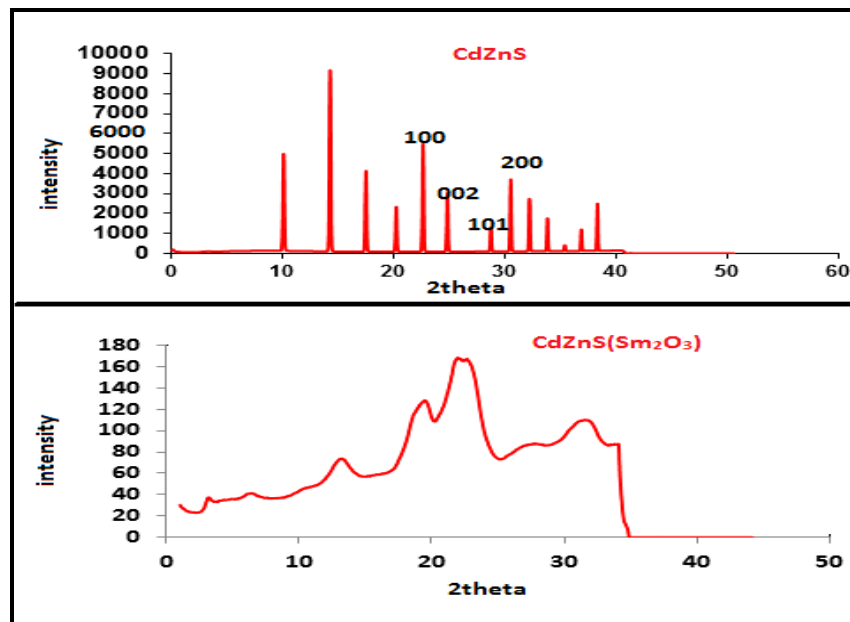


Fig.1(A),(B) XRD Pattern of CdZnS and doped CdZnS(Sm₂O₃) Thin films

B. Optical Studies

The optical band gap of undoped and doped, CdZnS thin films was measured using UV-VIS spectrophotometer. Fig. 1.3 show UV-VIS transmission spectra for both undoped and doped CdZnS film in the wavelength range 350 to 900 nm. Plots of $(\alpha h\nu)^2$ with photon energy $h\nu$ are shown in fig. Using the plots optical band gap of CdZnS was calculated. For undoped films it comes out to be 2.5eV whereas for doped films it is 2.4eV, 2.42eV, respectively. Thus the band gap of CdZnS thin film decreases on doping.

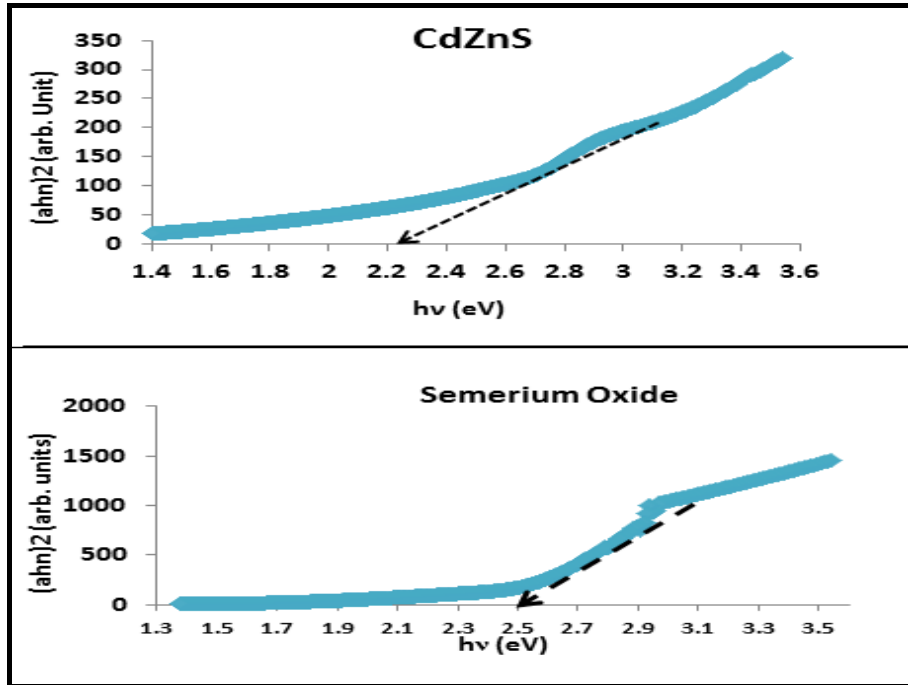


Fig.2(A),2(B) plots of $(ah\nu)^2$ vs $h\nu$ CdZnS and doped CdZnS(Sm₂O₃) films

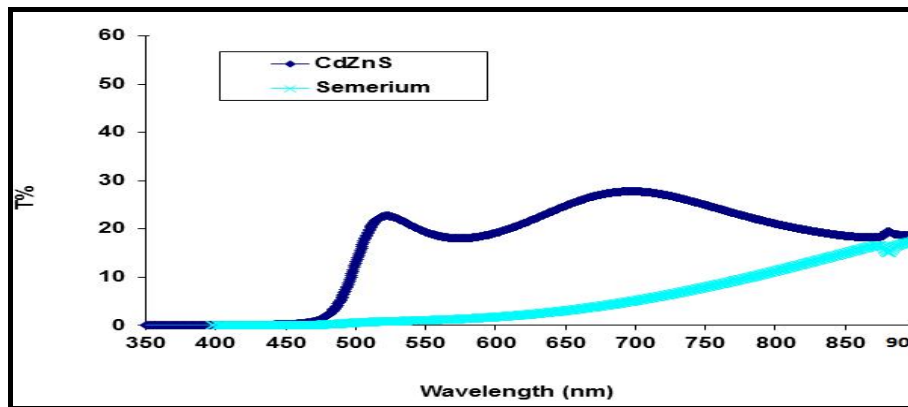


Fig.2(C) Transmission spectra of CdZnS and doped CdZnS (Sm₂O₃) films

C. Photoconductivity

Dark and photo conducting currents was measured by making silver contacts on the surface of films. I-V characteristic was drawn under dark and photo exposed conditions. The result shows that the CdZnS films are highly resistive in nature. At room temperature the current increases with an increase in applied voltage. Moreover, the photocurrent is higher than dark current for the same applied voltage in all the samples. Thus at the films are photo conducting in nature. The plots show that the nature of variation of photo conducting current is different in different samples.

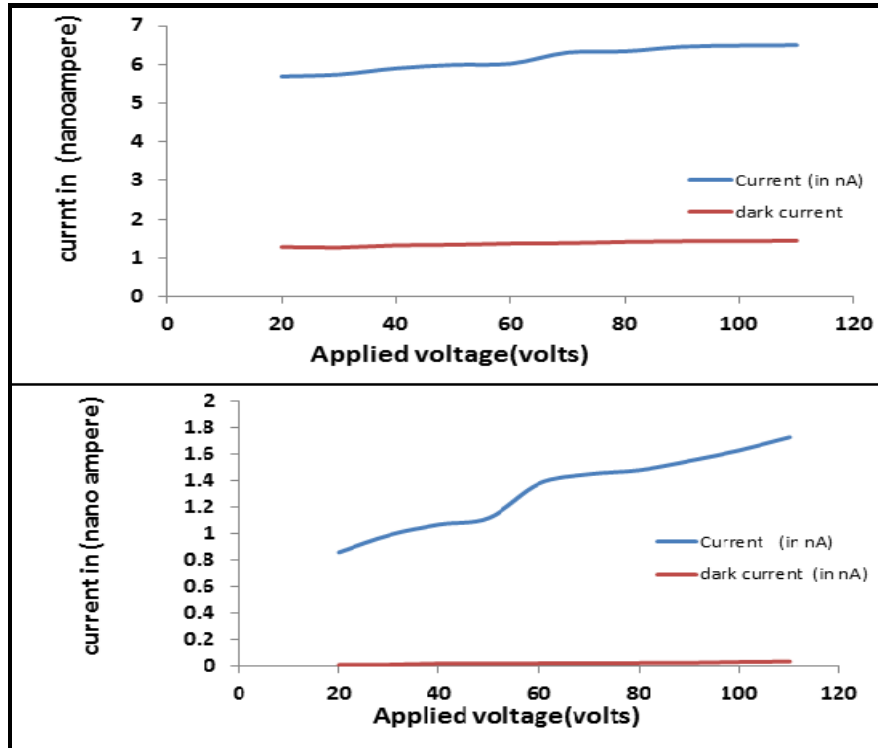


Fig. 3(a), (b) I-V characteristics of CdZnS and doped CdZnS (Sm₂O₃) films

IV. THICKNESS OF FILMS

This method depends on the increase of the weight of a film due to its mass increase after deposition and if we know the density of the film material and deposited area, then the film thickness (d) can be evaluated by relation, -

$$d = \Delta w / \rho A$$

Where, Δw = weight difference of film
 ρ = density of deposited material
 A = deposited area

The increase in film weight can be measured by a suitable microbalance. In the present work the thickness of the films measured are as follows;

S.N.	Sample	Dipping time (hrs)	Thickness (μm)
1	CdZnS	5 hrs.	18 μm
2	CdZnS(Sm ₂ O ₃)	6hrs.	19 μm

V. CONCLUSION

Doped and undoped thin films are prepared by chemical bath deposition (CBD). The grown films were characterized using (XRD), UV-VIS spectrophotometer and two probe methods. XRD confirms that undoped CdZnS film is poly

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crystalline in nature. Broad peaks on doping indicate the decrease in particle size on doping. Optical studies confirm good quality of grown material. Doping results decrease in optical band gap. Photo conducting studies show photocurrent to be larger than the dark current for the same voltage.

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