

Photovoltaic Characteristics Of Chemical Bath Deposition Grown Eu-Cds/Eu-Pbs Fabricated Solar Cells – Enhancement Studies

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Abstract: In the enhancement of photovoltaic properties of Eu: CdS/PbS solar cell plays the vital role in the present innovative approach. With the advent of nanocrystalline based approach problems like performance degradation due to Pb diffusion in CdS/PbS solar cells can be solved. In this study an effort has been made to improve the performance of CdS/PdS thin film based devices, by doping with rare earth Eu. In this study undoped and Pr doped CdS thin films were prepared using Chemical Bath deposition and characterized for structural, optical and Morphological properties on pre cleaned glass and ITO coated glass plates. The PbS thin films were prepared system by chemical bath deposition over the CdS nano thin film layers grown over ITO glass plates and their photovoltaic properties were studied using Photocurrent–voltage measurements at AM 1.5 at an illumination of 100 mW/cm². The results are reported. The increase of Eu concentration in the CdS layer has produced considerable enhancement in the microstructural and optical properties leading to performance efficiency. The possible mechanism are also discussed.

Index Terms: CdS thin film, europium doping, Eu doped CdS/PbS, structural, optical, photovoltaic properties

1. INTRODUCTION

Cadmium sulfide (CdS) is a well-known II-VI group semiconductor of much interest with high photoconductivity in the visible region, high electron affinity. The favorable electronic and electronic and optoelectronic properties of CdS nano thin films made this system interesting for sensors, solar cells, photo detectors, optical wave guides, nonlinear optical devices, and other opto electronic devices [1-3]. Though CdS is one of the most studied materials from past decades, its application as n-type window layer for high efficiency thin film hetero junction solar cells based on CdTe and Cu (InGa)Se₂ (CIGS offer many edges over other candidates of II VI family. CdS/PbS solar cells had shown significant promise, but the problem of lead diffusion into and CdS layer led to a long-term performance degradation and ultimately this hetero junction lost interest. However, the advent of nanocrystalline materials based approaches involving milder processing conditions, this problem can be easily avoided [5]. To improve the performance and efficiency of such thin film based systems, the properties of the layers should be modified. It has been experimentally proved that doping can be used as one of the possible ways to improve the electronic and optoelectronic properties of metal chalcogenide thin films. Many researchers have reported an enhancement in the optoelectronic properties of CdS thin film layers by doping with some cationic (In, Ni, Co) and anionic (Cl, Br) elements [6-10]. The photo generated electron–hole pairs are separated in the depletion region of the hetero junction creating a potential across the junction. If the junction is degraded then a stable performance could not be achieved. Currently efforts have been devoted to the preparation of high quality CdS and PdS nanostructured thin films. Few

low cost chemical techniques such as spray pyrolysis [12], successive ion layer adsorption and reaction (SILAR) [13], electrochemical growth method [14], and chemical bath deposition (CBD) [15] have exhibited amazing potential for preparing such thin films offering tailoring of surface properties. Among all of these methods, CBD is a simple technique to grow thin films that are uniform and can be easily scaled to industrial processings with ease. In this work undoped and Pr doped CdS thin films and PbS thin films were grown over glass substrates and their micro structural and absorption properties were studied and reported. For the preparation of hetero junction solar cells CdS were grown over ITO substrates of sheet resistance 10 ohms per square and the PbS thin films were grown over the CdS layers using CBD and their photovoltaic properties are reported.

2 PROCEDURE FOR EXPERIMENTATION

2.1 Chemicals Required

The typical CBD growth conditions of the CdS layer involves Cadmium Chloride (CdCl₂ 0.005 mol/L) and Ammonium Chloride (NH₄Cl) in 100 ml deionized water at room temperature. The solution mixture was stirred and heated to 70 °C. After heating the solution for 5 minutes 0.04 mol/L of liquid ammonia solution was added and stirred for 5 minutes. To this solution 0.03 mol/L of thiourea was added subsequently and stirred continuously at the same temperature. This solution serves as the CBD bath. Pre cleaned glass slides were used as substrates and were placed vertically in the CBD bath for a period of 60 minutes. After the immersion of substrate for desirable time they were removed and cleaned with deionized water. The liquid ammonia combines with Cd²⁺ ions and forms Cd(NH₃)₄²⁺ complex which releases Cd²⁺ ions steadily. The thiourea releases S²⁻ ions and acts as a sulfur source. These ions combine to form CdS layers over the surface provided. For the preparation of 1% and 3% Eu-doped CdS thin films the addition of 1% and 3% (0.005 mol/L) Europium Chloride to the CBD bath before adding liquid ammonia and the experiment was repeated. For the preparation of solar cells, PbS thin film was deposited over

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CdS layer formed over ITO substrates (sheet resistance of ITO is 10 Ω /sq). A 50 ml solution of 0.15 M lead nitrate [Pb(NO₃)₂] and 0.1 M thiourea [SC(NH₂)₂] was used for the deposition of PbS. The alkalinity of the solution was set using 0.5 M sodium hydroxide [NaOH]. The CdS coated ITO substrate was vertically immersed into the solution and the beaker containing the reactive solution was kept in a water bath maintained at 60 °C for 1 hr. 2.2 Final Stage

2.2 Characterization

Thickness of the prepared films was measured using an Alpha-step surface profiler. The structural properties of the grown layers were studied using X'pert PRO (PANalytical) X ray diffractometer employing CuK α radiation ($k = 0.15405$ nm) in the 2θ range of 10–80°. Morphological studies were undertaken using Hitachi (S-3000H) scanning electron microscope. The optical studies were performed using Perkin Elmer Lambda 35 spectrophotometer. For the solar cell studies the Photocurrent–voltage measurements were performed using a Keithley 4200 semiconductor parameter analyzer under AM1.5G illumination at 100 mW/cm².

3 RESULTS AND DISCUSSION

3.1 X-ray and Structural analysis

The X-ray diffraction patterns of undoped CdS, Nd doped CdS and PbS films respectively are presented in figure 1. The diffraction peak observed at 26.58° corresponds to the (002) plane of CdS wurtzite structure and matches the JCPDS card no. 41-1049. The XRD pattern of PbS also shows three characteristics peaks corresponding to (1 1 1), (2 0 0) and (2 2 0) orientations, in agreement with the standard JCPDS card No. 00-0050592 of cubic rock salt (NaCl) type structure [16]. Using the usual expressions the crystallite size, micro strain and the stacking fault probability was calculated by measuring the peak shift with the standard value [17]. The intensity of the prominent peak (002) is found to increase as the film doping concentration increases. Structural parameters of the CdS and PbS thin films were also calculated and shown in Table 1. As the CdS film thickness increases with increase of Pr doping concentration, the reduction in microstrain and dislocation density were observed which might have lead to the relaxation of the stress in the films. This relaxation produces freak between the substrate and the layer as the Pr doping concentration increases and hence the stacking fault decreases as given in the Table 2.

3.2 Morphological and compositional analysis

Figure 2 (a-c) shows the morphology of Eu: CdS thin films. These SEM micrographs clearly reveal the homogeneity of the CdS thin films. The surface morphology is found to be affected by the Eu doping slightly. It is also apparent from the SEM image shown in Fig. 2(a) that the undoped film has morphology formed using nearly spherical grains. Figures 2(b-c) show the SEM images of the films prepared after 1% Eu doping which indicate uniform covering of the substrate with the spherical shaped grains. At 3% Eu doping concentration also the morphology do not change and the uniform coverage of the grains are observed revealing the high quality of the nano thin film layers facilitating the mobility and diffusion of surface atoms [18].

3.3 Compositional analysis (EDX)

The elemental composition of chemical bath deposited CdS thin films were also studied using the EDX. Figure 2 (d, e) shows the typical EDX spectra of the undoped and 3% Eu-doped CdS thin films. The spectrum shows Cd and S peaks, for undoped and Eu peak confirming the presence of Cadmium (Cd), sulfur (S) and (Eu) europium in the doped sample. The films showed nearly stoichiometric composition. The EDX spectrum showed extra peaks corresponding to substrate.

3.4 Optical properties

The changes in optical transmittance (T) with the incident wavelength (λ) for the CdS thin films prepared using different Pr doping concentration are study using the transmission spectra shown in Fig. 3 in the wavelength region 400–1100 nm. It is clear that all films are highly transparent in the visible wavelength range and showed sharp ultraviolet absorption edge at approximately near 540 nm. The presence of multiple interference fringes in the transmittance spectrum denotes that the surface is smooth. In Fig. 3 the inset shows transmittance spectrum of PbS film and it shows a value of transmittance around 35%. The optical absorption spectra of undoped and Eu doped thin films are also recorded at room temperature from 400 to 1000 nm as shown in Fig. 4. This absorption spectrum shows that the absorption is high in the blue region of visible spectrum. The Fig. 4 inset shows absorption spectrum of PbS film and it shows a higher absorption in the visible region. Using the usual Tauc's relation the band gap was evaluated. Figure 5 shows the plot of $h\nu$ vs $(\alpha h\nu)^2$ of the films deposited at different Eu doping concentration. The calculated energy gap (E_g) is found to decrease from 2.48 eV to 2.43 eV with the increase of Pr doping concentration from 0% to 3%, showing the crystallinity improvement with the densely packing of atoms [19]. The inset of figure 5 shows the direct energy gap of PbS thin film deposited by chemical bath deposition method. The obtained band gap value of PbS is 1.54 eV which agrees with those reported [20]. Optical constants of CdS thin films such as refractive index (n) and extinction coefficient (k) were calculate using the reported relations [18]. Fig. 6 and Fig. 7 show the variation of both n and k of CdS films deposited with different Eu doping concentration. The refractive index of the films decreased with the increase of doping concentration. The increase of Eu may impede the propagation of light through the film [21]. The extinction coefficient of the films varied in the range from 0.24 to 0.30 [22,23,24].

5 FIGURES AND TABLES

Table 1 Thickness and structural parameters of CdS, Eu-CdS and PbS thin films

Eu doping in CdS film	Thickness (μ m)	Crystal lite size (nm)	Dislocati on density ($\delta \times 10^{15}$ lines. m ⁻²)	Micro Strain ($\epsilon \times 10^{-3}$ lines ⁻¹ . m ⁻¹)	Stacking fault probabilit y (α) $\times 10^{-4}$
0%	0.59	29	1.27	4.3	2.9
1%	0.61	30	1.05	3.9	2.4
3%	0.68	36	0.78	3.2	1.8
PbS	0.75	41	0.54	2.3	1.3

Table 2 Parameters of the solar cell structures in Fig. 8

parameters	Eu doping in CdS film		
	Eu 0%	Eu 1%	Eu 3%
$V_{oc}(V)$	0.33	0.32	0.33
$I_{sc} (mA/cm^2)$	6.96	7.91	8.72
FF	0.34	0.36	0.38
η (%)	1.16	1.32	1.66

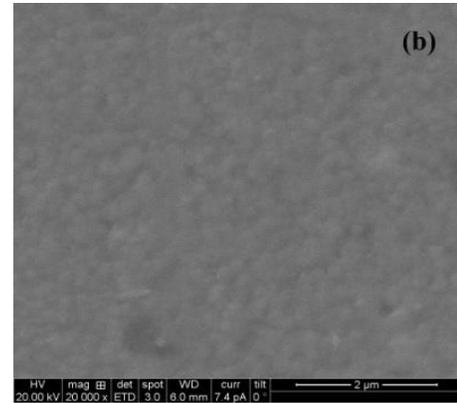


Figure 2 (b) SEM images of CdS thin films 0%

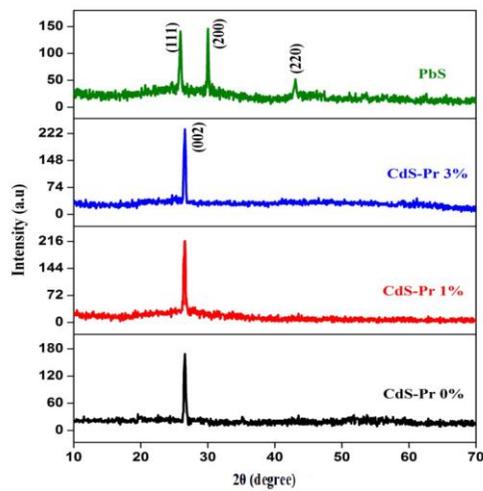


Figure 1 XRD patterns of Cds and PbS thin films

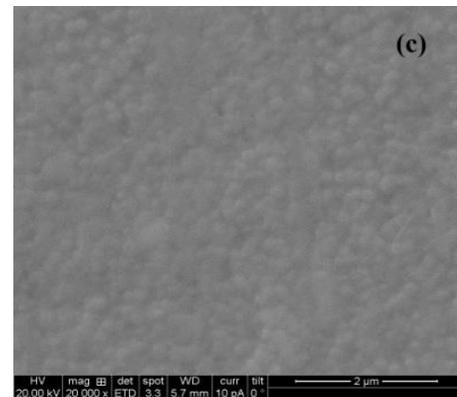


Figure 2 (c) 3% Eu doped CdS

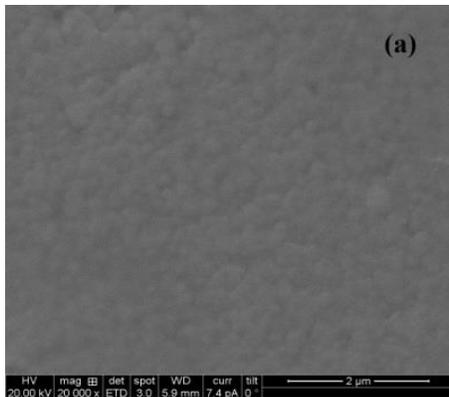


Figure 2 (a) SEM images of CdS thin films undoped 0%

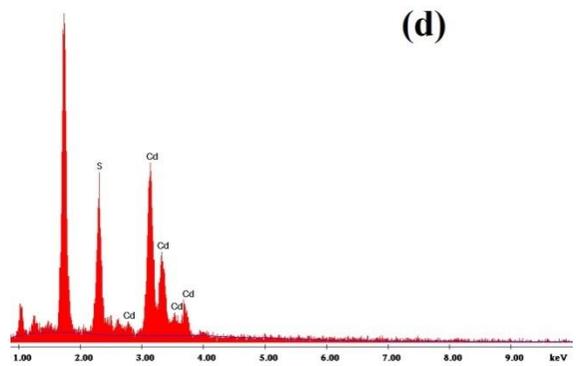


Figure 2 (d) 0% Eu doped EDX spectrum

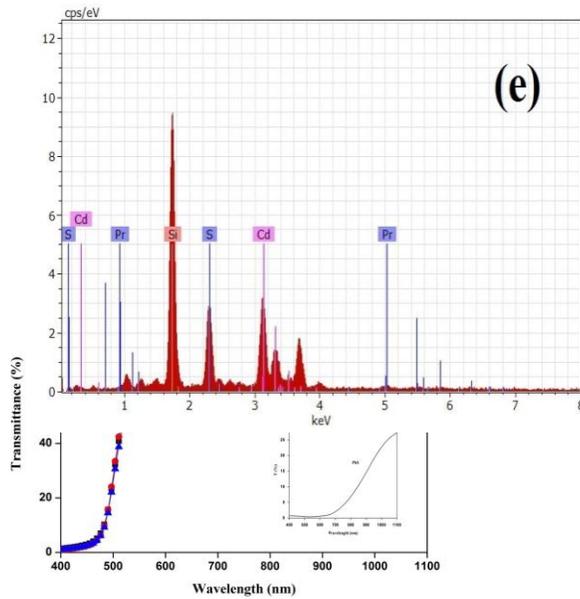


Fig.3 Transmittance of Eu:CdS thin film

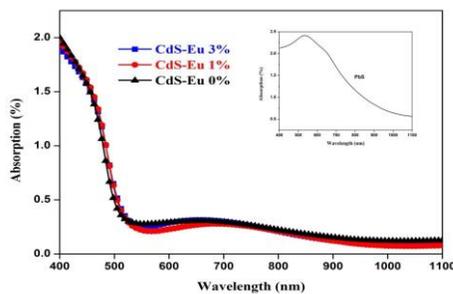


Fig.4 Absorption spectra of Eu:CdS thin film

Fig.4 Inset shows Absorption spectra of PbS thin film. The optical absorption spectra of undoped and Eu doped thin films are recorded at room temperature from 400 to 1000 nm as shown in Fig. 4. This absorption spectrum shows that the absorption is high in the blue region of visible spectrum. The inset Fig. 4 shows absorption spectrum of PbS film and it shows a higher absorption in the visible region. Tauc's relation (relation between absorbance and band gap) describes the dependence of optical density with wavelength and band gap as well as nature of optical transition [22].

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \dots\dots\dots (5)$$

Here, A is the characteristics independent constant, n is a constant number that depends on the nature or type of optical transition, hν is the photon energy, E_g is the energy band gap and α is the absorption coefficient. The constant number (n) has value 1/2 for direct transition and direct band gap optical materials like CdS [13, 22]. The E_g values of undoped and Eu doped CdS films determined from the Fig. 5 are found to be 2.47 and 2.5 eV respectively. These values of CdS band

Fig. 3 the inset shows transmittance spectrum of PbS film and it shows a value of transmittance around 25%.

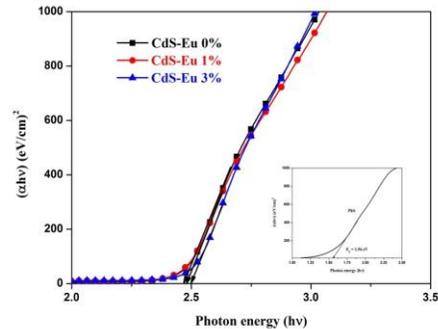


Fig.5 Energy Band gap of Eu: CdS thin film

Fig.5 Inset shows Energy Band gap of PbS thin film. The gap is found to be in excellent agreement with the reported values in the literatures [23, 24]. Figure 5 inset shows the direct energy gap of PbS thin film deposited by nebulizer spray technique. The obtained band gap value of PbS is 1.56eV which is perfectly matched with band gap value reported for PbS [25]. The variation of band gap between the Eu doped and undoped CdS thin films is small in the present study. The optical constants of undoped and Eu doped CdS thin films were evaluated using the following relations [26],

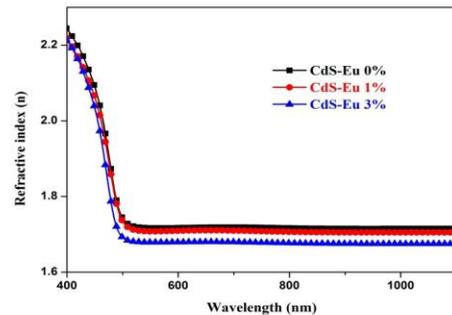


Fig.6 Refractive Index Variation of Eu:CdS thin film

$$n^2 = N + (N^2 - n_a^2 n_s^2)^{1/2} \dots\dots\dots (6)$$

where,

$$N = \frac{(n_a + n_s)}{2} + 2n_a n_s T$$

n_a, n_s and n are the refractive indices of air, substrate, and the CdS films, respectively. T is the transmittance value at a particular wavelength.

$$k = \frac{\alpha \lambda}{4\pi} \dots\dots\dots (7)$$

Where, α, λ, k are the absorption coefficient, wavelength, and the extinction coefficient, respectively. Fig. 6 and Fig.7 show the variation of both n and k of CdS films deposited with different doping concentration. The refractive index of the films decreased with the increase of

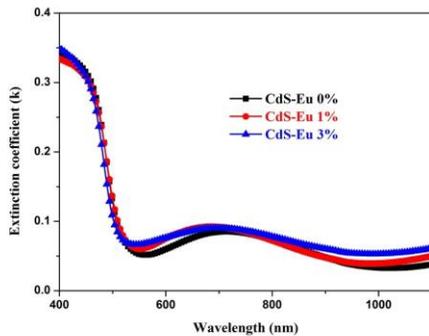


Fig.7 Extinction Coefficient of Eu:CdS thin film

doping concentration. The extinction coefficient of the films varied in the range from 0.33 to 0.35. The value of refractive index and extinction coefficient of CdS are found to be in excellent agreement with reported in the literatures [13, 22,23,24].

3.4. Photovoltaic studies

The CdS based PV cells were fabricated with undoped and Eu doped CdS on ITO coated glass substrate by CBD method. The photovoltaic performances of the ITO/Eu-CdS/PbS/Al solar cells are shown in Figure 8. The open-circuit voltage (V_{oc}) is found to increase from 0.31 to 0.36 V and the short circuit current density (J_{sc}) is increased from 6.83 to 7.72 mA/cm^2 with the increase of doping concentration. These results revealed that as the doping concentration increases the open circuit voltage also increase.

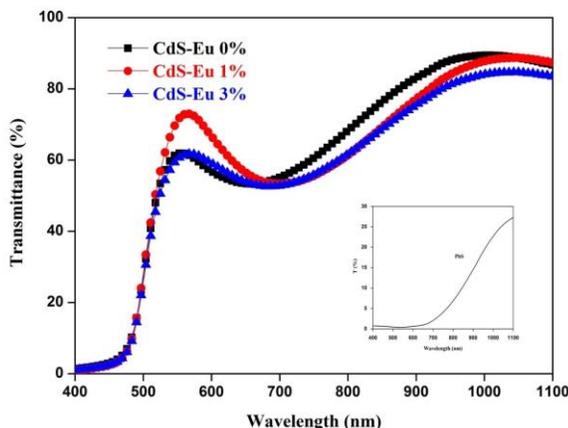


Fig.8. I-V Performances for Eu:CdS/PbS

4 CONCLUSION

Eu-CdS, PbS and CdS/PbS heterostructures were successfully prepared using simple chemical bath deposition method. Europium doping to n-CdS layer has shown improved photovoltaic properties of the ITO/n-Eu-CdS/PbS/Al heterostructure. XRD confirmed the formation of hexagonal phase with a preferred orientation in the (0 0 2) plane. The PbS film showed cubic rock salt structure with (200) preferred orientation. Crystallite size of the Pr doped CdS is found to increase with Eu concentration, and it is found to be 37 nm for the 3% Eu concentration. The surface uniformity was excellent for all the films and Eu doping retained surface uniformity and improved mobility for photo generated carriers. Optical studies

revealed that the optical transmittance and energy band gap decreased with the increase of Eu doping concentration. The solar conversion efficiency of the fabricated solar cells is found to increase from 1.14 up to 1.66 %, as Eu doping concentration is increased from 0% to 3% and the possible mechanism are discussed.

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