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Thin Film and Photo-Electrochemical Studies of ZnSe and CdZnSe Alloys

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Abstract: **The *Abstract:* In these studies, pure ZnSe and ternary CdZnSe thin films were deposited onto glass and stainless- steel substrate by Chemical Bath deposition method. The structure and surface morphology of these as- deposited films were analyzed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques. The structural studies revealed that ZnSe and CdZnSe thin films were polycrystalline in nature and cubic (Zinc blend) structures. The structural parameters like lattice constant, crystallite size, internal strain, dislocation density were calculated. The SEM micrographs showed these films were composed of spherical shaped crystallites and EDX studies confirmed the elemental composition. Optical investigations showed high absorption coefficients and the energy band gap decreased from 2.81eV to 2.27eV when Cd^{+2} are incorporated in ZnSe lattice. Photoelectrochemical parameters were obtained for semiconductor-electrolyte junction selecting ZnSe and CdZnSe as photoanodes and Polysulphide as an electrolyte. The photocurrent, photo potential and quantum conversion efficiency were found to be enhanced significantly after adding Cd^{+2} to ZnSe lattice.**

Index Terms: **ZnSe, CdZnSe thin films, XRD, SEM, EDX, PEC.**

I. Introduction

The research on conversion of optical energy into a clean and renewable energy leads to development of various photovoltaic devices and photoelectrochemical cells. The semiconductor-liquid interface PEC cell consists of photoactive semiconductor electrode immersed in an electrolyte solution containing redox couple and counter electrode (Chandra Babu K. et al.,1994). The semiconducting materials like CdS, CdSe, ZnS, ZnSe, ZnTe, CdTe , HgSe, etc were used as photoactive electrode to get good conversion efficiency(García-Barrientos A., et al.,2018; Ayeshamariam, A., et al.,2014; Lokhande C.D., et al.1998; Marcus Jones,et al.,2009). Not only in solar cell buffer layer but these chalcogenide semiconductors are popular in optoelectronic applications such as blue green Lasers (Gupta P., et al.,1995), radiation detectors (Burger A., et al.,1984), electroluminescent and biomedical imaging devices (Ajaya K.S,.2011). Zinc Selenide (ZnSe) is a wide band gap material with higher luminescent efficiency and alloying it with Cadmium Selenide provides an opportunity to tune the optical and electronic properties for its use in PEC cells (Ju-Hyun, A.; et al.,2007).

Chalcogenide thin films are deposited by various methods like vacuum evaporation (Kishore V., et al.,2005), molecular beam epitaxy (Schreder B., et al.,2000; Hua-Chiang Wen,et al.,2010), electro deposition (Senthil Kumar .,et al.,2019), SILAR (Gudage Y.,et al.,2010) , arrested precipitation technique (Chaitali S. Bagade, et al.,2001) and Chemical bath deposition method (Kamble1 V. K., et al.,2015;.Pawar,A., .,2013). Considering the simplicity, low costing, and large area deposition utility, we have selected Chemical bath deposition method to synthesize pure ZnSe and CdZnSe thin films. Here we present, (1) the investigations on structural, surface morphological, optical properties of pure ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films and (2) the study of these films as photoanode in PEC cell.

II. MATERPIALS AND METHODS

The deposition of pure ZnSe thin films was carried out on thoroughly cleaned glass micro slides and stainless-steel substrate using Chemical Bath deposition method. AR grade Zinc Sulphate ($ZnSO_4$) was used for Zn^{2+} source and Selenium metal powder refluxed with Sodium Sulphite (Na_2SO_3) for 9 hours at 80^0C was used for Se^{2-} source. Triethanolamine (TEA) was used as a complexing agent and pH of the reaction mixture was adjusted to 10.5 by adding the adequate quantity of sodium hydroxide (NaOH). The deposition parameters were optimized to get smooth, uniform and strongly substrate adherent thin films of ZnSe. To get ternary $Cd_{0.5}Zn_{0.}5Se$ thin films Cadmium Sulphate ($CdSO_4$), Zinc Sulphate ($ZnSO_4$) and Sodium Selenosulphate (Na_2SeSO_3) were used in proper stoichiometric ratio. Structural determination and hence microstructural properties analysis of

Table1. Microstructural Properties of ZnSe and CdZnSe thin films

Thin Film	Lattice Parameter a,(A.U)	Microstrain (ξ x10^{-3}) line^{-2} m^{-4}	Dislocation Density δX10^{15} lines/m^2	Crystallite size D, (A.U)		Weight%		
				XRD	SEM	Cd%	Zn%	Se%
ZnSe	5.64	3.01	6.66	120	207	0.00	83.64	16.36
$Cd_{0.5}Zn_{0.5}Se$	6.08	2.51	4.61	144	264	34.96	34.81	30.23

these thin films was done by using EMPYREAN X-ray diffractometer with CuKα radiation (λ= 1.5405A^0) in the scanning range of 2Θ (20^0 to 80^o). The surface morphology was studied using JEOL JSM 7600F FEG-SEM operating at an accelerating voltage 0.1v to 30kv. The optical absorption spectra were obtained by using ELICO SL27 UV-Spectrophotometer at room temperature in the wavelength range of 300nm to 900nm.

The ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films deposited on clean Stainless-steel substrate were used as photoelectrodes in PEC cell. To investigate the current- voltage and power output characteristics of ZnSe and $Cd_{0.5}Zn_{0.5}Se$ photoelectrodes, they were dipped in the 1M polysulphide electrolyte (The aqueous electrolyte preparation was carried out by adding 1M sulphur (S), 1M sodium sulphide (Na_2S) and 1M sodium hydroxide (NaOH) in succession) in H-shaped glass corvette set with graphite rod as counter electrode.

III. RESULT AND DISCUSSION

A. *Structural Properties*

Figure 1 shows the XRD pattern of ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films deposited on glass substrate. ZnSe shows orientations along (1 1 1), (2 0 0), (2 2 0), (3 1 3) planes and confirms the cubic structure in accordance with JCPD card No. (1463) but Cadmium alloyed CdZnSe thin films shows orientations along (111) ZnSe plane and also (111) cubic and (2 2 0) hexagonal planes of CdSe with much dominant peaks along (1 1 1) cubic orientation. JCPD Card No. (19-191) and (8-459).

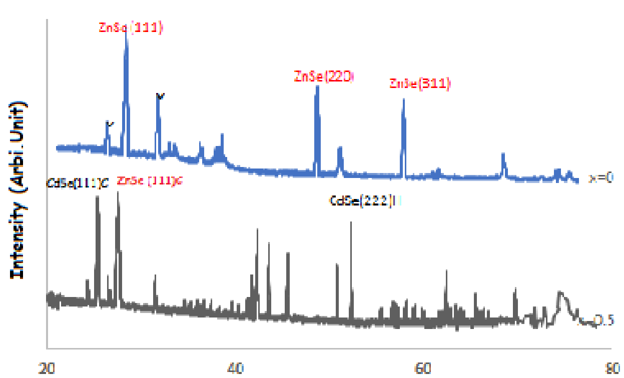

Fig.1 XRD spectra of ZnSe , $Cd_{0.5}Zn_{0.5}Se$ thin films

The lattice parameter d increases from 3.257 A^0 to 3.512 A^0 when Cd was incorporated into ZnSe lattice. The average crystallite size was calculated for the highest intensity peak by Debye - Scherrer's formula shows increase the Cd^{2+} ion, addition of Cd in ZnSe expands the cell uniformly (Hankare P. P, et al.,2006). The microstrain which is disagreement in lattice created during the deposition process and the dislocation density of CdZnSe films was found lower than that of ZnSe films resulting improvement in the stoichiometry which in turn results the volumetric expansion of thin films (Mahalingam, T., et al.,2012). (Table 1)

B. *Surface Morphological Properties*

Scanning Electron Microscopy is useful technique to understand the surface morphology of the thin films. Fig.2 shows micrographs of ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films which describe homogeneous, well adherent films with spherical grains for ZnSe films whereas spherical with slightly elongated grains for $Cd_{0.5}Zn_{0.5}Se$ films. The small, spherical grains are of nearly same diameter of 207nm which represent Cubic phase of ZnSe. The $Cd_{0.5}Zn_{0.5}Se$ films show both cubic and hexagonal phases with increased grain diameter of 264nm. (Kale R.B., et al.,2007). The EDX analysis was done along with SEM for Zn, Se and Cd only. The results give the elemental composition of the thin films which were nearly same as taken in solution and are presented in Table 1.

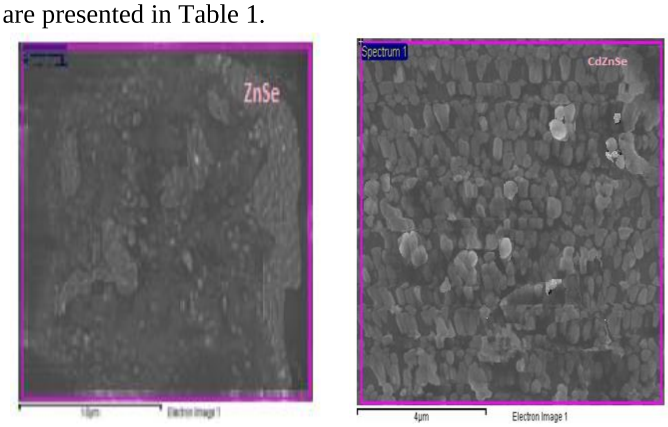

Fig.2 SEM Micrographs of (a) ZnSe (b) $Cd_{0.5}Zn_{0.5}Se$

Table1. Microstructural Properties of ZnSe and CdZnSe thin films

C. *Optical Properties*

The absorption spectra of ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films (Fig.3) indicate that both the films show good absorbance in the visible and infrared region. The spectra also revel long absorption range covering the wavelength 300nm to 990 nm which makes these materials useful for various optical components. In order to estimate the band gap energies, the graphs of $(\alpha h\nu)^2$ Vs photon energy hν were plotted as per Tauc Relation (Fig. 4)

(Tauc, J., et al.,1947). The energy band gap decreases from 2.81eV to 2.27eV because doping of Cd in ZnSe decreases the inter-crystalline spaces among the crystallites. The linear dependence of the absorption edge shows direct type of transition. This direct allowed transition, tuneable band gap of the materials can be best choice for solar photo electrochemical cell applications.

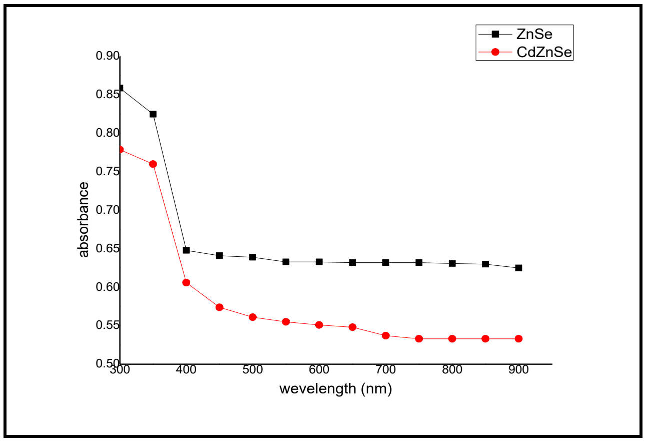

Fig.3 Absorbance curves of ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films

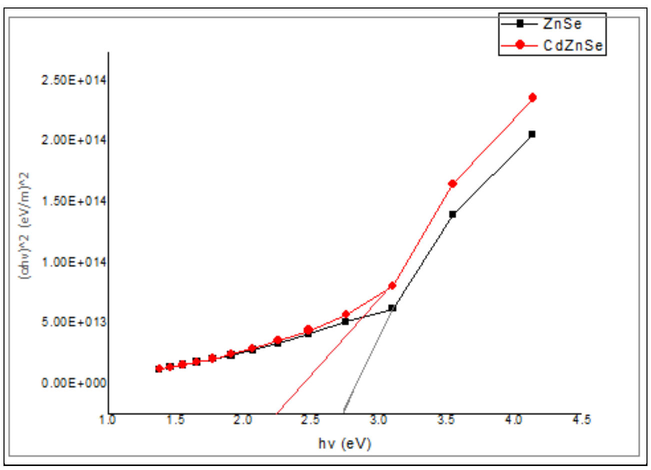

Fig.4 Tauc plots for ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films

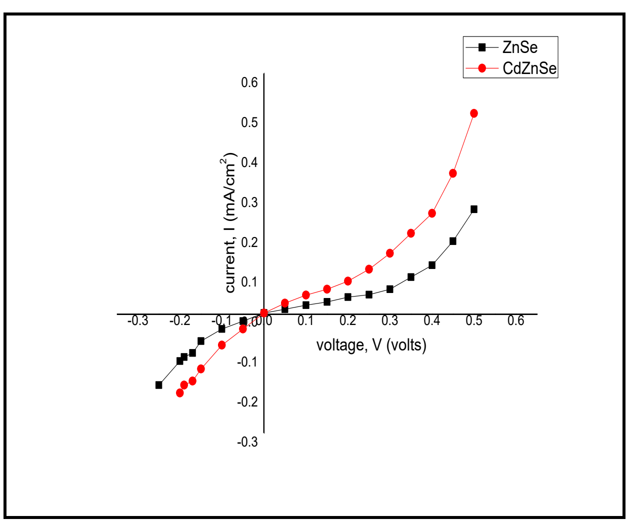

Fig.5 I- V Characteristics in dark

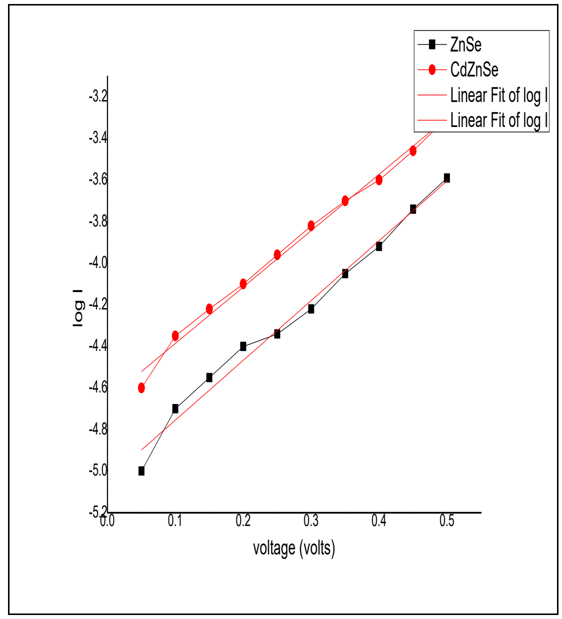

Fig.6 Plots of log I against V

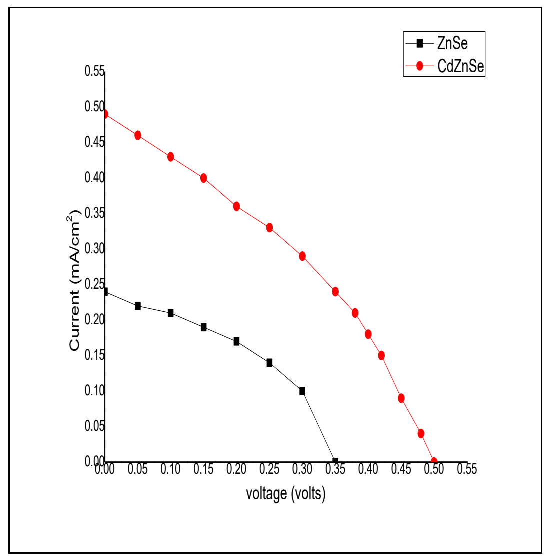

Fig.7 Power output curves

The power output curves were recorded for both the ZnSe and CdZnSe films and are shown in Fig.7. Under constant light illumination, absorption of photons takes place by these semiconducting photoanodes and the electrons in valance band gets excited to conduction band. These electrons will flow to graphite electrode through external circuit and gives open circuit voltage (V_{oc}) and short circuit current (I_{sc}) (Soundararajan D, et al.,2010). The increase in the open circuit voltage of CdZnSe than ZnSe can be understood from the improved grain structure after addition of Cd in ZnSe. The PEC cell performance parameters such as fill factor (FF), efficiency (η), series resistance (R_s) and shunt resistance (R_{sh}) were computed using the following relations from the power output curves and presented in Table 2.

$FF = (V_m \times I_m) / (V_{oc} \times I_{sc}) \times 100\%$

η = Output Power/ Input power

$\eta = ((V_m \times I_m) / P_{in}) \times 100\%$

Table 2. Solar cell parameters of ZnSe and CdZnSe photoanodes in PEC cell

Sample	**ZnSe**	**CdZnSe**
n_d	2.87	2.71
R_s (Ω)	1428	671
R_{sh} (kΩ)	3.33	1.53
V_{oc} (volts)	0.35	0.5
I_{sc} (mA/cm^2)	0.24	0.49
V_m (volts)	0.22	0.30
I_m (mA/cm^2)	0.16	0.29
FF	41.9	35.51
η%	0.176	0.435

CONCLUSION

The Chemical bath deposition method was used to form ZnSe and CdZnSe thin films for its use as photoanode in PEC cell. The addition of Cadmium in Zinc Selenide results in improvement of various thin film and photo-electrochemical cell properties. XRD studies shows crystallite size increases from 120 A^0 to 144 A^0 with decrease in dislocation density as 6.66 x 10^{15} lines/cm^2 to 4.61 x 10^{15} lines/cm^2 for these polycrystalline ZnSe to CdZnSe thin films. The FEG-SEM micrographs gives that the films were smooth, homogeneously distributed over the entire glass surface and the crystallinity enhances for CdZnSe films. The UV-Visible spectrophotometer studies indicated the decrease in energy band gap for CdZnSe thin films. The PEC cells fabricated using ZnSe and CdZnSe with Polysulphide electrolyte shows increment in V_{oc} and I_{sc} values for cadmium doped zinc selenide photoanodes results in increased efficiency (0.435%) for $Cd_{0.5}Zn_{0.5}Se$ electrode. Hence, better solar cell output characteristics can be obtained with $Cd_{0.5}Zn_{0.5}Se$ photoanode in PEC cell.

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