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Structural and morphological characterization of CdSe:Mn thin films

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Abstract. CdSe:Mn thin films were grown by chemical bath deposition. The pH of the solution was maintained at 11. Dry films so obtained were annealed in vacuum (10^{-1} Torr) for about 2 h at 400°C. The annealed samples were subjected to morphological and structural characterization using scanning electron microscope and XRD. XRD was used for structural characterization whereas scanning electron microscope shows the surface morphology of the films. XRD spectra reveal that the grown CdSe films are polycrystalline in nature and have cubic structure. The average particle size decreases on doping CdSe with Mn ions. The FE-SEM images show spherical particles having uniform distribution. Optical characterization was done using PL studies and UV–Visible spectrophotometer. PL spectra show an increase in PL intensity on doping. Optical band gap also decreases on doping.

Keywords. Morphology of films; X-ray diffraction; semiconductors.

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1. Introduction

Synthesis of binary metal chalcogenides of II–VI semiconductors in nanocrystalline form has experienced an enormous development in recent years owing to their interesting size-dependent optical and electrical properties [1,2]. In particular, nanostructures of CdSe have received considerably more attention due to its increasing fundamental, experimental and applied interests [3]. CdSe nanocrystals are useful in understanding the phenomenon of quantum confinement effect and are used in the fabrication of devices like PV cells, lasers, TFTs, light-emitting diodes and other nanoscale devices [4–8]. Blue shift in the band gap of this material, with decreasing grain size, has led to many applied investigations. CdSe nanocrystalline films have been prepared by various techniques including chemical bath deposition (CBD) [1]. CBD is a well-known method for preparing semiconductor layers and has been used mainly for metal selenide. Chemically deposited films can be used in photovoltaics. The films prepared by CBD are usually composed of closely spaced nanocrystals [9]. The band-gap engineering of films is possible by tailoring the nanocrystellite size, which can be done by varying the deposition parameters.

In the present work, we have successfully synthesized nanograins in CdSe and nanosphere in CdSe:Mn (2%) doped films on glass substrates. The structural, morphological and optical properties of pure and Mn-doped CdSe thin films were measured.

2. Materials and methodology used

Extra pure chemicals received from the manufacturers were used for the synthesis of these films. High-quality $MnCl_2$-doped CdSe films were prepared by chemical bath deposition method using cadmium acetate $(Cd(CH_3COO)_2) : 2H_2O$, manganese chloride $(MnCl_2)$, selenium ions (Se^{2-}) and sodium sulphide as starting materials. Double-distilled water was used as a solvent. Aqueous solution of 1 M $Cd(CH_3COO)_2 : 2H_2O$, 2% $MnCl_2$ and 1 M sodium selenosulphate was prepared separately. Selenium selenosulphate solution was then added slowly into the mixture of manganese chloride and cadmium acetate solution with constant stirring till it turns into a dark orange solution. pH of the solution was maintained at 11 by adding 30% ammonia. Thereafter, 5 ml of triethinoamine was added to this solution. The substrate was left in the bath for 2 h to have a

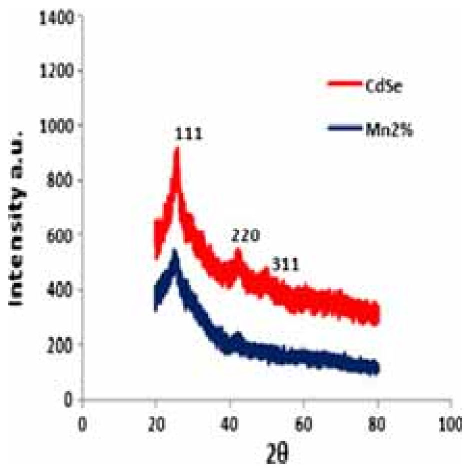

Figure 1. XRD patterns of pure and 2% Mn-doped CdSe thin films.

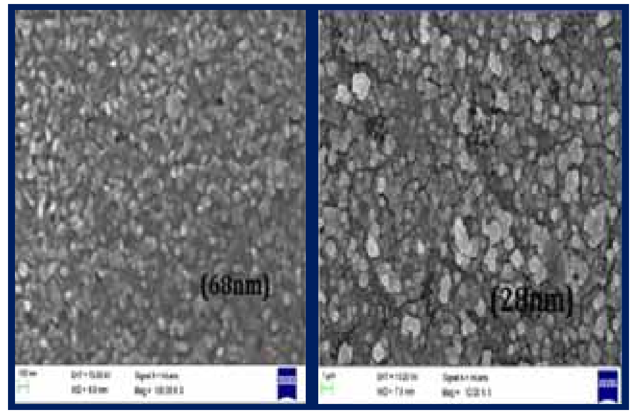

Figure 2. SEM image of pure and 2% Mn-doped CdSe films.

substantial growth of the film. After the deposition was completed on the substrates, films were taken out and cleaned with double-distilled water and dried in open atmosphere at room temperature. Annealing of the films was done at 400°C in vacuum.

3. Results and discussion

3.1 *Structural studies*

XRD of pure and Mn-doped CdSe were recorded by scanning 2θ from 20° to 80°. In the case of pure CdSe, the peaks are detected at $2\theta = 25.90°$, 42.07° and 49.69°, respectively, whereas in Mn (2%) doped films, the peaks are observed at 24.80°, 41.83° respectively (figure 1). Thus, there is a shifting of peak position on doping. The particle sizes of the films were determined using the Debye–Scherer formula,

$$D_{hkl} = K_{\lambda}/\beta \cos\theta, \tag{1}$$

where K is a constant which is taken to be 0.94 and β is the full-width at half-maxima (FWHM) of the XRD peaks at 2θ. XRD was recorded with an incident wavelength λ (=1.54 Å). XRD peak indicates crystalline nature. The particle size is calculated using the prominent peak indexed as (1 1 1) plane. Particle size of pure CdSe is 36 nm and for Mn-doped CdSe, it comes out to be 10 nm. Thus, particle size decreases on increasing doping concentration [10,11]. The FWHM of the XRD peaks may also contain contributions from the lattice strain. The average strain in CdSe and 2% Mn-doped films is calculated using Stokes–Wilson equation,

$$\varepsilon_{\text{strain}} = \beta\,(\cot\theta)/4. \tag{2}$$

All the results are shown in table 1.

3.2 *Scanning electron microscope and elemental analysis*

Scanning electron microscopy (SEM) is a convenient technique to study nanostructure of thin films. Figures 2a and 2b show the FE-SEM images of the annealed CdSe and 2% Mn-doped CdSe. The nanograins and crystals without hole and crack are visible. It shows that the almost spherical nanoparticles and grains are homogeneously distributed. Energy-dispersive X-ray analysis (EDX) shows the presence of Cd, Se and Mn

Table 1. Structural parameters of pure and 2% Mn-doped CdSe films.

Material	2θ(°)	Interplaner spacing *d*-values	Plane (*hkl*)	FWHM (rad.)	Particle size (nm)	Average strain (β) ($\varepsilon_{\text{strain}}$)
CdSe	25.90	3.4720	1 1 1	0.12350	36	0.080
	42.07	2.1437	2 2 0	0.11900		
	49.69	1.8433	3 1 1	0.04210		
CdSe:Mn	24.80	3.0256	1 1 1	0.16377	10	−0.484
	41.83	1.0870	2 2 0	0.46315		

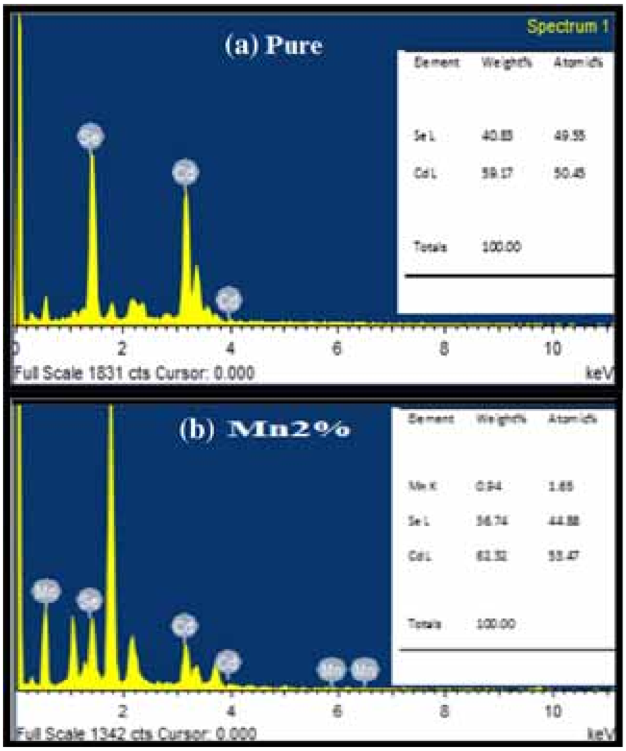

Figure 3. EDX spectra for pure CdSe and 2% Mn-doped CdSe.

(figure 3). These results indicate that material deposition in both samples is exactly the same as desired [CdSe and CdMnSe (2%)].

3.3 *Optical study*

3.3.1 *UV–Visible spectrophotometer*

Optical properties are studied by recording the transmission spectra of these films. Figure 4 shows the transmission data of n-CdSe thin films deposited at 80°C of bath solutions. The optical band gaps of pure and doped CdSe thin films were measured using UV–Visible spectrophotometer. UV–Visible transmission spectra for pure and 2% Mn-doped CdSe film in the wavelength range 200–1000 nm were recorded. Plots of $(\alpha h\upsilon)^2$ with photon energy $h\upsilon$ are shown in figure 4. Using these plots, optical band gap of CdSe was calculated. For undoped films, it comes out to be 1.74 eV whereas for 2% Mn-doped films it is 1.52 eV. Thus, the band gap of CdSe thin film decreases on doping [10].

3.4 *Photoluminescence (PL)*

Photoluminescence (PL) studies of CdSe and 2% Mn-doped CdSe were carried out at room temperature. Figure 5 shows room-temperature PL spectra of pure and Mn-doped CdSe films. PL spectra for all samples show two peaks. Peaks for CdSe were obtained at lower wavelength viz. 299 nm. The figure shows that PL intensity improved when sample was doped

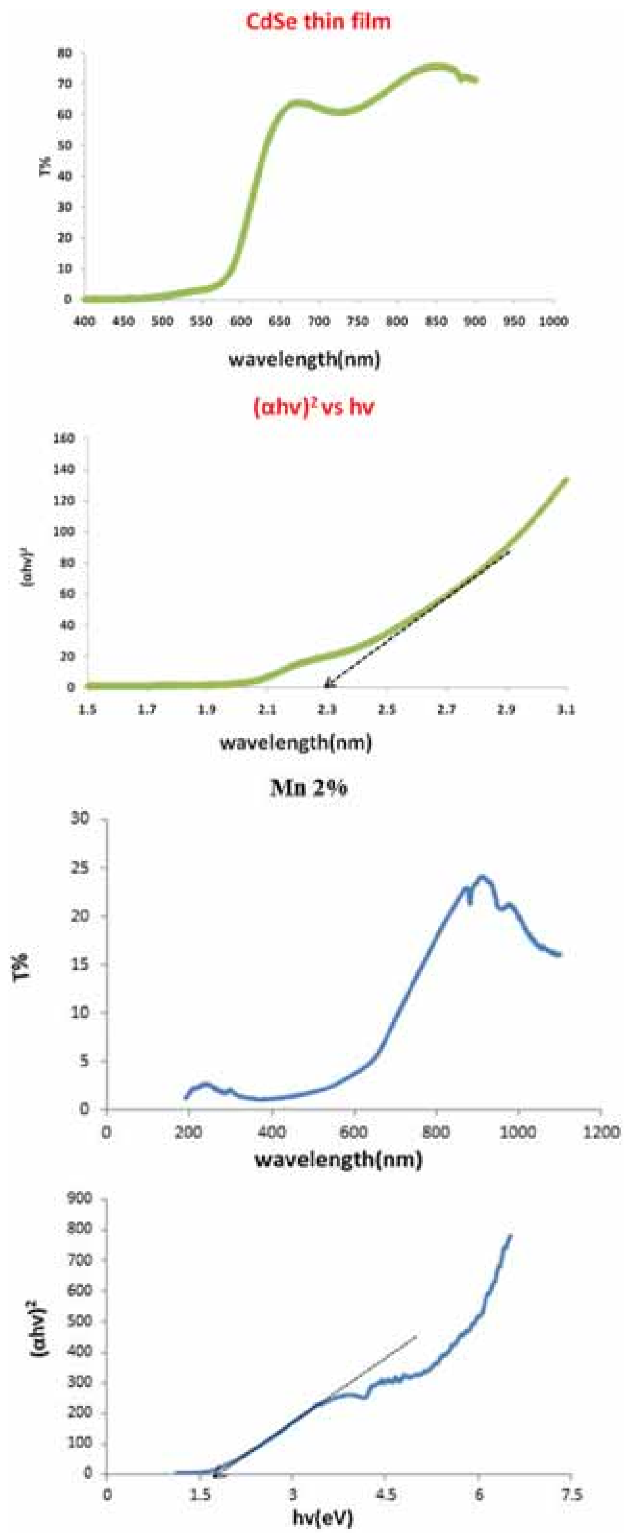

Figure 4. Energy band gap and transmission spectra of pure and 2% Mn-doped CdSe films.

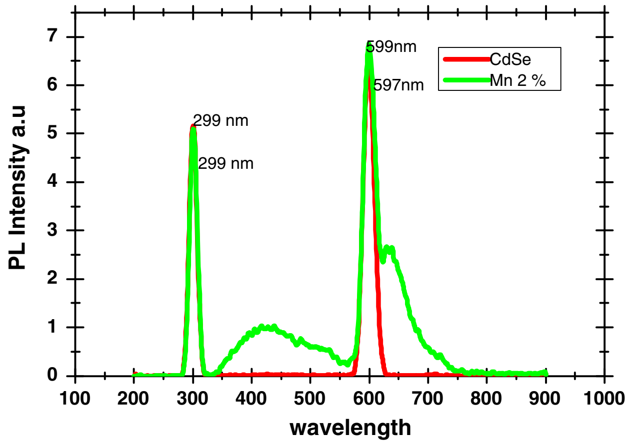

Figure 5. PL spectra of pure and 2% Mn-doped CdSe films.

with Mn. Thus, peaks become more intense after doping [12,13].

4. Conclusions

From the above results, it is concluded that films of pure and doped CdSe are successfully deposited by chemical bath deposition method. The grown material, CdSe, shows cubic phase having an energy band gap of 1.74 eV which decreases on doping. Annealing of films was found to increase the crystallinity of the films. XRD study confirms that the particle size decreases on doping with Mn. The optical study indicates that band gap decreases on doping. These results were related to the formation of defect states in forbidden gap due to the incorporation of Mn in the host lattice. PL spectra show an increase in PL intensity on doping.

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