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STUDY OF Mn DOPED CHEMICAL BATH DEPOSITED NANOCRYSTALLINE CdS THIN FILMS

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Abstract

In this paper we report the study of Mn doped CdS ($Cd_{1-x}Mn_xS$) thin films grown on commercial glass slide substrate by chemical bath deposition technique at 70±2ºC. The effect of Mn content (x value) on structural, morphological and some optical properties have been studied. The as-deposited $Cd_{1-x}Mn_xS$ thin films were characterized using X-ray diffractometer (X-PERT PRO), SEM and UV-VIS spectrophotometer. All the films show nano-crystallinity with hexagonal structure. The average grain size obtained is in between 157 nm and 93 nm with increase in Mn content. It was found that the peak intensity of XRD peaks decreases with the increase in Mn content. The effect of Mn content on morphological properties have been studied. The value of energy bandgap obtained in between 2.31 eV and 2.47 eV for varying Mn content from x= 0 to x= 0.8 respectively. The other optical properties were under consideration.

Keywords: Mn-CdS, chemical bath deposition, thin films, Mn doping.

1. INTRODUCTION

Cadmium manganese sulfides $Cd_{1-x}Mn_xS$ have properties in between CdS and MnS. Cadmium sulfide (CdS) is semiconductor with good optical absorption properties in the range of visible light, and the direct band gap of 2.42 eV at room temperature. For this reason, cadmium sulfide has been applied to many photonic devices such as photovoltaics, photodetectors, laser and light emitting diode [1,2,3]. Whereas, manganese sulfide (MnS) is a magnetic semiconductor material having bandgap 3.1 eV that is of potential interest in short wavelength optoelectronic applications such as in solar selective coatings, solar cells, sensors, photoconductors, optical mass memories and antireflection coating [4,5,6,7,8] .

Addition of Mn to the most widely used CdS buffer layer material enhances the electronic and optical properties of optoelectronic devices. It has been widely used as a wide bandgap window material in hetero-junction photovoltaic solar cells and photoconductive devices. Keeping these aspects in view, more attention is being given in producing good quality CdMnS thin films for comprehensive optical studies and their various applications.

A number of film deposition methods such as spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition, SILAR and chemical bath deposition (CBD) have been used for preparing II-VI compounds [9,10,11,12,13,14].

In this study, we were prepared the Mn doped CdS thin films for varying Mn content by a modified CBD technique. The effects of Mn content on structural, morphological and some optical properties have been investigated.

2. EXPERIMENTAL DETAILS

The $Cd_{1-x}Mn_xS$ thin films were prepared by CBD technique on commercial glass slide for various Mn concentration (x= 0, 0.2,…0.8). The starting materials used were $CdSO_4$ (0.06M) as a Cd^{2+} ion source, $MnSO_4$ (0.2M) as Mn^{2+} ion source, thiourea (0.6M) as an S^{2-} ion source and triethenolamine (TEA) complexing to control the Cd^{2+} and Mn^{2+} ion concentrations. An alkaline solution of ammonia was used to adjust pH of the reaction mixture. All the chemicals used were of Analytical Reagent grade. The process involves a controllable chemical reaction at a low rate, by adjusting the pH value and temperature of the working solution. The experimental arrangement consists of a special substrate holder which is attached to a high torque motor having a constant speed of 60 r.p.m. The temperature of chemical bath was adjusted with a hot plate and temperature controller (72±2ºC), while magnetic stirrer is applied to promote ion-by-ion heterogeneous growth on the substrate. The as deposited thin films were prepared on carefully cleaned glass substrates. Cleaning of substrate is important in deposition of thin films, cleaning steps and growth procedure is reported elsewhere [15,16,17]. The pH value of working solution was adjusted by a pH meter for different deposition time (10-60min.). After deposition the substrates were removed from the chemical bath and cleaned in double distilled water.

The crystallographic structure of the films was analyzed with a (XPERT-PRO) X-ray diffractometer using Cu-Kα radiation with wavelength, 1.5418Å. The thickness of thin film was measured by the weight difference method at room temperature.

The average grain size in the deposited films was obtained from a Debye-Scherrer formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). Optical properties were measured at room temperature by using Perklin-Elmer UV-VIS lambda-35 spectrometer in the wavelength range 200-1000nm.

3. RESULTS AND DISCUSSION

3.1 Structural properties of $Cd_{1-x}Mn_xS$ thin films:

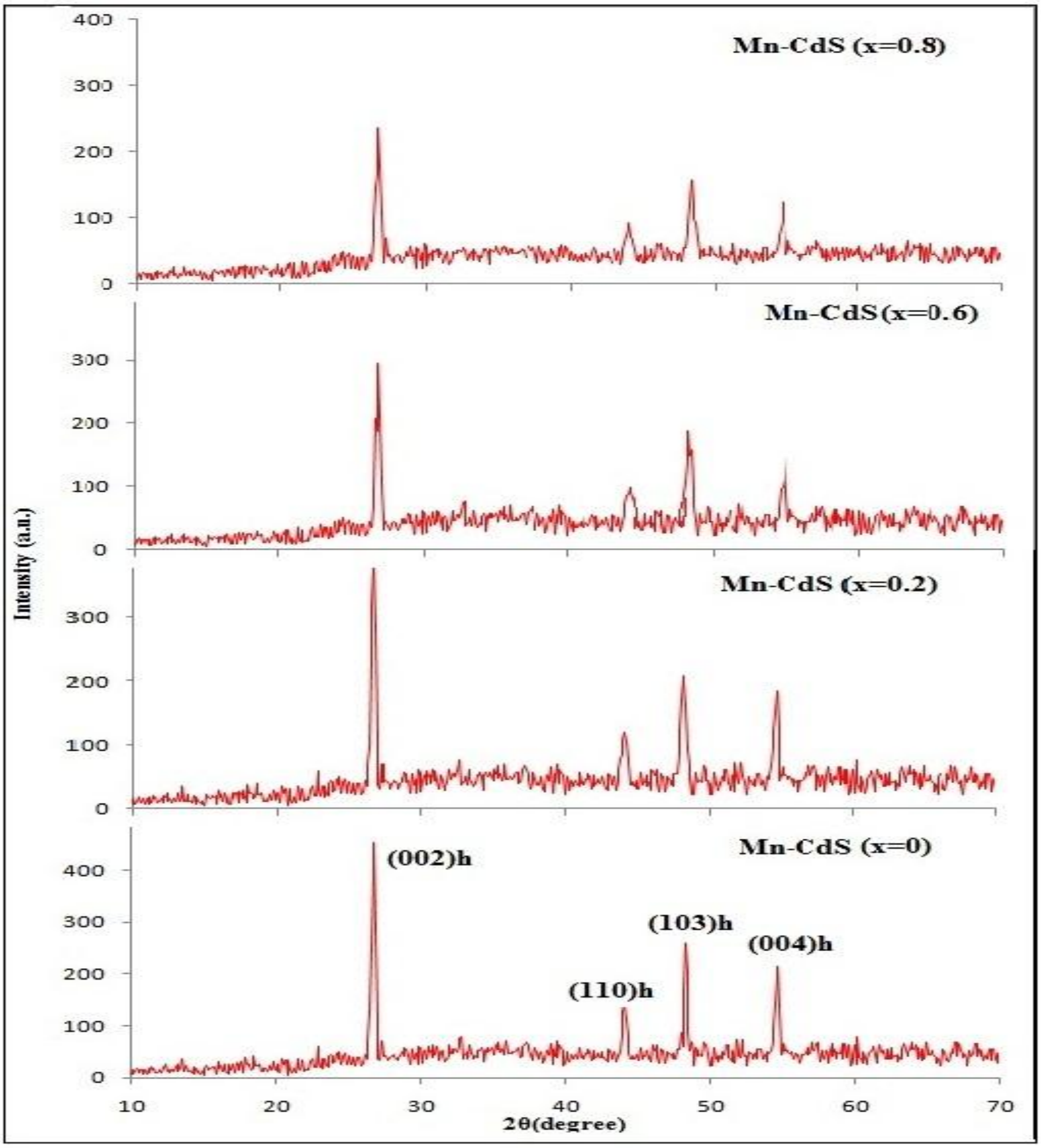


Figure 1. *XRD pattern of $Cd_{1-x}Mn_xS$ films for varying Mn content for x= 0 to x= 0.8*

Figure 1 shows the XRD pattern of $Cd_{1-x}Mn_xS$ films for Mn content between x=0 and x=0.8. A comparison of the peak position (2θ values) of the JCPDS XRD spectra data suggests that the as-deposited films have hexagonal (wurtzite) structure with the peaks corresponding to (002), (110), (103), (004). The presence of multiple peaks in

XRD pattern indicates that the as-deposited thin films are polycrystalline in nature. It was observed that the peak height decreases with an increase of Mn content which was recorded previously [18]. It was also observed that, the crystallinity of the CdS film was deteriorated with increasing Mn content which indicates that Mn might have been immersed into the matrix of CdS nanoparticles [19,20].

The average grain size (g) has been obtained from the XRD patterns using Debye-Scherrer's formula,

$$g = K\lambda / \beta \cos\theta$$

Where, K is a constant taken to be 0.94, λ is wavelength of X-ray used (1.542Å), β is full width at half maximum (FWHM) of the peak and θ is Bragg's angle. The average grain size was observed in between 157 nm and 93 nm for Mn content between x= 0 and x= 0.8.

The average value of lattice constant for hexagonal structure has been calculated using formula,

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

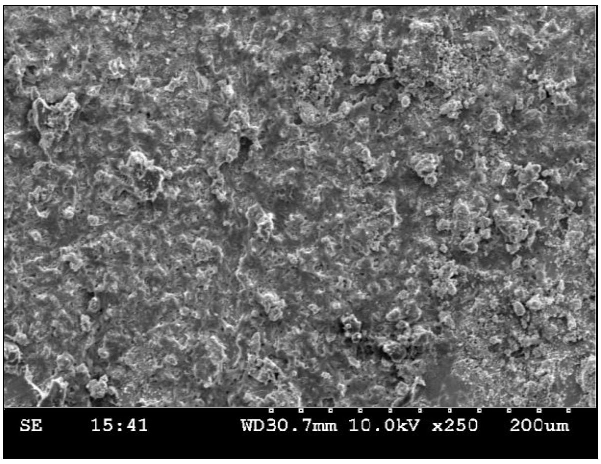
Where, d_{hkl} is the interplanar spacing of the crystallographic planes. The average value for a = b = 4.13 Å and c = 6.65 Å, which is close to the standard values (*a* = *b* = 4.14 Å and *c* = 6.72 Å). Table 1 shows the detailed summary of lattice constant, grain size and optical band gap of $Cd_{1-x}Mn_xS$ thin films for varying Mn content.

Table 1. *A summary of lattice constant, grain size from XRD and optical bandgap for varying Mn content.*

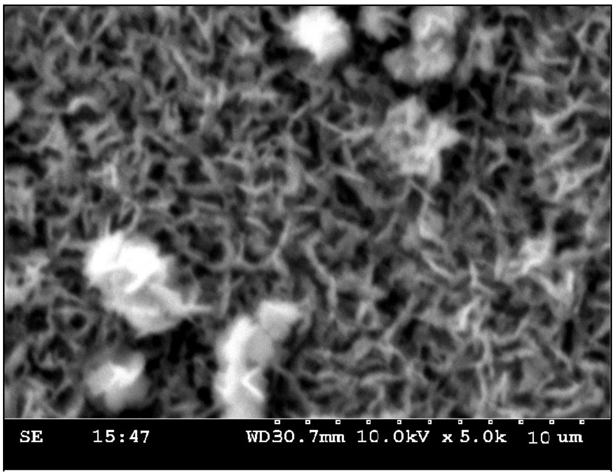
Mn content (x value)	Lattice constant		Grain size (XRD) g nm	Band gap Eg (eV)
	Hex			
	a Å	c Å		
x = 0 (CdS)	4.1363	6.6816	157	2.47
x = 0.2	4.1245	6.6542	164	2.41
x = 0.4	4.1181	6.6308	126	2.42
x = 0.6	4.1252	6.6320	112	2.38
x = 0.8	4.1120	6.6511	93	2.31

3.2 Morphological properties of $Cd_{1-x}Mn_xS$ thin films:

The surface morphology and the micro structural features of the as deposited $Cd_{1-x}Mn_xS$ thin films have been studied by Scanning electron microscopy (SEM). The SEM micrograph shows smoother and more uniform films with fibrous structure as Mn content increases (Figure 2).



(a) x=0.2



(b) x=0.8

Figure 2. *SEM of $Cd_{1-x}Mn_xS$ films for Mn content (a) x=0.2 and (b) x= 0.8*

The films obtained were smooth, uniform, adherent, and yellowish in color. It is observed that the grain size decreases with increase in Mn content. The improved fibrous films may useful for gas sensing applications.

3.3 Optical properties of $Cd_{1-x}Mn_xS$ thin films:

The optical studies plays vital role in any optoelectronic application. The optical absorbance spectra of Mn-doped CdS thin films were studied in the wavelength range of 400–1000 nm as shown in Figure 3. The spectra shows the weak absorbance and strong transmittance at VIS-NIR region which is advantageous feature of Mn-doped CdS thin films for a window layer in solar cells as well as a good material for construction of poultry roofs and walls and for coating eyeglasses.

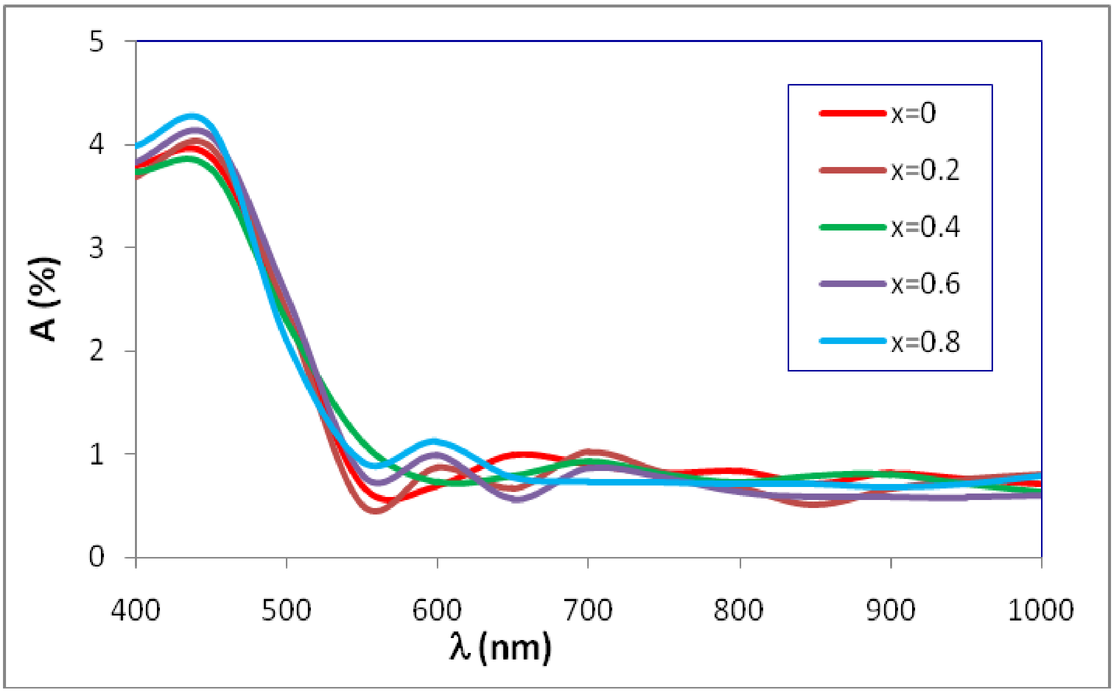


Figure 3. *Optical absorbance of nickel sulfide thin films for different concentration.*

The energy band gap of Mn-doped CdS thin films were calculated using the Tauc's relation [21] as:

$$\alpha h\nu = A\ (h\nu - Eg\ )^{\ n}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, Eg is the band gap, n = 0.5 for direct band gap transition and A is constant which is different for different transitions.

The band gap Eg was determined from absorbance data by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis at α =0. The band gap energy Eg obtained for each Mn content is different. For higher Mn content (x=0.8) the band gap is 2.31eV and for lower Mn content (x=0) it is 2.47eV. The band gap of other films is intermediate (Figure 4 and Table 1). In this study, the decrease in band gap of as deposited thin films from 2.47 eV to 2.31 eV with increasing Mn conent is observed. Similar results were observed in literature for different semiconductor thin films [22,23,24,25,26].

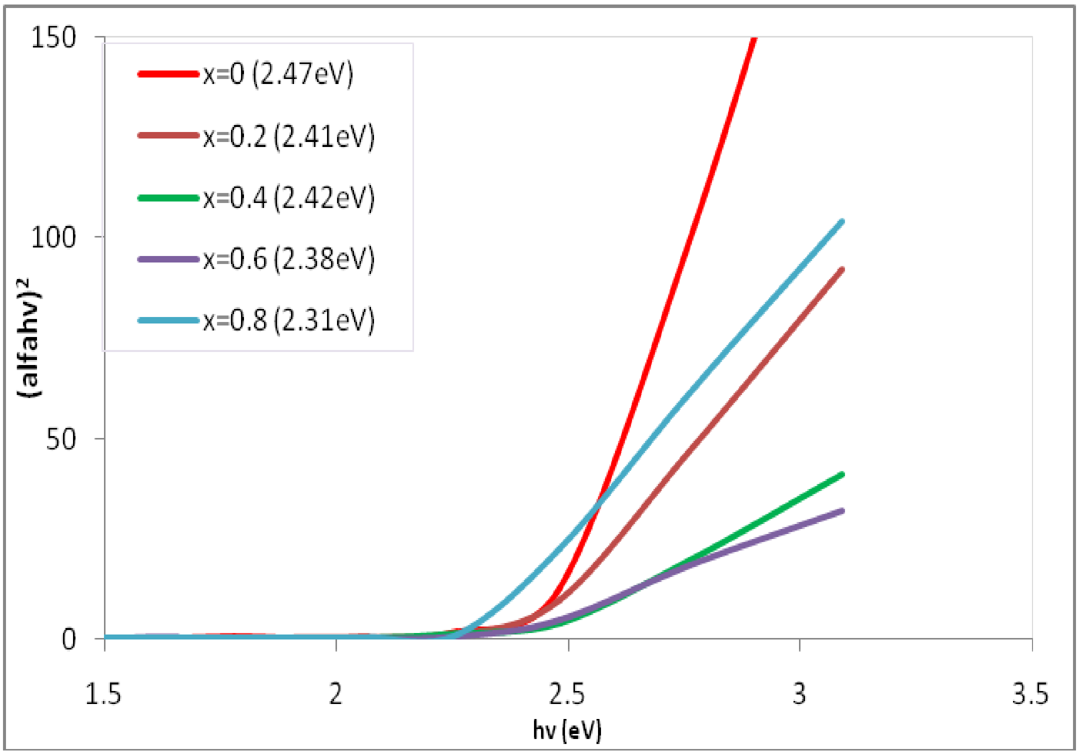


Figure 4. *Plot of $(\alpha h\nu)^2$ vs $h\nu$ for all CdZnS thin films.*

4. CONCLUSION

$Cd_{1-x}Mn_xS$ nano-crystalline thin films have been grown successfully by modified CBD technique. The effect of Mn doping on structural, morphological and optical properties have been studied. The multiple peaks observed in XRD study reveals the polycrystalline nature of the obtained films. The SEM image confirms the fibrous (nano-wires) nanostructure of the films which may useful in sensor applications. The Mn content affects the grain size. It is also observed that the bandgap of the as-deposited film was decreases with increase in Mn doping. Due to strong transmittance at VIS-NIR region and wider bandgap, the films were suitable for optoelectronic devices and window layers in solar cells

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