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Investigation of Effect of Mn Concentration on Physical Properties of CdS Thin Films

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Abstract: CdS thin films have been successfully deposited on commercial glass slide substrate by chemical bath deposition technique at 70±2ºC. The effect of Mn concentration (x value) on structural, morphological, optical and electrical 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. The XRD study reveals the nano-crystalline thin films with hexagonal structure. The peak intensity of XRD peaks decreases with increase in Mn content. It is observed that as Mn content increases the average grain size varies between 189 nm and 107 nm. Morphological properties have been discussed. The value of obtained in between 2.28 eV and 2.46 eV For varying Mn content from x= 0 to 0.8 the energy bandgap and resistivity decreases apparently.
Keywords: CDS, thin films, Mn doping, chemical bath deposition.

I. INTRODUCTION

Mn doped cadmium sulfides ($Cd_{1-x}Mn_xS$) thin films have properties in between CdS and MnS. Cadmium sulfide 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 work, we prepared the Mn doped CdS thin films for varying Mn concentration by a modified CBD technique. The effects of Mn content on structural, morphological, optical and electrical properties have been investigated.

II. 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, 0.4, 0.6 and 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]. 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. The electrical resistivity was obtained using Four-probe setup.

III. RESULTS AND DISCUSSION

A. *Structural properties of $Cd_{1-x}Mn_xS$ thin films*

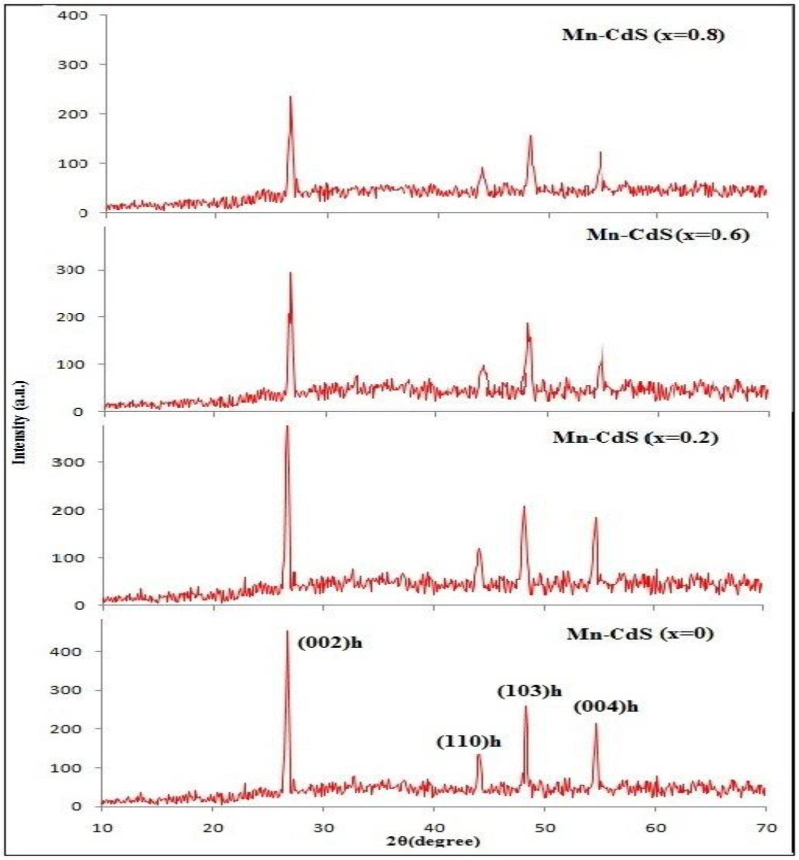


Figure 1. XRD pattern of $Cd_{1-x}Mn_xS$ films for varying Mn content x= (0 to 0.8)

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. 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 [17-20].

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 189 nm and 107 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,

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

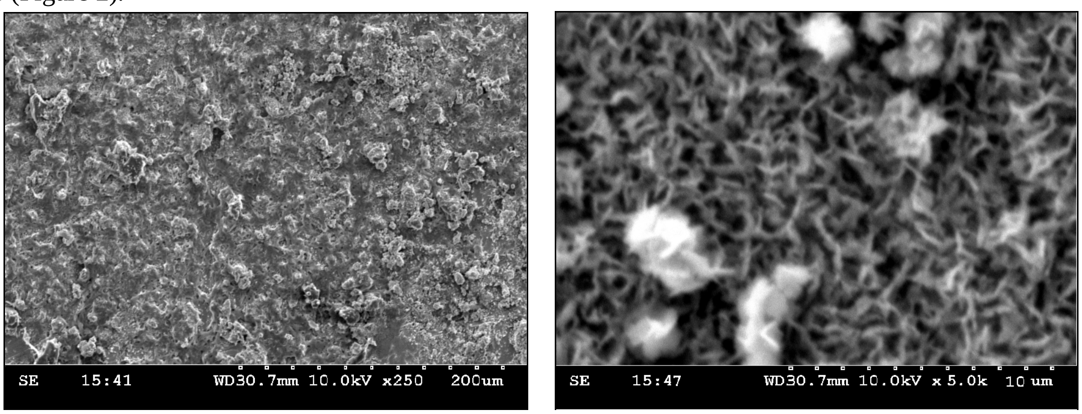
Where, d_{hkl} is the interplanar spacing of the crystallographic planes. The average value for a = b = 4.13 Å and c = 6.65 Å, which is close to the standard values ($a = b = 4.14$ Å and $c = 6.72$ Å). Table 1 shows the detailed summary of lattice constant, grain size and optical band gap of $Cd_{1-x}Mn_xS$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

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

Mn content (x value)	Grain size g nm	Band gap Eg (eV)
x = 0 (CdS)	189	2.45
x = 0.2	164	2.39
x = 0.4	156	2.41
x = 0.6	132	2.34
x = 0.8	107	2.28

B. 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 crack free, smoother and more uniform films with fibrous structure as Mn content increases (Figure 2).



(a) *(b)*

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.

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

The optical investigation 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.

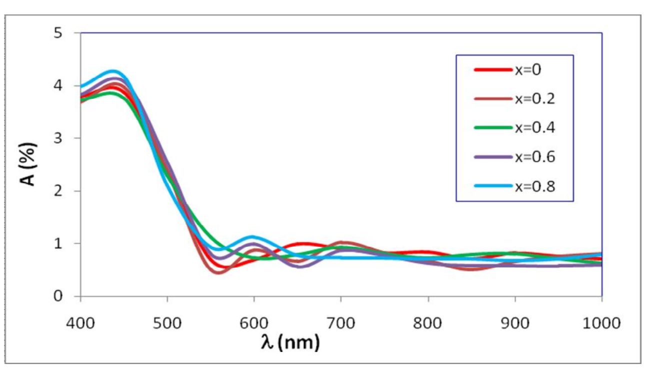


Figure 3. Optical absorbance of $Cd_{1-x}Mn_xS$ thin films for different concentration.

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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 = absorption coefficient
hv = photon energy
Eg = band gap
n = 0.5 for direct band gap transition and
A = 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 2.28eV and for lower Mn content (x=0) it is 2.45eV. 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 2.45 eV to 2.28 eV with increasing Mn conent is observed. Similar results were observed in literature for different semiconductor thin films [22-27].

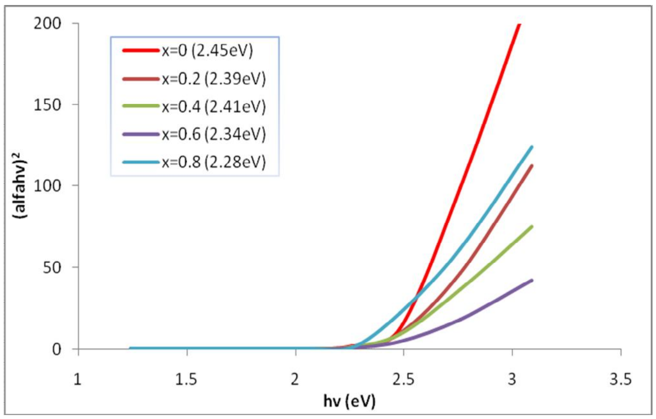

Figure 4. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for all $Cd_{1-x}Mn_xS$ thin films.

D. Electrical properties of $Cd_{1-x}Mn_xS$ thin films

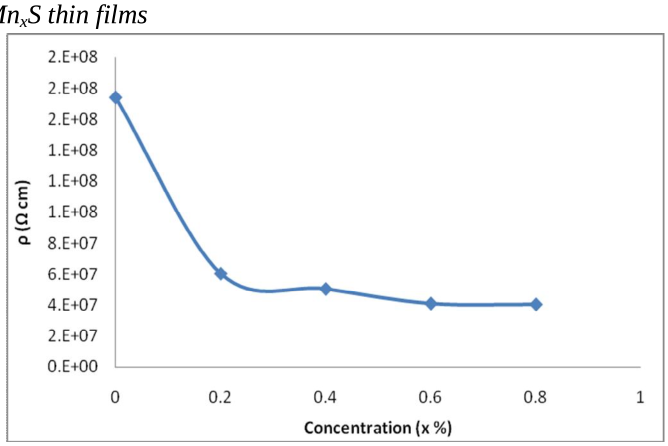

Figure 5. Variation of Mn concentration (x) vs ρ (Ω cm) for $Cd_{1-x}Mn_xS$ thin films.

The dark resistivity of Mn doped CdS thin film is shown in fig. 5. This clearly indicates that the resistivity decreases with Mn concentration which reflects the increase in conductivity.

IV. CONCLUSION

Mn doped CdS ($Cd_{1-x}Mn_xS$) nano-crystalline thin films have been grown successfully by modified CBD technique. The effect of Mn doping on physical properties have been investigated. 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 applications as well buffer/ window layers in solar cells.

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