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RESEARCH ARTICLE

SOME STUDIES ON CHEMICAL BATH DEPOSITED $Cd_{1-x}Mn_xS$ THIN FILMS

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Abstract

In the present research paper simple and cost effective chemical bath deposition method is used to deposit $Cd_{1-x}Mn_xS$ thin films. Film thickness of the deposited series was estimated by weight and difference method. The film thickness was found to increase with increase in composition up to x=0.6. All the films show polycrystalline crystal structure by XRD analysis. The crystallites of the $Cd_{1-x}Mn_xS$ thin films were decreased on increasing the doping concentration of Manganese. The intensity of XRD peaks corresponding to (100), (101), (203), (102), (110) and (200) reflections significantly decreased with increase in Mn doping concentration but the intensity of (002) peak for x=0.6 was significant. All the film shows that optical absorption decreased significantly with increasing in wavelengths. The significant blue shifting was observed for the composition x=0.6, having very low absorption.

Keywords: $Cd_{1-x}Mn_xS$ thin films, film thickness, XRD, peak intensity.

Introduction

The area of research is expanding day by day in development of selected combinations of chalcogenides semiconductor thin films to be operate over wide range of sun's spectrum with comparatively wide optical band gap.

Among the several chalcogenides, CdS and MnS have been studied thoroughly as individual binary systems for thin film applications (Goede and Heimbrodt 1998; Zuo, et al., 2007; Lokhande et al., 1998; Fan *et al.*, 2003; Chowdhuri et al., 2011). The best of our knowledge is concerned, very few work have been reported on the study of $Cd_{1-x}Mn_xS$ ternary system.

In the present study deal with the preparation of $Cd_{1-x}Mn_xS$ thin films on commercial glass substrates and study their physical, spectroscopic, electrical transport properties. Photoelectrochemical solar cell performance has been studied in the application part of $Cd_{1-x}Mn_xS$ ternary system deposited on ITO glass substrates (Tepparo, *et al.*, 1997; Sombuthawee, *et al.*, 1978; Chaki *et al.*, 2012; Mane and Lokhande 2000; Haynes 2013; Pawar 2011)

Experimental details

Preparation of MnS Thin Film:

The objective of the study was doping of manganese (Mn) in CdS thin films using CBD method. Therefore the preparation MnS thin films are the firstly preferred. The study of various reported literatures on preparation of Mns thin films it was planned to prepare MnS thin films by using chemical bath deposition procedure described as (Goede and Heimbrodt 1998; Zuo, *et al.*, 2007; Tepparo *et al.*,1997; Lokhande *et al.*, 1998).

The high purity AR grade Chemicals (Sd Fine-CHEM Limited) were used for synthesis of the film. $MnSO_4$ (Manganese sulphide) and $(NH_4)_2CS$ (thiourea) were used as Mn^{+2} and S^{-2} ion sources respectively. pH of the reaction mixture was controlled by using ammonia. The ammonia also acts as complexing agent. In the reaction bath, 10 ml of manganese sulphate (1 M) was mixed with 1ml concentrated ammonia. The mixture result into Mn^{2+} free radicals as a complex. In this reaction mixture 10 mL of thiourea (1 M) was added slowly with constant stirring. To this mixture 20 ml distilled water was added with. The pH of the mixture was adjusted to 10.5 by slow addition of ammonia. The glass substrates (Blue star or crown glass) were cleaned with detergent and distilled water using high frequency ultrasonic cleaner and dried in desiccators. The pre cleaned glass substrate was kept in vertical position in the bath containing solutions. The reaction bath was kept untouched until the completion of the reaction.

In order to prepare the $Cd_{1-x}Mn_xS$ thin films, the bath conditions such as deposition temperature, deposition time, pH of the solution mixture and molarities of the reagents were kept constant as determined in the deposition of CdS thin films, only varying the $CdCl_2$ or $CdSO_4$ and $MnSO_4$ or $MnCl_2$ in the proportion of 1-x and x respectively. The molar concentration of thiourea was kept 1M constant. AR grade 99.99% purity chemicals were purchased from SD fine Chemical Limited, Mumbai. The stock solutions of 0.75 M $CdSO_4$, 0.75 M $MnSO_4$ and 1M (NH_2CSNH_2) were prepared. These solutions serve as Cd^{+2}, Mn^{+2} and S^{-2} ions respectively. The experimental solutions with different proportions have been taken in chemical bath for deposition of $Cd_{1-x}Mn_xS$ thin films.

Results and Discussion

Film Thickness:

Film thickness of the series of the films was estimated by using weight and difference method. The variation of film thickness with composition was shown in figure 1. The film thickness was found increased with increase in composition up to x=0.6. Above x=0.6 the variation of film thickness with composition was found constant.

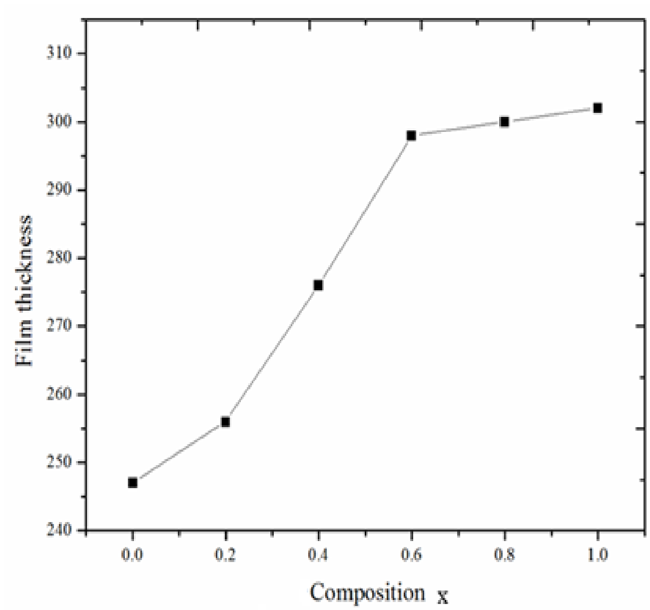

Figure 1 Film thickness (μm) is plotted as function of Composition x of $Cd_{1-x}Mn_xS$ thin films

Structural Studies of $Cd_{1-x}Mn_xS$ Thin Films:

The deposited thin films were characterized by X- ray diffractometer. The XRD pattern of $Cd_{1-x}Mn_xS$ thin films was presented in figure 2. All the films show polycrystalline crystal structure. The crystallites of the $Cd_{1-x}Mn_xS$ thin films were found decreased on increasing the doping concentration of Manganese. The obtained XRD spectra compared with standard JCPDS (ICCD -1999) international diffraction data. The observed diffraction patterns were well fitted with the standard JCPDS card data: 77-2306 of CdS and 76-2049 for MnS. $Cd_{1-x}Mn_xS$ thin films exhibit the hexagonal as well as cubic crystal structure. The prominent peaks were observed at (100), (002), (101), (203), (102), (110), (200) and (004) diffraction planes. The above designated peaks are assigned to 2θ = 25.31, 26.586, 29.59, 31.20, 36.06, 52.10 and 54.58 diffraction angles respectively.

The planes (101), (002), (100) exhibited the wurtzite (hexagonal type) structure. Anuar Kassim et. al. (2010) [27] have been reported the similar crystal structure of CdS. The effect of Mn doping was significantly observed on the XRD spectra of $Cd_{1-x}Mn_xS$ thin films. The increase of Mn doping concentration in the composite, intensity of XRD peaks corresponding to (100), (101), (203), (102), (110) and (200) reflections significantly decreased. However the intensity of (002) peak for x=0.6 was significant. The (002) peak provides the lattice matching to the chalcogenide component system such as $CuInGaSe_2$ and $CuIn(Se_xS_{1-x})_2$ which are used in solar cell devices for getting better solar cell efficiency (Chaki *et al.*, 2008). The MnS thin film with x=1.0 show the hexagonal as well as cubic polycrystalline nature.

The average grain size was calculated by using Scherrer's relation. The variation of average grain size verses composition (x) was displayed in table 1 and presented in figure 3. The nature of the curve indicates that grain size was observing increased on increasing composition (x). The significant increase in grain size was observed when the composition reached to 0.6.

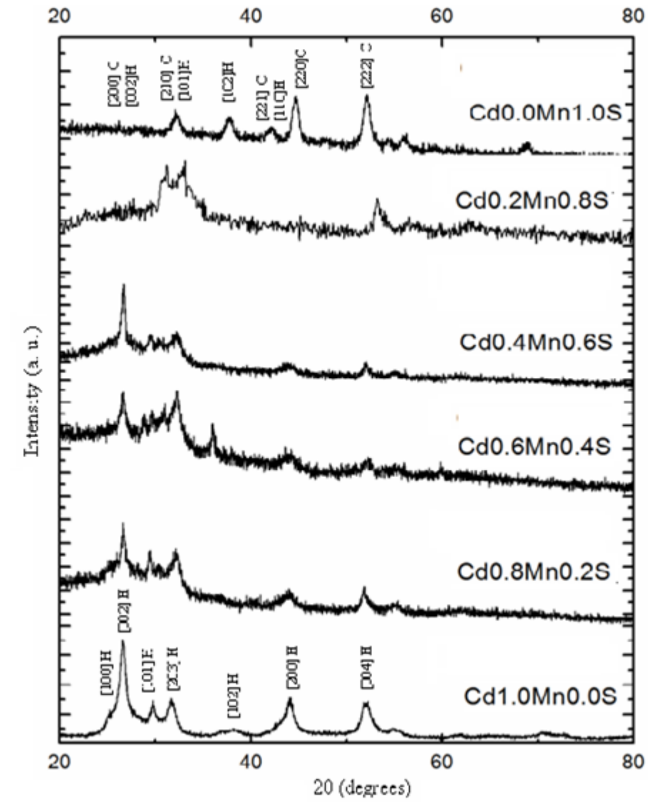

Figure 2 XRD patterns of $Cd_{1-x}Mn_xS$ thin films

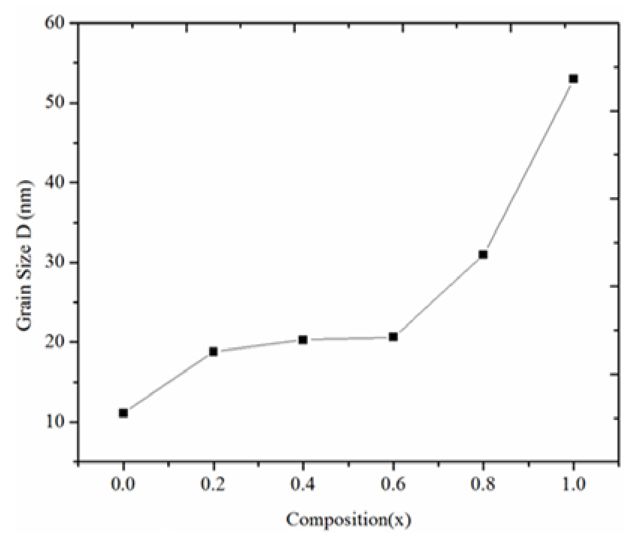

Figure 3. Variation of average grain size (nm) vs. Mn composition (x)

Composition (x)	Film Thickness (µm)	Grain size (nm)	Lattice Constant 'a'	Lattice Constant 'c'
0.0	247	11.10	4.104	6.588
0.2	256	18.81	4.112	6.686
0.4	278	20.3	4.121	6.682
0.6	294	20.63	4.112	6.686
0.8	300	30.97	4.113	6.686
1.0	306	53	4.069	6.621

Table 1: Variation of film thickness, Grain Size and lattice constants with composition x.

Absorption Study:

Optical absorbance data of $Cd_{1-x}Mn_xS$ thin films was recorded by using UV-Visible spectrophotometer (Systronics Double Beam 2201). The percentage absorption was plotted verses wavelength and presented in figure 4. All the film shows that optical absorption decreased significantly with increasing in wavelengths.

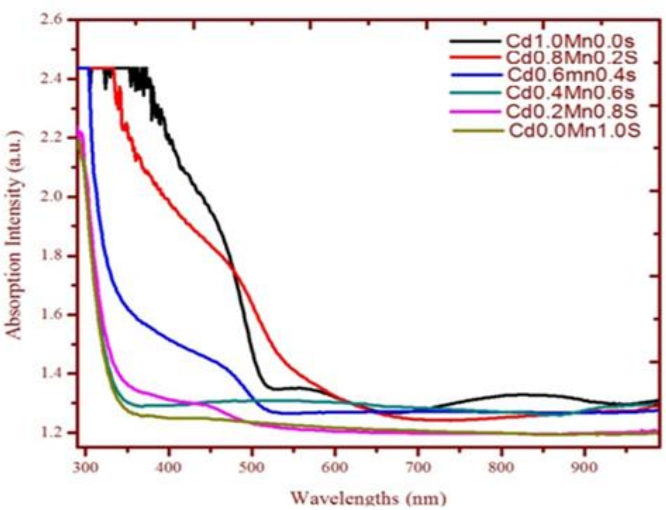

Figure . 4 Absorption Spectra of $Cd_{1-x}Mn_xS$ Thin Films

The absorption was observed higher in the 290 to 390 nm range. After 390 nm optical absorption was found significantly decreased and becomes nearly constant in the 390 to 990nm range for x=0.0 and x=0.2 compositions. The percentage (%) absorption was observed decreased with increase of Mn impurity in the $Cd_{1-x}Mn_xS$ thin films and can be clearly understand from figure 4 (approximately from 390 to 320 nm). The significant blue shifting was observed for the composition x=0.6, having very low absorption. (Borse *et al.*, 2007) reported that blue shifting of absorption edge towards shot wavelengths indicate that decrease in optical absorption in the blue portion of the solar spectrum (Gumus *et al.*, 2005; Munde and Ravangave 2017; Dargad 2015). The lower absorption in blue as well as ultraviolet portion of electromagnetic spectrum leads to conclusion that, the absorption of short wavelength photons may be reduced.

This leads to prevent absorption losses in $Cd_{1-x}Mn_xS$ thin film which is major advantage for solar cell application. It also concluded that the x=0.6 composition can be operate in the wide region of the electromagnetic spectrum from ultra violet to near infrared. Therefore $Cd_{1-x}Mn_xS$ film of composition x=0.6 may be very advantages as a solar cell window layer material.

The % transmittance was plotted versus wavelengths in nanometer and shown in Fig. 5. The optical transmittance was higher in the visible region (350 - 900 nm) and was found increased from 5 to 68 %. In the composition x=0.6, the observed transmittance was 48 %. However nature of the curve shows that this composition may be advantages for design of solar cell device application.

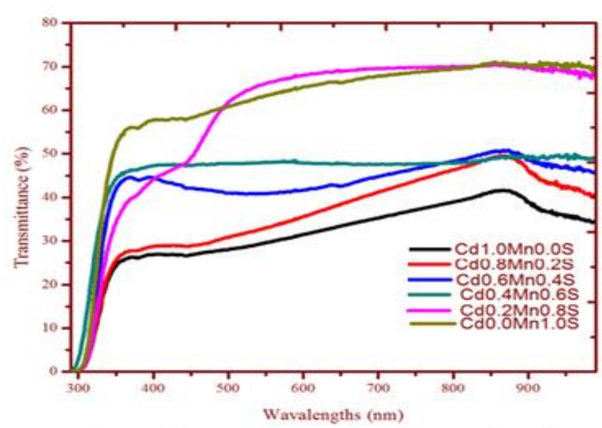

Figure 5 Percentage Transmittance plotted vs. wavelengths (nm) for $Cd_{1-x}Mn_xS$ thin films

Conclusion

- A series of $Cd_{1-x}Mn_xS$ thin films were deposited by chemical bath technique.
- The crystallite size of the $Cd_{1-x}Mn_xS$ thin films were decreased with increasing the doping concentration of Manganese.
- The significant increase in grain size was observed when the composition reached to 0.6.
- The absorption was observed higher in the 290 to 390 nm range.
- The optical transmittance was higher in the visible region.
- The films can be used in solar cell device applications.

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