Physical and Spectroscopic Characterization of Chemically Deposited Cd_{1-x}Mn_xs Thin Films

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Abstract: Chemical bath deposition technique (CBD) was used for deposition of $Cd_{1,x}Mn_x$ s Thin Films. Initially bath parameters were optimized by physical observation of sustainable Deposition of CdS thin films. The deposited films have been characterized by using X-ray diferactometer, Scanning electron microscopy, EDAX and spectrophotometer. The film thickness was estimated using weight and difference method. Film thickness was found increased with increase in Mn concentration in CdS material. All the films show polycrystalline crystal structure. The observed diffraction patterns were well fitted with the standard JCPDS card data: 77-2306 of CdS and 76-2049 for MnS. $Cd_{1x}Mn_xS$ thin films exhibit the hexagonal as well as cubic crystal structure. The micrograph shows that the films deposited cover the whole substrate with uniform surface morphology. The significant effect of Mn doping has been observed from SEM micrographs of the $Cd_xMn_{1-x}S$ thin film. Very small amount of Mn doping can show significant change in the microstructure of the SEM. The nanowire morphology was found changed into granular morphology. The absorption spectra show significant blue shifting for the composition x=0.8, having very low absorption. The optical transmittance was higher in the visible region (350 - 900 nm) and was found increased from 5 to 68 %. The optical band gap was found increased on Mn doping. The x=0.8 exhibit 3.58eV band gap. The maximum transmittance and higher band gap shows that Cd0.2Mn0.8S Composition can be used for solar cell applications. Key Words: CdMnS thin films, Chemical Bath Deposition, Optical Properties.

I. Introduction

The area of research is expanding contuniously in development of selected combinations of chalcogenide semiconductor thin films to be operate over wide range of solar 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 [1-5]. The best of our knowledge is concerned, very few work have been reported on the study of $Cd_{1-x}Mn_xS$ ternary system. The variation of optical band gap and structure have been reported using deposition temperature of CBD deposited MnS thin films [6].

Various methods have been employed for deposition of CdS and CdS doped thin films. Chemical Bath Deposition is simple, very economic, less instrumentation, non-vacuum easy to operate and needs small space. It is suitable for any type of substrates [7]. L. S. Ravangave and U. V. Biradar (2013) reported the synthesis of high resistivity $Cd_xZn_{1-x}S$ thin films using CBD technique and dark resistivity of CdS thin film, order of ≥ 105 Ω cm reported [8]. In the present work we employed CBD technique for deposition of Cd_{1-x} Mn_xS thin films and study the effect of Mn concentration on structural, Morphological and optical properties.

II. Material And Method:

Initially the bath parameters (Temperature, pH, molar concentration and deposition time) were optimized by physical observation of deposited CdS thin films. The optimized parameters were used for deposition of $Cd_{1-x} Mn_x S$ thin films. The high quality analytical grades Chemical were used. CdSO₄ and MnSO₄ have been used as Cd⁺⁺ and Mn⁺⁺ ion sources. Thiourea (NH2)2 CS is used as S ion source. The stock solutions of 0.75 M CdSO4, 0.75 M MnSO4 and 1M (NH₂CSNH₂) were prepared. The experimental solutions with different proportions of MnSo₄ (x=0.0, 0. 2,0.4,0.6,0.8 and 1) have been taken in chemical bath for deposition of Cd_{1-x}Mn_xS. Six baths were prepared. The pH of the entire bath kept at optimized value 11 by drop wise addition of NH₄OH. The baths were kept in constant temperature bath maintained at 55±2. The pre cleaned substrates were removed and wished twice using deionized water. The deposited films were dried in air and annealed at 100 °C for 1 hours. Above prepared Cd_{1-x}Mn_xS films were characterized using X-ray diffractometer, SEM, spectrophotometer.

I Physical Study:



III. Results And Discussion:

Fig. 1 Thickness of the Cd1-xMnxS thin films vs Mn Concentration

Figure 1 shows that variation of film thickness verses Mn content in the CdS material. It was observed that film thickness increased on do dopping concentration of $MnSO_4$ after x=0.2 composition.

II XRD Study:

Figure 2 represents the XRD spectra of deposited $Cd_{1-x}Mn_xS$ thin films. 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 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 $2\theta = 25.31$, 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. Rajathi S. et. al. 2012) [9] and Kumar T. et. al. (2009) [10] 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 fig. 3 represents the variation of grain size with molar concentration of Mn. The grain size was estimated by using equation(1). It was found that grain size increases wit increasing Mn content in the composite from 26 to 58 nm. The Cd0.2Mn0.8S sample exhibits 44nm grain size. This leads to conclusion that the deposited films are nano structured.





Fig.2 XRD pattern of deposited $Cd_{1-x}Mn_xS$ thin films.

II Surface Morphology of Cd_{1-x}Mn_xS Thin Films:

In order to study the influence of Mn doping on the surface morphology of $Cd_xMn_{1-x}S$ thin film the deposited film were scanned by using Scanning electron microscopy (SEM Model: Quanta 200 ESEM). The SEM images of six different $Cd_xMn_{1-x}S$ thin films were presented in figures 3.27 (for x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). All the films were scanned at 10000 magnifications. The micrograph shows that the films deposited cover the whole substrate with uniform surface morphology. The excellent wire type morphology was found changed to flower type and then granules as the increase in Mn concentration. The Cd0.2Mn0.8S composition shows excellent flowers morphology with uniform regularity.



Fig. 4 Represents the SEM Images of $Cd_{1-x}Mn_xS$ thin films

III Optical Study of Cd_{1-x}Mn_xS Thin Films:

Optical absorbance data of $Cd_xMn_{1-x}S$ 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. The significant blue shifting was observed for the composition x=0.6, having very low absorption. Borse S. V. 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 [11]. 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 $Cd_xMn_{1-x}S$ thin film which is major advantage for solar cell application. It also concluded that the x=0.8 composition can be operate in the wide region of the electromagnetic spectrum from ultra violet to near infrared. The % transmittance was plotted

versus wavelengths in nanometer and shown in Fig. 3.30. The optical transmittance was higher in the visible region (350 - 900 nm) and was found increased from 5 to 70 %. In the composition x=0.8, the observed transmittance was 70 %. However nature of the curve shows that this composition may be advantages for design of solar cell device application. The variation of band gap verses composition was presented in fig 7. The band gap was obtained from absorption data by plotting $(\alpha hv)^2$ on ordinate and hv on abscissa and using equation (2)

where Eg is optical band gap energy, hv is the photon energy, n is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and $Cd_xMn_{1-x}S$ thin film with composition x=0.8 shows maximum 3.58 eV band gap. The composition x=0.8 exhibit maximum band gap 3.58 eV and maximum blue shift of absorption edge towards short wavelength indicate that the composition is to be applicable as window layer. Similar finding were reported by Bhattacharjee et al., (2002) [12].



IV. Conclusion

 $Cd_xMn_{1-x}S$ thin films successfully deposited using chemical bath deposition technique. The XRD spectra concluded that hexagonal symmetry of the deposited $CdxMn_{1-x}S$ compositions. The SEM images shows improvement of surface morphology on addion of Mn content. The study of optical spectra sws that present composition may be used in the application of solar cell design.

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