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Optimization of Growth Parameters for Deposition of $Cd_{1-x}Mn_xS$ (x=0.4) Nanocrystalline Thin Films by Chemical Bath Deposition Technique

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ABSTRACT

The growth and study of $Cd_{1-x}Mn_xS$ (x = 0.4) nanocrystalline thin films on glass substrate using chemical bath deposition techniques with the Mn doping has been presented. We report the film deposition and optimization of the growth parameters that maximizes the thickness of the deposited film in alkaline solutions. The preparative parameters such as bath temperature, deposition time, pH, precursor concentration etc. were optimized to get good quality films. The deposited film showed an optical transmittance of about 80% with band gap 2.81 eV for a molar composition of x=0.4. The film thickness was found decreased with increase in Mn^{2+} concentration. Further, deposited films were characterized by using UV-visible spectrophotometer. The film thickness was estimated using gravimetric weight difference method. The composition of the films was estimated by using EDAX and surface morphology was studied by using FESEM characterizations.

1. Introduction

The groups II-VI compounds have considerable interest as they have application in large variety of area in semiconductor science and technology [1-3]. Cadmium manganese sulphide (CdMnS) belongs to II-VI group compound [4]. Nanocrystalline thin film of CdMnS can be used as window material for solar cells [5,6]. Its wide band gap is important for their application in solid state solar cells, LEDs and non-linear optical devices [7-9].

The use of CdMnS thin film attracted much attention because of its easily tunable energy gap and lattice parameter by varying the material compositions [10]. Many researchers are tried to deposit CdMnS thin films from an aqueous alkaline and non-aqueous medium [11]. A variety of techniques have been widely used in the fabrication of CdMnS thin films like, electro-deposition, spray pyrolysis, chemical bath deposition (CBD), etc.,. Nowadays, development in nanoscience and nanotechnology for industrial applications requires efficient, low temperature and low-cost deposition techniques to obtain desired quality thin films. CBD is one of the important aqueous medium processes and can be performed using a range of precursors and deposition conditions like, temperature, time, concentration of reactants etc. The CBD technique is a simple, low cost method to form uniform, adherent and reproducible large area thin film especially used in solar cells and optoelectronics [12].

We report here the alkaline deposition of CdMnS thin films and investigation of effect of various deposition parameters on film properties. The quality of thin films prepared by CBD technique critically depends on growth conditions such as temperature of bath, concentration of precursors, pH of solution and nature of complexing agent [13-15]. Further, obtained films were characterized by using UV-visible spectrometer, FESEM and EDAX to investigate the various optical, structural and elemental compositions. The thickness of the films was calculated by using gravimetric method.

2. Experimental Methods

All chemicals used in present work were AR grade without any further purification. For deposition of $Cd_{1-x}Mn_xS$ (x = 0.4) thin films, cadmium chloride ($CdCl_2$) and manganese chloride ($MnCl_2$) have been used as Cd^{2+} and Mn^{2+} ion sources, respectively. Thiourea $(NH_2)_2CS$ is used as S^- ion source and double distilled water used as solvent for the preparation of solution. The pH of bath solution was adjusted by drop wise addition of liquid ammonia (NH_3). All these chemicals were thoroughly mixed and stirred with a glass rod. The molar concentration of precursors was varied from 0.25 M to 1.5 M in steps of 0.25 keeping ammonia solution concentration constant. To obtain the optimal temperature for good quality films, the bath temperature was varied from 50 °C to 90 °C in interval of 10 °C. To optimize the concentration of Cd^{2+}, Mn^{2+} and S^- ion precursors in bath solution, a 25 mL beaker was used as container for the reaction. This container acts as chemical deposition bath. Cadmium chloride, manganese chloride and thiourea were first mixed in 25 mL beaker. Afterwards ammonia solution is added drop wise in coating solution to control the pH. The pre-cleaned glass substrates were kept inclined in the chemical bath. This 25 mL beaker, container was immersed in a constant temperature water bath maintained at 80 °C for 60 min. After deposition of CdMnS thin films, the substrates were taken out, washed with distilled water and then dried.

3. Results and Discussion

The thickness (t) of the film is calculated using gravimetric method by using following standard relation,

$$t = \frac{m}{A\rho} \quad (1)$$

where, m is mass difference of films weighted before and after deposition, A be the area of deposition and ρ is the material density. The thickness of obtained films is observed in the range of 700-2500 nm. The variation of $Cd_{x-1}Mn_xS$ (x=0.4) film thickness for various concentrations of precursors is shown in Fig. 1. It is observed that initially, film thickness increases with precursor's concentrations and attains the maximum thickness (~2500 nm) for 1 M concentration. Beyond 1 M concentration, the film thickness is observed to be decreased.

In order to study the effect of deposition time on film thickness, the films were deposited for range of deposition time. The Fig. 2 shows the variation of film thickness as function of deposition time. Initially film thickness increases, as time increases the film layer goes increasing and well adherent to the substrate. Further, time increases beyond 60 min., film thickness decreases slowly. The thickness of film was found to vary

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between 1500 nm to 2200 nm with deposition time 30-105 min. The highest thickness 2200 nm is obtained for 60 min. of deposition at constant temperature 80 °C.

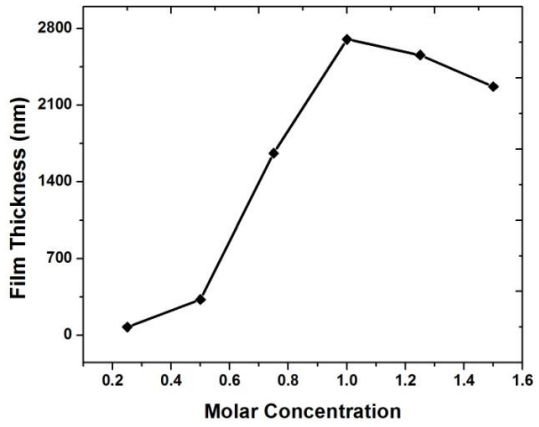

Fig. 1 Variation in film thickness as function of molar concentration

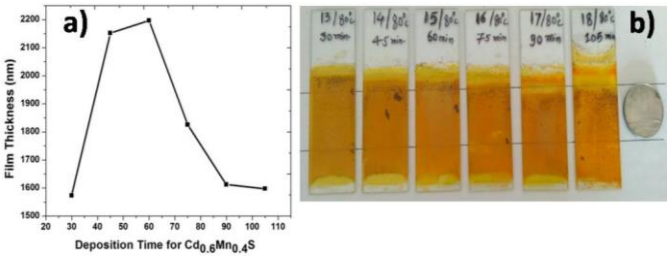

Fig. 2 Variation in film thickness as function of deposition time

In chemical bath deposition process, bath temperature plays important role to control film thickness. Fig. 3 shows the variation of film thickness as a function of bath temperature. The bath temperature recorded from 50 °C to 90 °C. The film thickness observed to be increased for increase in bath temperature from 50 °C to 80 °C. Highest film thickness optimized for film deposited at 80 °C. Beyond optimized temperature, thickness drops due to the less adhesion to the substrate surface. Beyond >80 °C temperature, the film thickness decreases because at higher temperature the rate of nuclei formation from Cd^{2+}, Mn^{2+} and S^{2-} ions increases and bath solution becomes deficient in Cd^{2+}, Mn^{2+} and S^{2-} ions, resulting in lowering thickness. Also, the solubility constants are depending on bath temperature [16].

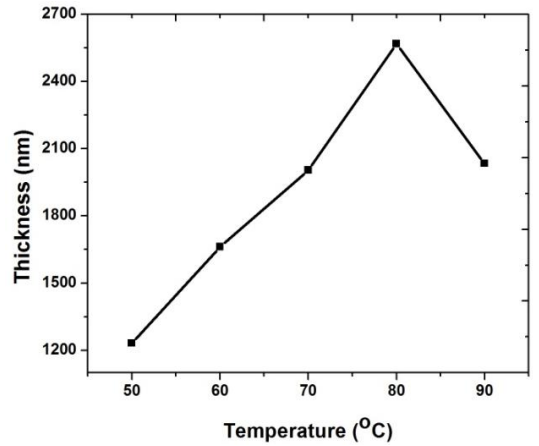

Fig. 3 Variation in film thickness as a function of bath temperature

The effect of complexing agent liquid ammonia on film thickness is shown in Fig. 4. The film thickness increases as pH of bath solution increases from 7.5 to 10. Afterwards, pH tends to more basic nature, the film thickness observed to be decreased from 2500 nm to 1900 nm. The maximum thickness of thin film was obtained at pH=10. Initially adherent film of optimized thickness of 2500 nm was obtained at 1 M concentration of precursors for 60 min deposition time at bath temperature of 80 °C.

Fig. 5 shows EDAX spectra of deposited CdMnS film. It confirms the formation of CdMnS in film matrix. The Cd, Mn and S ratios for the film have been determined by EDAX technique. No appreciable changes were observed in initial composition taken in reaction bath and in final composition of elements in the film formation. Inset FESEM micrograph of nanoflower structure of CdMnS films. Micrograph shows the uniform distribution of CdMnS over the substrates. FESEM micrograph was used to calculate the grain size of the film by using Cottrell method [17]. The average grain size obtained from this method varies from 70-95 nm. The grain size falls mostly in nanometer range.

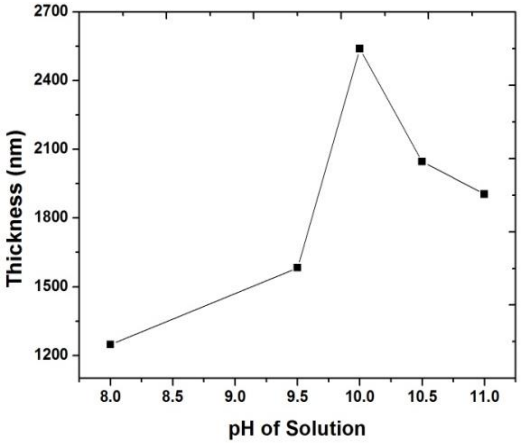

Fig. 4 Effect of variation in pH of solution on film thickness

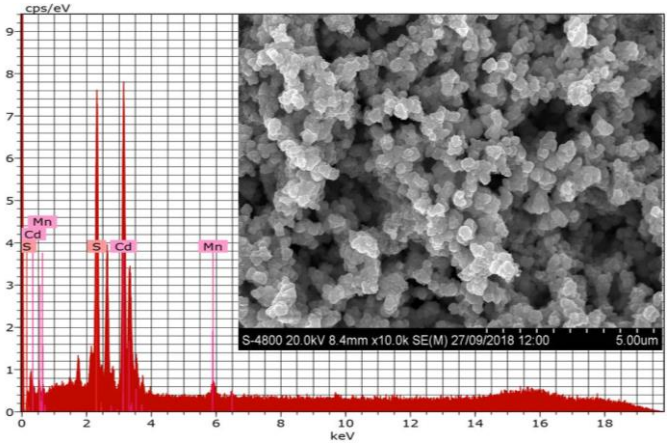

Fig. 5 EDAX spectra of CdMnS. Inset image shows FESEM micrograph of nanoflower structure of CdMnS films

The absorption spectra of deposited samples were obtained at room temperature as function of wavelength. The optical absorption of CdMnS film was measured in the wavelength range 300-800 nm regions. Fig. 6(a) shows the variation of optical absorbance with wavelength. The optical properties of as deposited CdMnS thin films was studied at room temperature using UV-visible spectrophotometer in the wavelength range 300-800 nm.

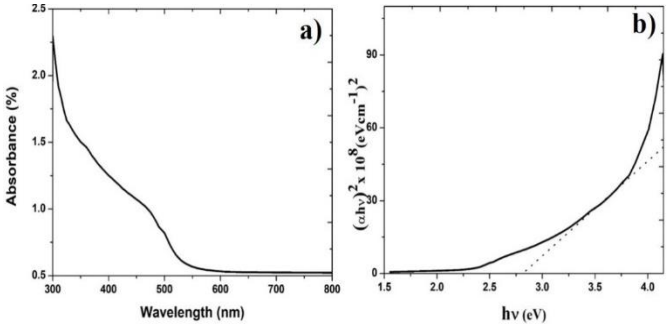

Fig. 6 a) Absorption spectra of $Cd_{1-x}Mn_xS$ (x = 0.4) film and b) energy band gap of $Cd_{1-x}Mn_xS$ (x = 0.4) films

The absorption spectra were used to calculate energy band gap. The plot of square of the absorption coefficient versus the photon energy is shown in Fig. 6(b). The band gap of the CdMnS film was determined by using Tauc plot and is observed to be 2.81 eV at the intercept of the extrapolation on photon energy axis.

The composition of the ternary CdMnS was estimated from the Vegards formula [14], $E_g = 2.42 + 0.69x + 0.62x^2$, where, $E_g(x)$ is the band gap of the composition of the ternary CdMnS defined at x. The calculated value of x was 0.4288 which is in good agreement with theoretical value of x≈0.40.

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4. Conclusion

The $Cd_{1-x}Mn_xS$ (x=0.4) films were successfully deposited using chemical bath deposition technique. In order to get good quality films, bath temperature, pH, deposition time, and molar concentration is optimized. The optimized optimum temperature is 80 °C; pH of coating solution is in the range of ~10-10.5. The optimum film thickness was obtained for precursors concentrations of 1 M and 60 min. deposition time. The formation of CdMnS is confirmed through EDAX analysis and nanocrystalline structure of film is studied using FESEM. The grain size as calculated by FESEM were in the range of 70-95 nm. The obtained band gap for composition x=0.4 was 2.81 eV. The obtained films have wide area application in semiconductor technology like, magnetic material, solar cells, sensors, etc.,.

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References

[1] R.N. Bhargava, Materials growth and its impact on devices from wide band gap II–VI compounds, J. Cryst. Growth 86 (1988) 873-879.
[2] I. Hernandez-Calderon, Optical properties and electronic structure of wide band gap, in: M.C. Tamargo, II-VI Semiconductor materials and their applications, Taylor and Francis, New York, 2002, pp.113 -170.
[3] B.S. Munde, R.B. Mahewar, L.S. Ravangave, Study of spectroscopic properties of $Cd_{0.6}Mn_{0.4}S$ chemical bath deposited thin film for solar cell applications, Int. J. Res. Anal. Rev. 5 (2018) 962-966.
[4] B. Krishnan, S. Shaji, M.C. Acosta-Enríquez, E.B. Acosta-Enríquez, R. Castillo-Ortega, et al., Group II–VI semiconductors, in: M. Pech-Canul, N. Ravindra (Eds), Semiconductors, Springer, Cham, 2019, pp.397-464.
[5] J.A.R. Baltazar, I.C. Villanueva, R.R. Bon, F.J.W. Rodriguez, A. Cuán, et al., Study of the diluted magnetic semiconductor CdMnS synthesized by magnetic field and chemical bath, XIV Int. Eng. Cong. (CONIIN) IEEE, Universidad Autonoma de Queretaro, Queretaro, Mexico, 2018.
[6] S.M. Al-Jawad, Optoelectronic characteristics and optical properties for Cd1-xMnxS nanocrystalline thin films prepared by chemical bath deposition, Int. J. Appl. Innov. Eng. Manag. 3 (2014) 329-333.
[7] F. Iacomi, I. Salaoru, N. Apetroaei, A. Vasile, C.M. Teodorescu, D. Macovei, Physical characterization of CdMnS nanocrystalline thin films grown by vacuum thermal evaporation, J. Optoelectron. Adv. Mater. 8 (2006) 266-270.
[8] D.H. Kim, D.J. Lee, N.M. Kim, S.J. Lee, T.W. Kang, et al., Ferroelectric and magnetic properties of CdMnS films prepared by coevaporation, J. Appl. Phys. 101 (2007) 094111:1-5.
[9] H. Sekhar, G.T. Rao, P.H. Reddy, D.N. Rao, Preparation, structural and its enhanced green upconversion luminescence in rare-earth doped CdMnS nanopowders, J. Alloy. Compd. 562 (2013) 38-42.
[10] S.I. Gubarev, Anomalous magneto-optical properties of $Cd_{1-x}Mn_xS$ crystals, J. Lumin. 52 (1992) 193-200.
[11] C.I. Oriaku, F.I. Ezema, J.C. Osuwa, Fabrication and optical constants of CdMnS ternary thin films deposited by chemical bath, Pac. J. Sci. Technol. 10 (2008) 413-416.
[12] T. Schneller, R. Waser, M. Kosec, D. Payne, Chemical solution deposition of functional oxide thin films, 1st Ed., Springer, London, 2013.
[13] R.S. Mane, C.D. Lokhande, Chemical deposition method for metal chalcogenide thin films, Mater. Chem. Phys. 65 (2000) 1-31.
[14] K.U. Isah, N. Hariharan, A. Oberafo, Optimization of process parameters of chemical bath deposition of $Cd_{1-x}Zn_xS$ thin films, Leonardo J. Sci. 12 (2008) 111-120.
[15] S.S. Kale, C.D. Lokhande, Thickness-dependent properties of chemically deposited CdSe thin films, Mater. Chem. Phys. 62 (2000) 103-108.
[16] S. Licht, Aqueous solubilities, solubility products and standard oxidation reduction potentials of the metal sulfides, J. Electrochem. Soc. 135 (1988) 2971-2975.
[17] A. Cottrell, An introduction to metallurgy, Universities Press, India, 1990.

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