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## Physical Properties of MnS Films Deposited by Nebulizer Technique

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### ABSTRACT

Manganese containing Diluted Magnetic Semiconductors (DMS) have recently attracted much attention due to their potential applications in solar selective coatings, solar cells, sensors, photoconductors etc. Among the available DMSs, Manganese Sulphide (MnS) is broadly studied because of its magneto-optical properties and wide band gap nature. In present study, first time, MnS thin films were deposited onto glass substrates by nebulizer technique using the precursor solutions of manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) and thiourea ( $\text{SC}(\text{NH})_2$ ) at a temperature of  $350^\circ\text{C}$ . The molar concentrations were varied from 0.25-1.5 M. The structural, optical and morphological studies of deposited films were carried out using x-ray diffractometer, UV-Vis-NIR spectrophotometer and scanning electron microscope, respectively. X-ray diffraction results revealed the crystallinity of MnS films improved with increasing precursor solution concentration. The absorption edges shift towards lower wavelength region, indicating a systematic raise in energy band gap with increasing precursor solution concentration up to 1.0 M which attributed to the lower defect density near the band edge. The broad emission peak at 420 nm corresponding to the band edge emission was observed in the PL spectra. The morphological study revealed the polycrystalline nature of the deposited MnS thin film.

**Key words:** Diluted magnetic semiconductors, nebulizer technique, structural property, optical property, surface morphology

### INTRODUCTION

Diluted Magnetic Semiconductors (DMS) are used in a wide range of applications owing to their unique electronic, optical and magnetic properties. Manganese Sulphide (MnS) is one of the promising DMS materials and has been extensively studied because of its unique magneto-optical properties. In DMS, the band electrons and holes are strongly interact with the localized magnetic moments and cause a variety of interesting phenomena (Goede and Heimbrodt, 1988). Generally, MnS films can be found in several polymorphic forms viz., rock salt type structure ( $\alpha$ -MnS), zinc blende ( $\beta$ -MnS) structure and wurtzite ( $\gamma$ -MnS) structure (Gumus *et al.*, 2007). It has been found that  $\beta$  and  $\gamma$ -MnS can transform irreversibly to stable  $\alpha$ -MnS in the temperature range of 373-673 K (Skromme *et al.*, 1995; Pramanik *et al.*, 1988). Till now, various methods have been adopted for the preparation of MnS thin films, such as Molecular Beam Epitaxy (MBE) (David *et al.*, 2003) thermal vacuum evaporation (Goede and Heimbrodt, 1988; Sombuthawee *et al.*, 1978), rf sputtering (Mayen-Hernandez *et al.*, 2003; Oidor-Juarez *et al.*, 2002), microwave irradiation (Wang *et al.*, 2005), Chemical Bath Deposition (CBD)

(Lokhande *et al.*, 1998; Fan *et al.*, 2003; Gumus *et al.*, 2007), SILAR method (Pathan *et al.*, 2007) and solvothermal method (Mu *et al.*, 2008). In the present investigation, first time we have attempted for the preparation of manganese sulphide thin films using nebulizer technique. This method is probably the most economical one for making thin films in addition to its relative ease in the preparation of large area MnS films compared with other sophisticated techniques (Mekhnache *et al.*, 2011; Yang *et al.*, 1998). In nebulizer technique, the film is prepared mainly by the decomposition of reactants on a substrate upon heat treatment. The advantage of nebulizer technique over conventional pneumatic spray pyrolysis is its low material consumption with better control of the spray and soft carrier gas flow which allows the deposition of very thin layers of pinhole free uniform thickness. The MnS films were prepared on glass substrates using nebulizer technique by varying the concentration of precursor solution at 350°C. The structural, optical and surface morphological properties of grown MnS films were studied.

## MATERIALS AND METHODS

Manganese sulphide thin films were prepared by employing the precursor solutions of manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) and thiourea ( $\text{SC}(\text{NH}_2)_2$ ) at different molar concentrations from 0.25-1.5 M. The precursor solution was prepared by dissolving equimolar manganese chloride and thiourea in 20 mL of de-ionized water and continuously stirred for 10 min at 50°C resulting a clear and homogenous solution. The pH of the precursor solution is 7. The nebulizer was connected with an air compressor and spray nozzle. The ultrasonically cleaned glass substrate was kept on the furnace and heated to 350°C. The prepared precursor solution was sprayed uniformly onto heated glass substrate. The solution flow rate was controlled ( $0.5 \text{ mL min}^{-1}$ ) by keeping the compressed air at a constant pressure of  $1.2 \text{ kg cm}^{-2}$ . The nozzle to substrate distance was maintained at 4 cm. The deposited films are homogeneous, pinhole free and well adherent to the substrate surface.

The structural property of thin MnS films were studied by X-Ray Diffraction (XRD) using  $\text{Cu-K}_\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation source (X'pert Pro PANanalytical) over a  $2\theta$  scan range of 10-80°. The effect of molar concentration on the changes in optical properties of MnS films were studied using UV-Vis-NIR spectrophotometer (Ocean optics HR 2000) in the wavelength range of 300-1000 nm. Surface morphological studies were carried out using a high resolution scanning electron microscope (HRSEM; FEG QUANTA 250). The room temperature photoluminescence (PL) study was performed using a fluorescence spectrophotometer (Varian Cary Eclipse).

## RESULTS AND DISCUSSION

**X-ray diffraction study:** Figure 1 shows the XRD patterns of manganese sulfide thin films deposited at 350°C by varying the precursor solution concentrations viz., 0.25, 0.5, 1.0 and 1.5 M. It is observed that all the deposited MnS films are found to be crystalline nature. The observed lattice spacings (d) match well with JCPDS data (card No.: 40-1288; 40-1289) corresponding to  $\beta$ -MnS (cubic) and  $\gamma$ -MnS (hexagonal) systems. One can observe from XRD patterns that the intensity of peaks increase with increasing molar concentration which revealed the enhancement in degree of crystallinity of films with solution concentration. However, a peak corresponding to MnO was observed in the XRD pattern ( $2\theta \approx 18.17^\circ$ ) (JCPDS card No.: 65-1844) for the film deposited at lower molar concentration and the intensity of this peak diminishes with the increase in molar concentration. This may be due to the less number of sulphur ions in the lower concentration to react with Mn ions. The crystallite size (D) of thin film was calculated using  $0.94\lambda/\beta\cos\theta$  (Scherrer formula), where  $\beta$  is Full Width at Half Maximum (FWHM) (in radians) of the XRD peak (Yoo *et al.*, 1990). The strain ( $\epsilon$ ) was determined using the equation:

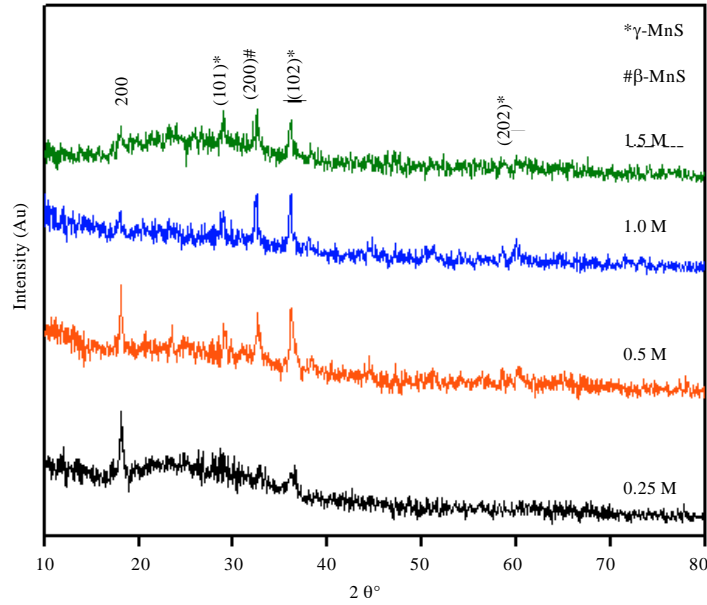


Fig. 1: X-ray diffraction patterns of MnS thin films deposited at various concentrations

Table 1: Structural and optical parameters of MnS thin films

Precursor solution concentration (M)	Crystallite size (nm)	Strain ( $\epsilon$ )	Energy band gap (eV)
0.25	10	0.09	2.43
0.5	44	0.07	2.70
1.0	56	0.04	3.27
1.5	21	0.06	2.33

$$\epsilon = \frac{\beta \cos \theta}{4}$$

The results are presented in Table 1. The improvement in the degree of crystallinity of films on glass substrate is demonstrated by an increase in the crystallite size with solution concentration. However, there is a slight reduction in the crystallite size of the film deposited at higher concentration of the solution (1.5 M) which may be due to the improper decomposition of manganese and sulphur ions. The decrease in strain with increasing solution concentration indicates the formation of high quality thin films. Generally, the origin of the strain is related to a stress generated by lattice misfit which depends on the deposition conditions. This type of stress has two components: Thermal stress due to the difference between the expansion coefficients of the film and substrate and internal stress due to the crystallographic flaws created in the film during deposition.

**Optical properties:** Figure 2 shows the absorbance spectra of MnS thin films deposited at different molar concentrations in the wavelength range of 300-1000 nm. It may be mentioned that the optical absorption spectra recorded in the visible and near infrared regions are related to the electronic transitions which are useful in understanding the electronic band structure of the

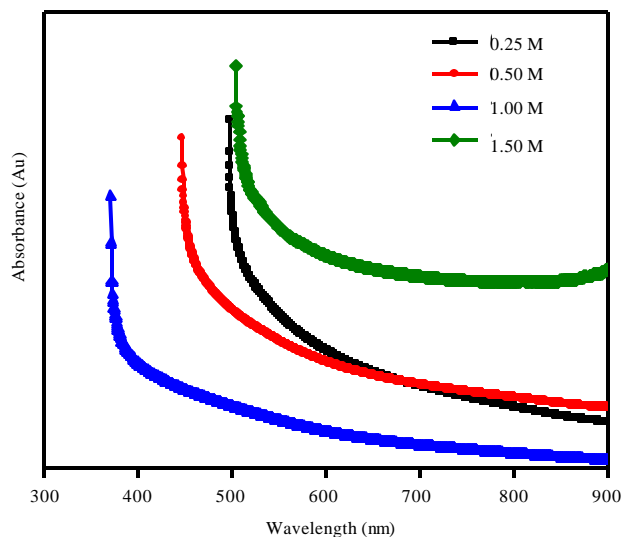


Fig. 2: Optical absorbance spectra of MnS thin films deposited at various concentrations

semiconducting films (El-Ocker *et al.*, 1990). It is observed that the films possess strong absorption in the visible region. In addition, the absorbance decrease with increasing molar concentration up to 1.0 M and further raise in solution concentration to 1.5 M causes the increase in absorption. It is also clear from the spectra that the absorption edges shift towards lower wavelength region, indicating a systematic raise in energy band gap with increasing precursor solution concentration up to 1.0 M due to the lower defect density near the band edge. This inference is consistent with our XRD results where we observe a grain growth in MnS films as a function of solution concentration up to 1.0 M. However, the absorption edge shifts to higher wavelength side for the MnS film deposited at 1.5 M. This could be attributed to the increased defect density near band edge which is in conformity with the rise in strain and fall in crystallite size of the film deposited at 1.5 M as observed from the XRD data (Table 1). The energy band gap,  $E_g$ , of the film was extracted from the traditional Tauc plot of  $(\alpha h\nu)^2$  versus photon energy  $E(= h\nu)$  and is shown in Fig. 3 as a function of the solution concentration. It may be mentioned that MnS is a direct band gap system and hence the Tauc plot is expected to show a linear behaviour in the higher energy region which corresponds to a strong absorption near the absorption edge. Extrapolation of the linear portion to zero absorption edge results in  $E_g$  of the films and the values are presented in Table 1. Initially, the energy band gap increased from 2.43-3.27 eV with increasing solution concentration up to 1.0 M which revealed the enhancement in crystallization of the films. Further increase in solution concentration (1.5 M) leads to the reduction in  $E_g$  of the film from 3.27-2.33 eV which attributed to the presence of unstructured defects and the increase in density of localized states (El-Zahed *et al.*, 2002).

**Photoluminescence study:** Figure 4 represents the room-temperature PL spectra of MnS thin films deposited at different molar concentrations of 0.25, 0.5, 1.0 and 1.5 M. The films were excited in the wavelength of 210 nm. The PL intensity is determined by the radiative recombination of excitons. The photoluminescence process is a charge transfer process, since the photo-luminescence emission associated with the combination of electrons from the conduction band, the holes in the

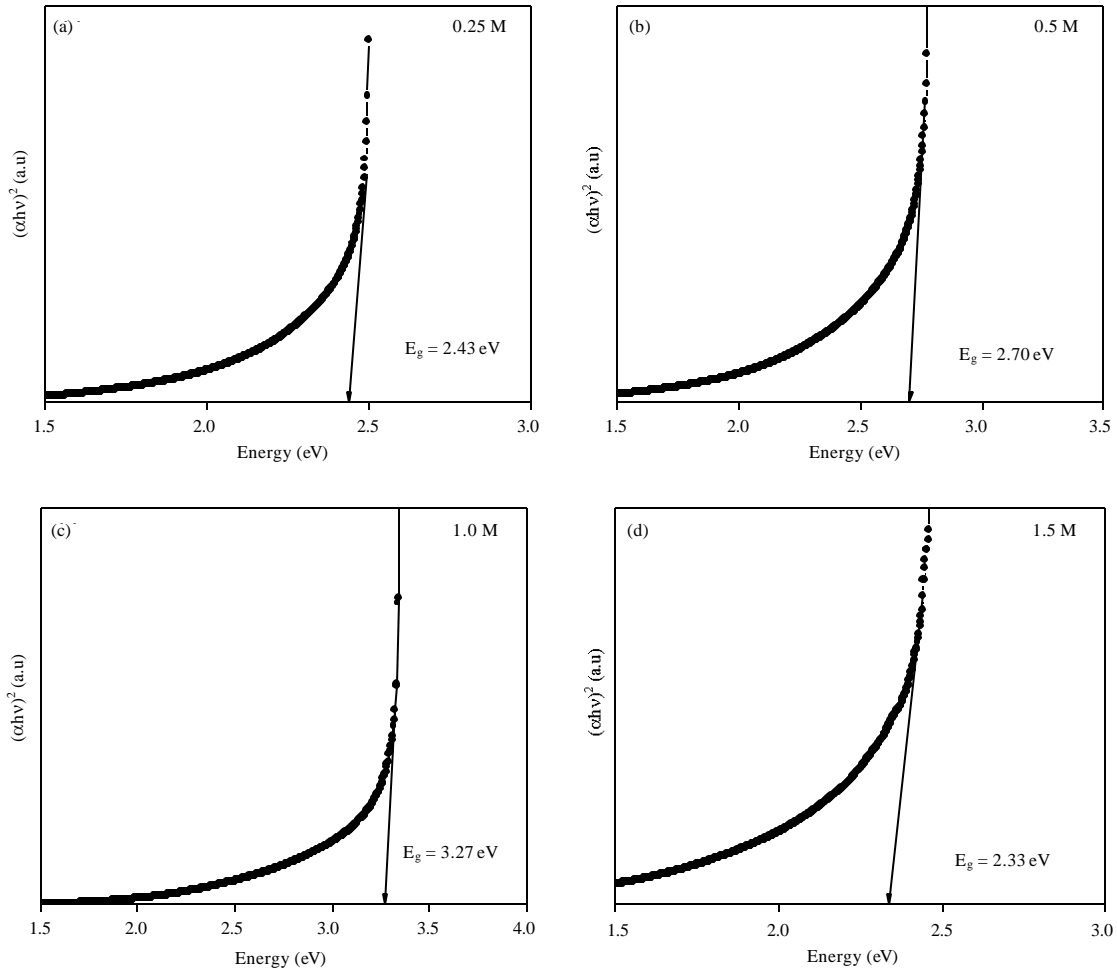


Fig. 3(a-d): Tauc plot of MnS thin films deposited at various concentrations (a) 0.25, (b) 0.5, (c) 1.0 and (d) 1.5 M

valence band and the change of the near-band-edge (Peng *et al.*, 2000; Zhao *et al.*, 2008). One can easily see from PL spectra that the broad emission peak at 420 nm (3 eV) corresponds to the band edge emission which is similar to the band gap of the bulk MnS (Tao *et al.*, 2007). We do not observe any defect related emission in PL spectra which confirmed the better quality of deposited films. In addition, it is observed from the photoluminescence spectra that the slight shift in peak position towards lower wavelength region upon increasing the solution concentration up to 1.0 M (due to band gap widening) and the further raise in concentration to 1.5 M causes the PL peak shift towards higher wavelength side (due to band gap narrowing). This is indeed consistent with our optical energy band gap data, where we observe both the band gap widening and narrowing with molar concentration.

**Surface morphological study:** High Resolution Scanning Electron Microscope (HRSEM) was used to study the surface morphology of MnS films. Figure 5a-b shows the HRSEM images of MnS films deposited at 0.5 and 1.0 M concentrations. It is observed from the micrograph of the film

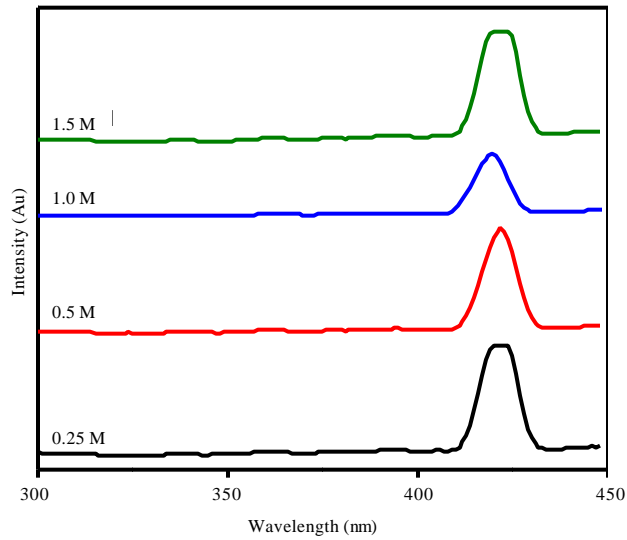


Fig. 4: Photoluminescence spectra of MnS thin films deposited at various concentrations

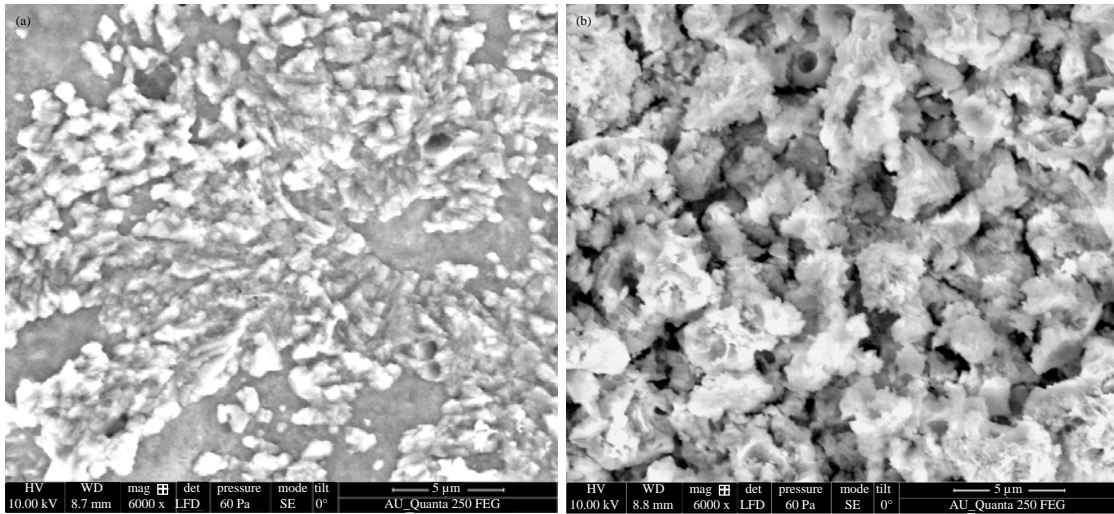


Fig. 5(a-b): SEM images of MnS films deposited at various concentrations: (a) 0.5 M and (b) 1.0 M

deposited at 0.5 M (Fig. 5a) that the compact and randomly oriented particles were distributed on the substrate surface. These particles are coalesce to form the larger crystal grains with different sizes when the concentration was increased to 1.0 M (Fig. 5b) which revealed the better crystalline nature of the films. This is also in conformity with the result of XRD, where we observe the grain growth of MnS films with molar concentration up to 1.0 M. In addition, a flower like architecture is seen in few places of the SEM image (Fig. 5b) which agreed with the report of Tao *et al.* (2007).

### CONCLUSION

In conclusion, we have described a simple approach called nebulizer method for the preparation of good quality MnS thin films. X-ray diffraction results revealed the crystallinity of MnS films

improved with increasing precursor solution concentration. The absorption edges shift towards lower wavelength region, indicating a systematic raise in energy band gap with increasing precursor solution concentration up to 1.0 M which attributed to the lower defect density near the band edge. The broad emission peak at 420 nm corresponding to the band edge emission was observed in the PL spectra. In addition, the slight shift in PL peaks attributes the variation in energy bad gaps of the films. HRSEM results showed the better crystalline quality of deposited film. Thus, we believe that the simple nebulizer technique can be used to grow the device quality MnS films.

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