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Research Article

# DEPOSITION AND CHARACTERIZATION OF MnS THIN FILMS BY CHEMICAL BATH DEPOSITION METHOD

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## ABSTRACT

The chemical bath deposition technique was used to deposit MnS thin films onto indium tin oxide glass substrate. During the deposition, manganese sulphate and thiourea were supplied $Mn^{2+}$ and $S^{2-}$ ions, respectively. X-ray diffraction and atomic force microscopy were used to investigate the structural and morphological properties of films, respectively. The band gap energy was determined using UV-VIS spectrophotometer. The influence of bath temperature was investigated to determine the best conditions for deposition process. The deposited films showed cubic structure of MnS. The highest peak observed was (200) plane. The number of peaks referred to MnS increased as the bath temperature was increased from 35 to 65 °C based on the XRD patterns. For the films deposited at lower bath temperature, the grains were small and thinner films to be formed. Conversely, for the films prepared at higher bath temperature, the grains were larger and thicker films to be formed. From the optical properties analysis, the band gap energy was to be dependent on the bath temperature.

**Keywords:** Chemical bath deposition, Manganese sulphide, Thin films, X-ray diffraction.

## INTRODUCTION

Recently, extensive research has been devoted to prepare various kinds of semiconductor thin films such as $MoSe_2$[1], CdSe[2], ZnS[3], CuS[4], $Cd_{1-x}Fe_xSe$[5] and $Cu_4SnS_4$[6] by using several deposition methods. Manganese sulphide thin films have been used in variety of applications such as solar cells, sensor, photoconductors, optical mass memories and solar selective coatings. Over the past few years, many methods such as radio-frequency sputtering[7], hydrothermal[8], SILAR[9] and chemical bath deposition method[10-13] have been used to prepare manganese sulphide thin films. Among various deposition methods, chemical bath deposition method has been identified as simple and low cost thin films deposition method with many advantages. Up-to-date, chemical bath deposition method has been successfully used to deposit various thin films including PbS[14], CdTe[15], ZnSe[16], CdS[17], $Ni_4S_3$[18] and $As_2S_3$[19]. Chemical bath deposition method is based on the controlled precipitation from solution of a compound on a suitable substrate. The substrates are immersed either in an alkaline or acidic solution which containing the metal ion, chalcogenide source and a complexing agent.

The present work reports the preparation and characterization of MnS thin films onto indium tin oxide glass substrates using chemical bath deposition method. The chemical bath contains manganese sulphate and thiourea which provide $Mn^{2+}$ and $S^{2-}$ ions, respectively. It is the first time, we report the influence of bath temperature (35 to 65 °C) on the MnS thin films in the presence of triethanolamine as a complexing agent. The results of the investigation on structural and morphological properties of thin films have been carried out by using X-ray diffraction and atomic force microscopy, respectively. The band gap energy and absorption properties were determined using UV-VIS spectrophotometer.

## MATERIALS AND METHODS

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). The manganese sulphide thin films were prepared from an alkaline bath using aqueous solutions of manganese sulphate [$MnSO_4$] and thiourea [$SC(NH_2)_2$] acted as a source of $Mn^{2+}$ and $S^{2-}$ ions, respectively. The triethanolamine was served as a complexing agent to chelate with $Mn^{2+}$ to obtain Mn-TEA complex solution. The indium tin oxide (ITO) glass was used as the substrate for the chemical bath deposition of MnS thin films. Before deposition, the ITO glass was degreased with ethanol for 15 min. Then, ultrasonically cleaned with distilled water for another 15 min and dried in desiccators. Deposition of MnS thin films was carried out using following procedure. 30 ml of manganese sulphate (1 M) was complexed with 5 ml of concentrated triethanolamine solution. To this, 30 mL of thiourea (1 M) was added slowly to the reaction mixture. The pH was adjusted to 11 by adding drop-wise ammonia/ammonium chloride (buffer solution). The cleaned ITO glass substrate was immersed vertically into beaker. In order to determine the best conditions for the deposition process, the films were deposited at different bath temperatures, ranging from 35 to 65 °C. During deposition process, the beaker was kept undisturbed. After the completion of deposition (7 h), the glass substrate was removed, washed several times with distilled water and dried naturally in desiccators for further characterization.

The structure of the films was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a $CuK_\alpha$ ($\lambda$=0.15418 nm) radiation source. Data were collected by step scanning from 20° to 70° with a step size of 0.05° ($2\theta$). The surface morphology, thickness and roughness were examined by recording atomic force microscopy images with a Q-Scope 250 in contact mode with a commercial $Si_3N_4$ cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software. The optical properties of the film were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer in the wavelength range of 300 to 800 nm. The film-coated indium tin oxide glass was placed across the sample radiation pathway while the uncoated indium tin oxide glass was put across the reference path. From the analyses of absorption spectra, the band gap energy ($E_g$) was determined.

## RESULTS AND DISCUSSION

The crystallographic properties have been investigated by X-ray diffraction (XRD) technique using $CuK_\alpha$ radiation. **Fig. 1** shows X-ray diffraction patterns of MnS thin films deposited at different bath temperatures. The films deposited at 35 °C show only single peak at 2 =34.1° corresponds to (200) plane. However, the number of peaks attributed to MnS increased to two and three peaks as the bath temperature is increased to 45, 55 and 65 °C, respectively. These results confirm that the deposition at higher bath temperature proved more favourable as the intensities of peaks corresponding to MnS increase. The peaks obtained are in good agreement with the Joint Committee on Powder Diffraction

Standards values belonging to the MnS[20] (Reference code: 00-065-2919) cubic structure. The lattice parameter values are a=b=c=5.22 Å. It is observed from Fig. 1 that the highest peak obtained corresponds to (200) plane. As the bath temperature is increased from 35 to 65 °C, the intensity of the peak corresponding to (200) plane increased, indicating that increasing bath temperature increases the crystallinity of thin films.

On the other hand, the presence of the indium tin oxide[21] (JCPDS reference No.: 01-089-4597) peaks in the XRD patterns are because of the glass substrate used during deposition. Four peaks occurred at $2\theta$ values of 21.3°, 37.4°, 60.5° and 65.2° corresponding to (211), (411), (622) and (543) planes were obtained. The peaks marked with solid diamonds are associated with reflections of the cubic structure of MnS and those marked with open diamonds can be ascribed to the cubic structure of indium tin oxide.

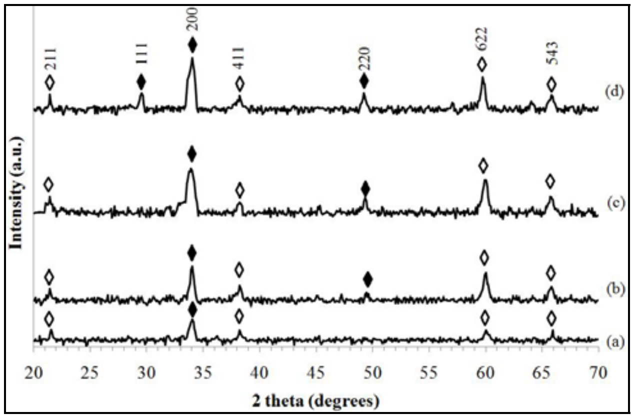


**Fig 1: X-ray diffraction patterns of MnS thin films deposited at different bath temperatures [(a) 35 °C (b) 45 °C (c) 55 °C (d) 65 °C (◊ $In_{1.875}O_3Sn_{0.125}$ , ♦ MnS)**

Atomic force microscopy (AFM) is a useful method analysis of the surface topography of the thin films. Fig. 2, Fig. 3, Fig. 4 and Fig. 5 show the AFM images of MnS thin films deposited on indium tin oxide substrates at various bath temperatures and the scanning area is 20 µm x20 µm. Fig. 2(a), 3(a), 4(a) and 5(a) show the two-dimensional while Fig. 2(b), 3(b), 4(b) and 5(b) display three-dimensional AFM images of MnS thin films deposited at 35, 45, 55 and 65 °C, respectively. The films deposited at 35 °C show incomplete grain coverage and low appearance of small grains (average grain size = 1 µm) over the substrate surface. The films deposition process on a substrate depends on the formation of nucleation sites and subsequent growth of the films from these centres. The films deposited at higher bath temperature (45, 55 and 65 °C) indicate better morphology compared to the films deposited at lower bath temperature (35 °C). The grains show complete coverage over the substrate surface. The grains size increases with increasing bath temperature. For the films prepared at 45 and 55 °C, the size of each grain differs from each other, varying from 1.5-2 µm, indicating irregular growth rate of the grains. The orientation of grain growth is also irregular as can be noticed from the specific increase of grain size at different areas of the substrate. On the other hand, the films prepared at 65 °C have the largest grains (average grain size = 2.5 µm) compared to the other films. During this stage, small grains agglomerate together to form larger grains.

The film thickness was measured using atomic force microscopy method. It can be observed that the thickness values of the thin films deposited at 35, 45, 55 and 65 °C are 971, 1314, 1542 and 2066 nm, respectively, indicating that the thickness increased as the bath temperature is increased. On the other hand, root mean square (RMS) roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness[22]. The films prepared at 35 °C have smoother surface (103 nm) due to the smaller grains size while the films deposited at 65 °C have rougher surface (139 nm) because of the films consist of irregularly shaped grains. The surface roughness values of the films deposited at 45 and 55 °C are 121 and 132 nm, respectively. It can be said that the surface roughness increases with increasing bath temperatures. Therefore, we can conclude that the MnS thin films grown on different bath temperatures obtained different surface roughness and thickness values.

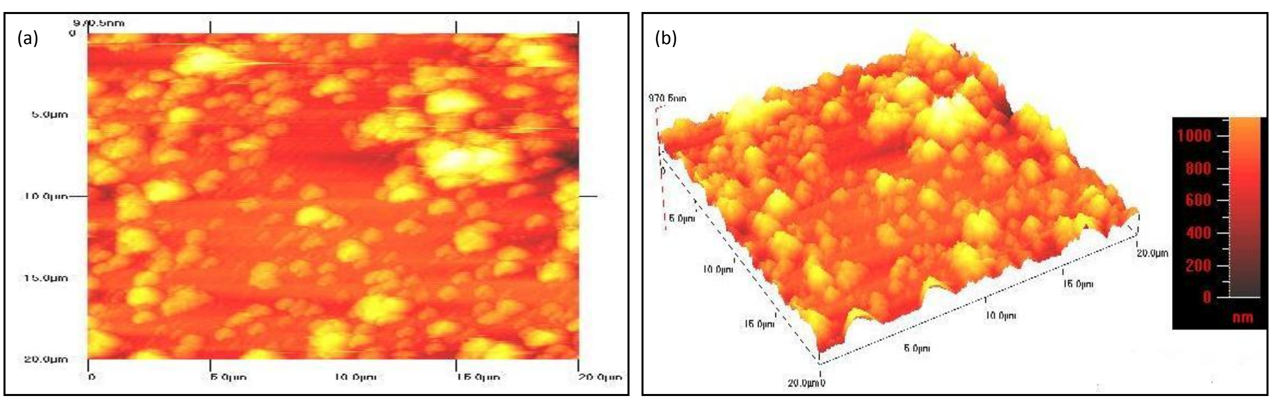


**Fig. 2: Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of MnS thin films deposited at 35 °C**

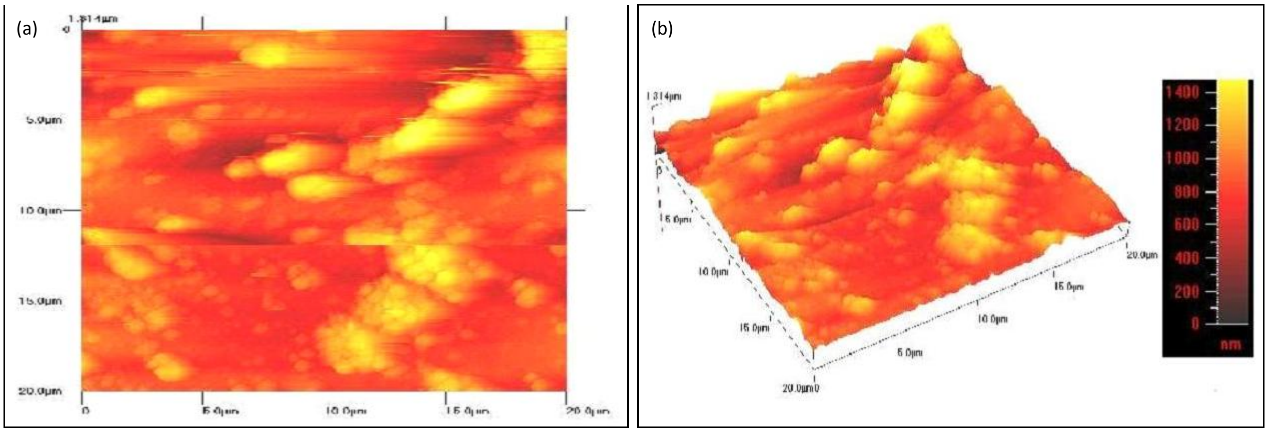


**Fig 3: Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of MnS thin films deposited at 45 °C**

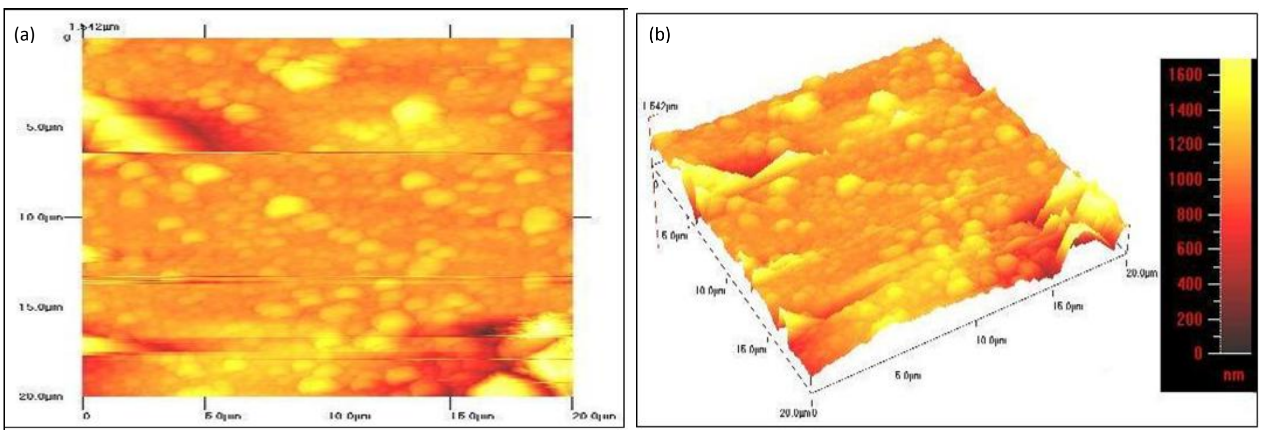


**Fig 4: Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of MnS thin films deposited at 55 °C**

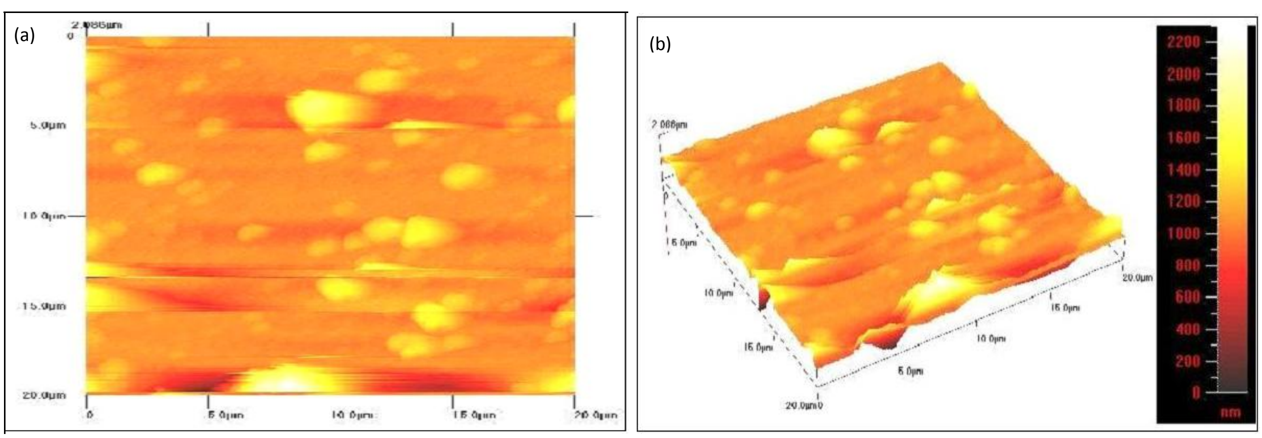


**Fig 5: Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of MnS thin films deposited at 65 °C**

In order to determine the band gap of thin films, the equation of Stern[23] was used.

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu} \qquad (1)$$

where $v$ is the frequency, $h$ is the Planck's constant, $k$ equals a constant while $n$ carries the value of either 1 or 4. The $n$ value is 1 for a direct gap material and 4 for indirect gap material. **Fig. 6** indicates the variation of $(Ah\nu)^2$ versus $h\nu$ for MnS thin films deposited at various bath temperatures. The direct band gap values are measured by extrapolating the straight-line portion over the $h\nu$ axis. It is seen that the band gap values are decrease (3.05, 3.0, 2.95 and 2.75 eV) when the bath temperature is increased from 35 to 65 °C. At higher bath temperature, the enhancement in crystallinity of the films leads to larger grains and also contributes to reduction in the band gap of the materials. The band gap of MnS thin films obtained in this work is close with that reported by Pathan et al.[9] and Agbo and Ezema[13].

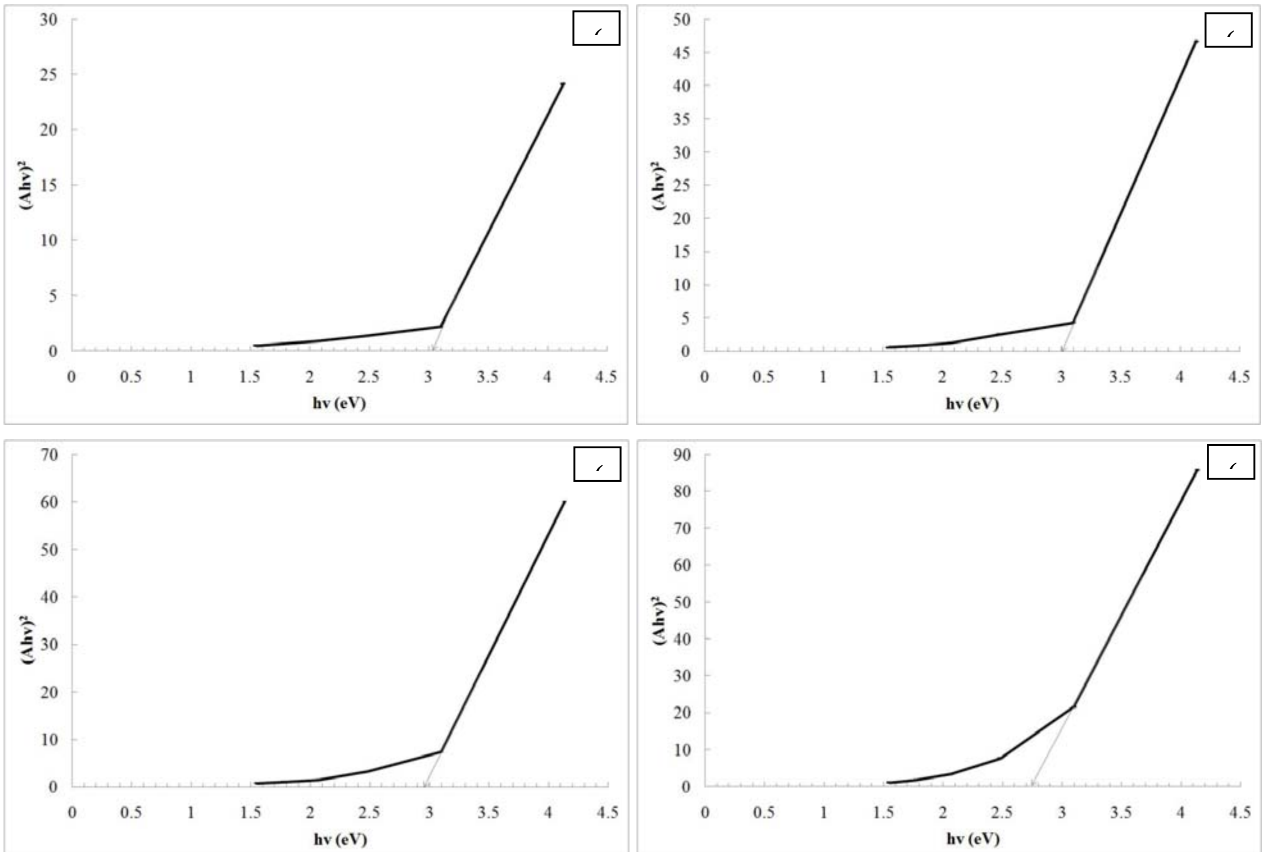


**Fig 6: Plot of $(Ahv)^2$ versus *hv* band gap for MnS thin films deposited at different bath temperatures [(a) 35 °C (b) 45 °C (c) 55 °C (d) 65 °C]**

**CONCLUSION**

The MnS thin films could be chemically deposited by using manganese sulphate and thiourea in the presence of triethanolamine as a complexing agent during deposition process. Based on XRD results, the thin films produced were polycrystalline in nature. The intensity of the (200) peak showed a significant increased as the bath temperature was increased from 35 to 65 °C. As expected, the crystallinity of the thicker films was better and more XRD peaks were observed. According to AFM images, the sizes of the grains and film thickness as well as surface roughness were noticed to increase as the bath temperature was increased. From the optical properties analysis, the band gap energy was to be dependent on the bath temperature.

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