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## Original Article

# Synthesis of manganese sulfide (MnS) thin films by chemical bath deposition and their characterization

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## ABSTRACT

Films of  $\gamma$ -MnS were deposited by chemical bath deposition (CBD) technique on glass slide substrates. The EDAX analysis showed that the film contains Mn and S elements without any other impurity. The EDAX weight percentage showed the film to be in perfect stoichiometry. The XRD showed that the synthesized MnS thin film possess hexagonal structure. The determined lattice parameters  $a = b = 3.9 \text{ \AA}$  and  $c = 6.4 \text{ \AA}$  were in match with the reported values. The crystallite size determined using XRD pattern employing Scherrer's formula and Hall-Williamson plot were 8.35 nm and 7.42 nm, respectively. The SAED shows ring pattern, clearly stating the thin film to be polycrystalline in nature. The SEM image of MnS thin film clearly reveals that the film surface is homogenous consisting of two sizes of spheres. Smaller spherical grain particles of size  $\sim 1.6\text{--}2 \text{ }\mu\text{m}$  covers the substrate and on top of covered small grain size particles are the large size spherical grain particles having size  $\sim 5.0\text{--}7.0 \text{ }\mu\text{m}$ . The 2D AFM image of MnS thin film shows coalescences between spherical grains. The optical absorbance analysis of the MnS thin film confirmed that the film possesses direct and indirect optical bandgap values of 3.67 eV and 2.67 eV, respectively. All the obtained results have been deliberated in this paper.

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## 1. Introduction

Materials known as dilute magnetic semiconductors (DMS) have shown potential applications and have become a focus of intense research activity as they exhibit an interesting combination of magnetism and semiconductivity. In DMS, the band carriers strongly interact with the localized magnetic moments thus showing a variety of interesting

phenomena [1]. Manganese sulphide (MnS) is a DMS material possessing wide optical bandgap of 3.1 eV making it suitable as a window/buffer material, as a solar selective coating, short wavelength optoelectronic material, sensors, photoconductors, optical mass memories and storage [2–6]. The MnS occurs in three crystalline forms, one is thermodynamically stable  $\alpha$ -MnS phase with an octahedrally coordinated rock salt structure, others are pink metastable tetrahedrally coordinated  $\beta$ - and  $\gamma$ -MnS with zinc blende and wurtzite structures,

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respectively [7]. The deposition of DMS materials in the thin films form has been the subject of intense research over the past few decades due to applications in variety of fields such as photoconductors, solar selective coatings, solar cells, antireflection coatings and optical mass memories [8,9]. Sensing to the importance of DMS in general and MnS in particular, the authors thought of depositing MnS thin films by simple chemical bath deposition (CBD) technique and characterizing the deposited films.

## 2. Experimental

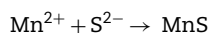
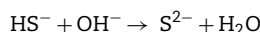
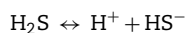
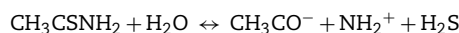
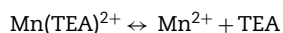
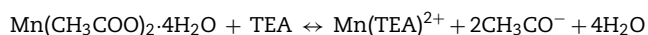
The manganese sulphide (MnS) thin films deposition was done on glass slide substrate by chemical bath deposition (CBD) technique. Various chemicals and its combinations were tried for the deposition of good quality MnS thin films by CBD technique. The best MnS thin films deposition by CBD technique was obtained by using the below chemical and synthesis procedures.

The A.R. grade chemicals viz. manganese acetate tetrahydrate ( $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ ) [Lobachemie, Mumbai, India], triethanolamine (TEA) ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ) [SISCO Chem, Mumbai, India], ammonia solution ( $\text{NH}_4\text{OH}$ ) [Chiti-Chem Corporation, Vadodara, India], hydrazine hydrate ( $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$ ) [SISCO Chem, Mumbai, India] and thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ) [Lobachemie, Mumbai, India] were used directly without any purification. Here manganese acetate and thioacetamide are the sources of  $\text{Mn}^{2+}$  and  $\text{S}^{2-}$  ions, respectively. Triethanolamine works as a complexing agent, whereas ammonia solution was used for adjusting pH of the bath solution to achieve the alkaline medium.

In the deposition of MnS thin films by CBD, firstly 20 ml of 1 M manganese acetate tetrahydrate ( $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ ) and 4 ml of 7.4 M triethanolamine ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ) (TEA) were vigorously mixed in 100 ml glass beaker for 5 min. After that, 20 ml of 1.5 M ammonia solution ( $\text{NH}_4\text{OH}$ ) was added to the solution and further stirred for 10 min. Then under constant stirring, 0.4 ml of hydrazine hydrate ( $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$ ) (80%) solution was mixed followed by 20 ml of 1.4 M thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ) and the solution was stirred for 10 min. The final solution was made 75 ml by adding double distilled water. The pH of the bath solution was found to be 10.5. The already cleaned microscope glass slides of dimensions  $76 \text{ mm} \times 26 \text{ mm} \times 1.35 \text{ mm}$  [Blue Ribbon, Microcil Manufacturers, Vyara, Gujarat, India] were used as substrates. The cleaning of the glass slide substrates was done by boiling it in chromic acid for 1 h and then keeping overnight in the acid. Next day the glass side was washed with detergent and finally ultrasonically cleaned in methanol, then dried in oven for 2 h at  $40^\circ\text{C}$ . The glass slide substrate was immersed in the prepared bath solution and kept vertical in the beaker for thin film deposition. The deposition was done at room temperature. After 6 h, the glass slide was removed, rinsed with double distilled water and allowed air drying. Good quality MnS thin film was deposited on glass substrate having an average film thickness of  $0.17 \mu\text{m}$ .

The thickness of the CBD deposited thin films were determined by gravimetric method, assuming the density of MnS thin film material as  $3.3 \text{ g cm}^{-3}$  [10] to be the same as that of

the bulk. The MnS thin film deposition mechanism follows the chemical reaction:



The stoichiometric composition of the CBD deposited MnS thin film was studied using energy dispersive analysis of X-rays (EDAX) attached to scanning electron microscope (SEM) JSM 5610. The surface morphology study was carried out using the SEM. The XRD measurement was performed in a Philip Xpert MPD diffractometer using  $\text{CuK}_\alpha$  radiation. The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) study was done by Philips Technai 20. The detailed surface morphology study of the synthesized MnS thin film was done by atomic force microscopy (AFM), Nano surf easy scan 2. The optical bandgap determination of the as-synthesized MnS thin film was done by employing Perkin-Elmer Lambda-19 UV-vis-NIR Spectrophotometer.

## 3. Results and discussion

### 3.1. Chemical composition

The stoichiometric chemical composition of the as-synthesized MnS thin film was determined by the EDAX technique. The obtained EDAX spectrum is shown in Fig. 1. The observed EDAX data of the weight percentage of constituent elements in the CBD as-synthesized MnS thin film are: manganese is 64.77% and sulphur is 35.23%. The values are in compliance with the standard values of manganese as 63.15% and sulphur as 36.85%. The EDAX spectrum did not

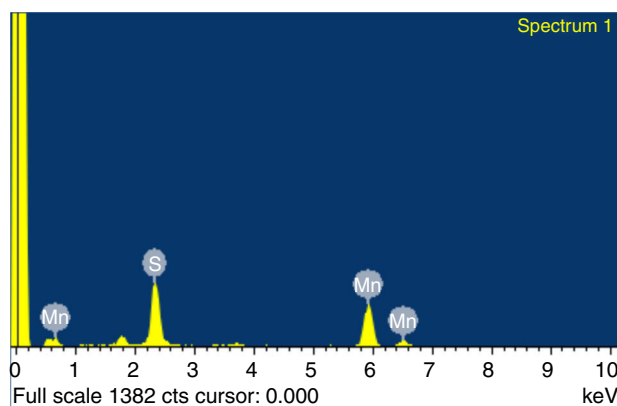
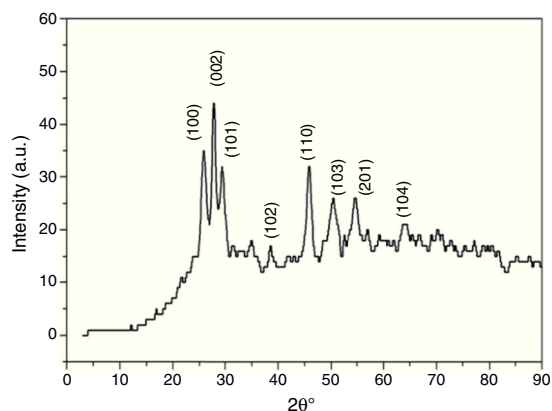


Fig. 1 – EDAX spectrum of as-synthesized CBD MnS thin film.



**Fig. 2 – The X-ray powder diffraction pattern of as-synthesized CBD MnS thin film.**

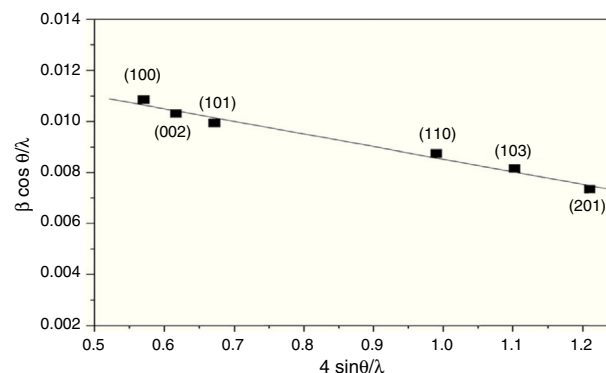
show any other elements, confirming that the synthesized MnS thin film is free from any impurity

### 3.2. Crystallographic structure

The crystallographic structure and lattice parameters of as-synthesized MnS thin film were determined using the XRD. The obtained XRD pattern is shown in Fig. 2.

The XRD peaks were indexed and crystallographic lattice parameters were determined by employing powder-X software. The peaks could be indexed as those of the  $\gamma$ -MnS with hexagonal structure. The determined lattice parameters were;  $a = b = 3.97 \text{ \AA}$  and  $c = 6.44 \text{ \AA}$ . The determined lattice parameters are matching with the reported standard lattice parameter values (JCPDS Card No. 40-1289) [5,11].

The crystallite sizes of the as-synthesized MnS thin film was determined from the XRD pattern employing the standard Scherrer's equation [12] and Hall-Williamson relation [13,14]. The Hall-Williamson plot is shown in Fig. 3. The obtained crystallite sizes using Scherrer's equation and Hall-Williamson plot are 8.35 nm and 7.42 nm, respectively. They are in good agreement with each other. The slope of the Hall-Williamson plot gives the amount of residual strain. The residual strain



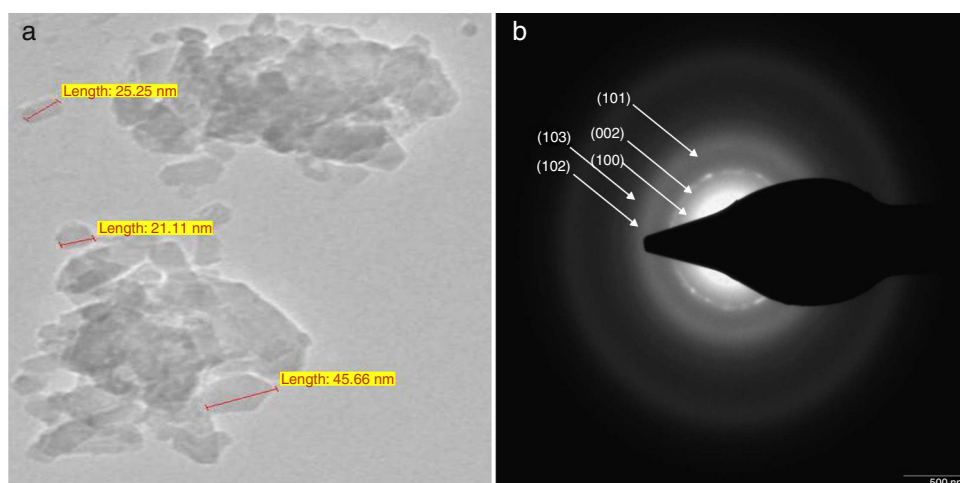
**Fig. 3 – Hall-Williamson plot of as-synthesized CBD MnS thin film.**

value in case of the as-synthesized MnS thin film is about  $-4.9 \times 10^{-3}$ . The negative value of the residual strain states that it is of compressive nature.

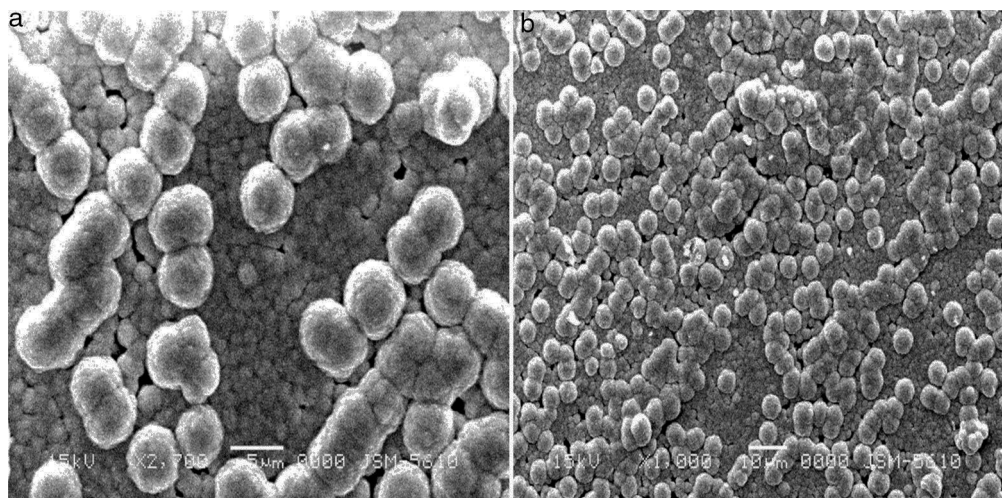
The TEM image and the SAED pattern of as-synthesized MnS thin film are shown in Fig. 4. This image shows that the film is homogeneous and uniform having no cracks or defects. The SAED image shows ring pattern, confirming that the as-synthesized MnS thin film to be polycrystalline in nature. The indexed SAED planes are in conformity with the respective XRD planes.

### 3.3. Surface analysis

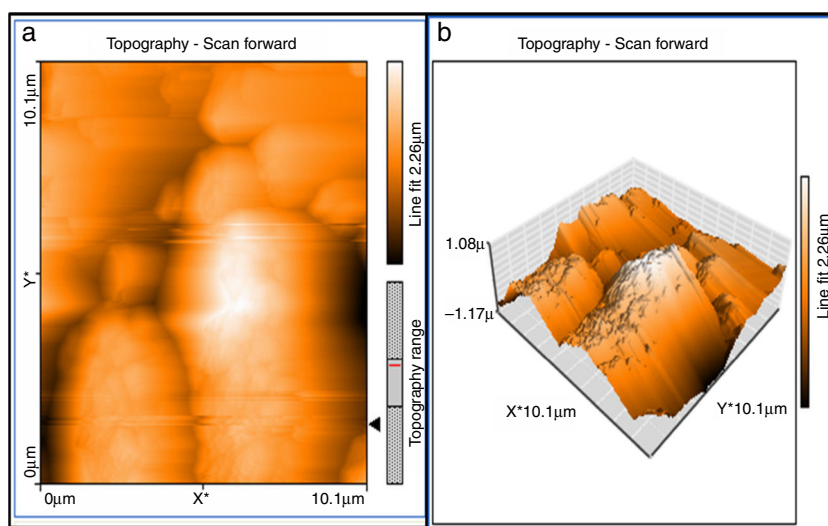
SEM images of the as-synthesized MnS thin film are shown in Fig. 5. The images clearly reveal that the thin film surface is homogenous having spherical grain particles. There are spherical grain particles of two different sizes. The small spherical grain particles size range from  $\sim 1.6$  to  $2 \mu\text{m}$ , which covers the substrate. On top of the small spherical grain particles there are large spherical grain particles of size ranging from  $\sim 5$  to  $7 \mu\text{m}$ . These large size grain particles might have grown from the coalescences of small particles. The SEM image analysis substantiate that the present MnS thin film formation by CBD technique takes place by the process of arrangement of



**Fig. 4 – (a) TEM image and (b) SAED image of as-synthesized CBD MnS thin film.**



**Fig. 5 – SEM images of as-synthesized CBD MnS thin film.**



**Fig. 6 – (a) Two-Dimensional (2D) and (b) Three-dimensional (3D) AFM images of as-synthesized CBD MnS thin film.**

spherical grain particles of two sizes. The SEM images clearly states that the present synthesis conditions are optimum for these two sizes of spherical grain particles.

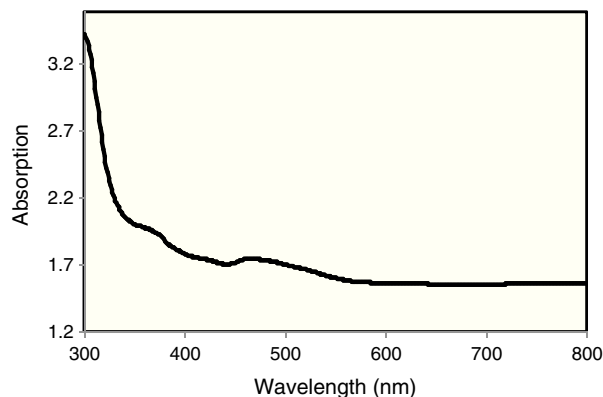
Fig. 6a and b shows two-dimensional (2D) and three-dimensional (3D) AFM images of the as-deposited MnS thin film, respectively. The 2D image of area  $10.1\ \mu\text{m} \times 10.1\ \mu\text{m}$ , shows spherical grains getting coalescences between themselves. The top view of the 3D image, Fig. 6b, recorded in area of  $10.1\ \mu\text{m} \times 10.1\ \mu\text{m}$  shows mountainous like structure. The mountains have extended characteristic with planar crest. Deep valleys are formed between the mountainous crest structures.

### 3.4. Optical properties

The optical absorption spectrum obtained for the MnS thin film synthesized by CBD technique is shown in Fig. 7. The film deposited on glass substrate was directly taken as sample and a plain glass slide worked as reference. The obtained spectrum clearly indicates that the synthesized MnS thin film

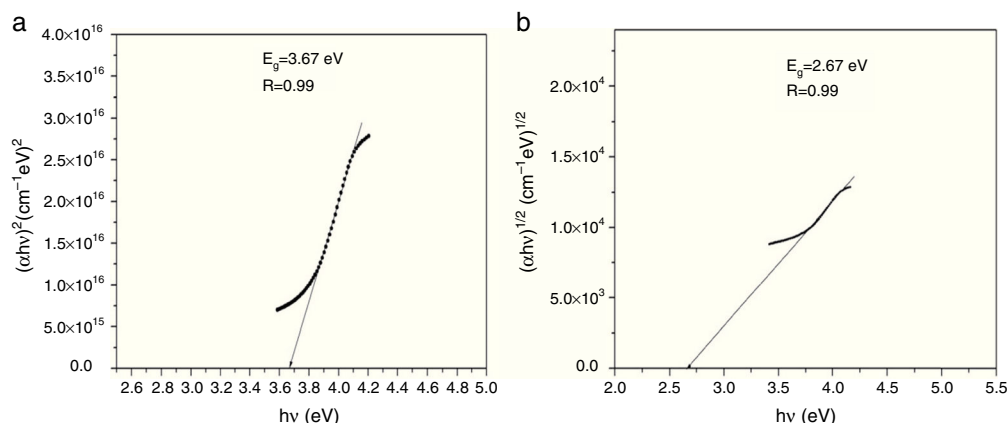
has absorption in the visible range with sharp absorption edge lying between wavelengths of 300–350 nm.

The plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for the as-synthesized MnS thin film is shown in Fig. 8a. The plot reveals that the CBD



**Fig. 7 – The absorbance spectrum of as-synthesized CBD MnS thin film.**





**Fig. 8 – Plots of (a)  $(\alpha h\nu)^2$  versus  $h\nu$  and (b)  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  for as-synthesized CBD MnS thin film.**

synthesized MnS thin film possess direct optical bandgap of 3.67 eV. This direct optical bandgap value is consistent with the reported value of 3.88 eV [15]. The plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  for the as-synthesized MnS thin film is shown in Fig. 8b. The indirect optical bandgap value obtained from the plot is 2.67 eV.

#### 4. Conclusions

MnS thin films were deposited by simple chemical bath deposition (CBD) technique. The synthesis was carried out at ambient condition using AR grade chemicals without any sophisticated instruments. The EDAX analysis confirmed that the CBD synthesized MnS thin film was near stoichiometric and does not contain any other impurity elements in them. The XRD analysis of the as-synthesized MnS thin film showed that the film possesses hexagonal structure. The determined lattice parameters  $a = b = 3.9$  and  $c = 6.4$  Å were in good match with the reported data. The crystallite size determined from XRD using Scherrer's equation and Hall–Williamson plot were 8.35 nm and 7.42 nm, respectively. The residual compressive strain determined from the Hall–Williamson's plot was  $-4.9 \times 10^{-3}$ .

The SAED pattern of MnS thin film show ring pattern clearly stating the sample to be polycrystalline in nature. The SEM images of CBD deposited MnS thin film clearly reveals that the film surface is homogenous having spherical grain particles. It is observed that there is good deposition coverage all over the glass substrate. There are spherical grain particles of two sizes. The smaller spherical grain particles cover the substrate and on top of covered small grain particles, are large size spherical grain particles.

The 2D AFM image of as-deposited MnS thin film shows spherical grains getting coalescences between them. The 3D image shows mountainous like structure. The mountains have extended characteristic with planar crest having deep valleys. The deep valleys are formed between the mountainous crest structures.

The optical energy bandgap determined for the as-synthesized CBD MnS thin film from the optical absorbance

spectrum gave the values for direct optical bandgap and indirect optical bandgap to be 3.67 eV and 2.67 eV, respectively.

#### Conflicts of interest

The authors declare no conflicts of interest.

#### Acknowledgements

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