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# Preparation of MnS thin films by chemical bath deposition and effect of bath temperature on their optical propertie

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**ABSTRACT**
MnS thin films were deposited onto glass substrates by chemical bath deposition at different temperatures (40°C and 70°C). The deposition parameters such as deposition time, pH and concentrations of solution were optimized. The films were prepared from the mixture as the solution of manganous acetate tetrahydrate as a manganese ion source, thiourea as a sulphur ion source and triethanolamine (TEA) as a complexing agent. The MnS thin films were characterized by optical absorption spectroscopy and band gap energy were determined. The band gap energy is found to be in the range of 2.81-3.1eV.

**Keywords**: Optical properties, CBD method, Band gap, Thin films, Chemical synthesis.

## INTRODUCTION

During the past few decades manganese chalcogenides (MnS, MnSe, MnTe etc.) have given much interest concerning their structural, chemical and physical properties [1-3]. Depending upon the deposition conditions, the structural, electrical and optical properties of these materials can be controlled in many ways [4]. The deposition of DMS materials in the thin films form has been the subject of intense research over the past few decades due to application in a variety of fields such as photoconductors, solar selective coatings, solar cells, antireflection coatings and optical mass

memories [5-6]. MnS thin films or powder can be found in several polymorphic forms: the rock salt type structure (α-MnS). Which is the most common form, by low temperature growing techniques it crystallizes into the Zincblend (β-MnS) or Wurtzite (γ-MnS) structure [7]. Many research groups have shown a great interest in the development of this material in the various deposition chemical and physical processes such as hydrothermal [8-10], radio-frequency sputtering [11-12], molecular beams epitoxy [13] and chemical bath deposition (CBD) [7, 14]. We have selected chemical bath deposition method because of its simple, inexpensive and convenient technique for large area deposition.

## METHODOLOGY

### 2.1 Materials

All the chemicals used for the deposition were analytical grade. It includes manganous acetate tetrahydrate [$C_4H_6MnO_44H_2O$], thiourea [$(H_2N)_2CS$], ammonia ($NH_3$), triethanolamine (TEA) [$(HOC_2H_4)_3$ N]. All the solutions were prepared in distilled water. During the deposition, the triethanolamine was used as a complexing agent while manganous acetate tetrahydrate acted as a source of manganese ions and thiourea acted as a source of sulphide ions, respectively.

### 2.2 Cleaning procedure of glass substrate

The deposition was carried out using commercial glass slides of dimensions 25 mm X 30 mm X 1.2 mm. To maintain homogeneity and better quality of films the substrate surface must be cleaned scrupulously. The slides were washed with detergent and then boiled in concentrated chromic acid (0.5 M) for 1 hour. The substrates were then washed with distilled water. The substrates were then taken out and immersed in distilled water prior to the deposition.

### 2.3 Synthesis of MnS thin films

The deposition was carried out in a reactive solution prepared in a 250 ml beaker containing equimolar solutions of manganous acetate tetrahydrate, and thiourea. TEA was used as a complexing agent and a pH of the reaction mixture was adjusted to ~ 10, with the help of ammonia solution. The resulting solution was thoroughly mixed and stirred. Finally distilled water was added to make up the bath solution 200 ml, while stirring continued. The bath temperature was fixed at temperature (40°C and 70°C). Pre-treated substrates were inserted vertically into the beaker. After deposition for 7 hours, the substrates were taken out, washed with distilled water and dried in air. The probable reaction mechanism was carried out for the formation of MnS.

$C_4H_6MnO_44H_2O+TEA \leftrightarrow Mn\ (TEA)^{2+} + 2CH_3CO^- + 4H_2O$

$Mn\ (TEA)^{2+} \leftrightarrow Mn^{2+} + TEA$

$NH_4OH \leftrightarrow NH_4 + OH^-$

$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CO^- + NH^{2+} + H_2S$

$H_2S \leftrightarrow H^+ + HS^-$

$HS^- + OH \leftrightarrow S^{2-} + H_2O$

$Mn^{2+} + S^{2-} \leftrightarrow MnS$

## RESULTS AND DISCUSSION

The optical absorbance of the MnS thin films were measured by using Systronics, AU-2701, UV- VIS, Double beam spectrophotometer in the wavelength range 300 to 1100 nm. The film indicates a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in the photo electrochemical cell. The absorption of these films was studied to evaluate the band gap ($E_g$). The fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band [17] was used to determine the nature and the optical energy band gap. The optical absorption is characterizes the relation between the absorption coefficient (α) and photon energy (hν) for different allowed transition as

$$\alpha h\nu = A\ (h\nu - E_g)^n \qquad (1)$$

Where α is the absorption coefficient, hν is the photon energy, $E_g$ is the optical band gap and A is the constant which is related to the efficient masses associated with the valence band and conduction band. To determine the possible transitions $(\alpha h\nu)^2$ versus hν was plotted. The corresponding band gap energies were obtained from extrapolating the straight portion of the graph on the hν axis at $(\alpha h\nu)^2=0$. Fig.2

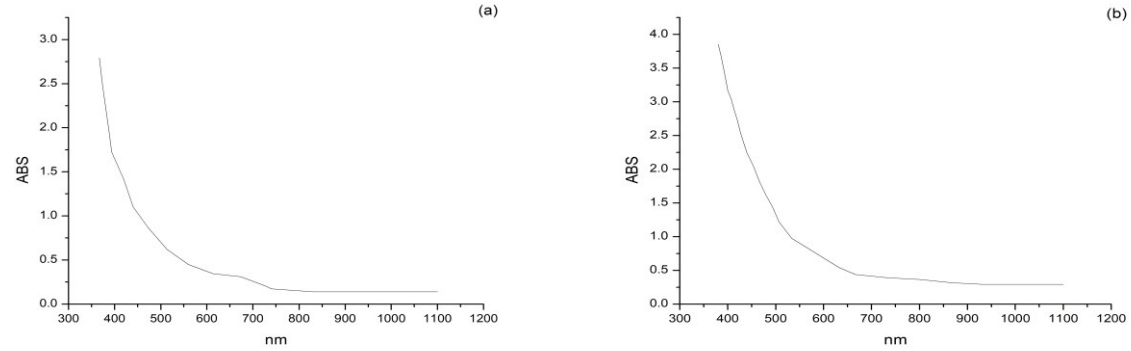


**Fig.1:** Optical absorbance spectra of the MnS thin film (a) 40°C (b) 70°C.

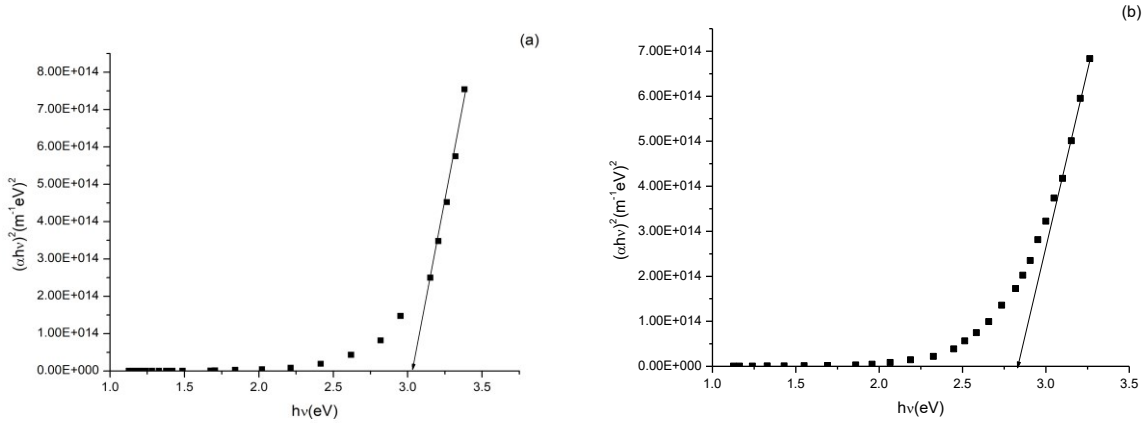


**Fig.2:** Plot of $(\alpha h\nu)^2$ versus hν showing the estimation of direct band gap energy (a) 40°C (b) 70°C.

plot of $(\alpha h\nu)^2$ versus hν shows band gap for MnS thin films deposited at different bath temperatures (40°C and 70°C). It is seen that the band gap values are decreases (3.1 to 2.81 eV) when the bath temperature is increased from 40°C to 70°C. The decrease in the band gap as a consequence of the increase in particle size is in conformation with the earlier studies. The obtained band gap width is consistent with the reported values [18].

## CONCLUSION

MnS thin films have been prepared successfully using a chemical bath deposition technique onto glass substrates. The optical absorbance spectra of the MnS thin film indicates a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in the photo electrochemical cell. It is seen that the band gap values are decreases (3.1 to 2.81 eV) when the bath temperature is increased from 40°C to 70°C. The decrease in the band gap as a consequence of the increase in particle size.

**Conflicts of interest:** The authors stated that no conflicts of interest.

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