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Synthesis of MnS2 Thin Films by Chemical Route: Physicochemical Properties

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ABSTRACT

In present work, manganese sulfide (MnS2) thin films have been deposited by chemical route at room temperature on commercial glass substrate. Employed chemical method is inexpensive, simple and does not require any sophisticated instrument for deposition. The chemical bath is prepared from the mixture as solutions of manganese acetate tetrahydrate [C4H6MnO44H2O] as a manganese source, thiourea [(H2 N) 2 CS] as a sulfur source and ammonia solution used as a complexing agent, respectively. The structural and morphological analysis has been investigated using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

Keywords: DMS, chemical route, X-ray diffraction, Scanning, Electron Microscopy (SEM).

I. INTRODUCTION

Various kinds of binary and ternary chalcogenides materials are in focus of extensive research [1]. Chalcogenides materials have applications in optoelectronic devices, solar cells, photoconductors and infrared detector devices, etc. respectively. The various chalcogenides such as ZnS, Cu₂S, MnS₂, MoS₂, WS₂ are commonly used. Among all the manganese sulfide (MnS₂) is especially used in mixing with Zn and Cd to form (Zn, Mn)S and (Cd, Mn)S composites used in various applications. Manganese sulphide thin films with main advantages like wide direct band gap, cheap processing. As far as we know, there are

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various methods of synthesis for managanese sulphide thin films like successive ionic layer adsorptions and reaction (SILAR), chemical bath deposition (CBD) and RF-sputtering etc. [2]. Chemical route is most feasible technique for film synthesis, since it is easy, simple and most-cost effective method of deposition [4]. In chemical route, manganese ions and a sulfurcontaining organic compound (thiourea) are processed in alkaline water medium. Ammonia is used as complexing agent in deposition as it reduces spontaneous precipitation by slowly releasing of metallic ions, which avoids precipitation. In this work, MnS2 thin film structures are reported by easy and simple chemical route at room temperature. Its structural and morphological studies are revealed by X-ray diffraction and Scanning electron microscopy, respectively.

II. EXPERIMENTAL DETAILS

Materials:

All The chemicals used are analytical grade. Manganese acetate tetrahydrate [C₄H₆MnO₄.4H₂O] used as a manganese source, thiourea [(H₂N)₂CS] used as a sulfur source and Ammonia solution was used as complexing agents and D.I. used as solvent. The pH of the solution was maintained by using ammonia solution.

Instruments:

For structural studies Philips PW1710 Diffractometer for the 2 θ ranging from 200 to 800 with Cu-K_{α} (λ = 1.5418 A°) radiation. The Scanning Electron Microscopy (SEM) analysis is used for surface morphology study.

Glass substrate cleaning:

Commercial glass slides of dimensions 25 mm x 30 mm x 1.2 mm are used for the deposition. For better homogeneity and quality of films, cleaned slides are essential. The slides cleansed with help of detergent, after they are boiled in concentrated chromic acid

(0.5 M) for 1 hour. The substrates washed with distilled water. Slides are immersed in distilled water before deposition.

Preparation of the MnS₂ thin films:

A total reactive solution prepared in a 100 ml beaker containing equimolar solutions of manganous acetate tetrahydrate (0.3M) as Mn source (50ml) and thiourea (0.3M) as a S sources (50ml). Solution is stirred well so that homogeneous solution was formed. The pH of the solution mixture was set with the help of ammonia to near about 10.6 with help of pH meter. The substrates were kept in the solution vertically at room temperature without stirring with the help of specially designed substrate holder for 24 hours. Dark brown deposited glass slides are removed gently. Finally substrates were washed in distilled water gently and dried in warm air.

III. RESULTS AND DISCUSSION

For Structural identification X-Ray Diffraction (XRD) was carried out within the range of angle 2θ between 10° to 80°. The MnS₂ thin films XRD pattern of deposited at room temperature for 24 hours deposition time is shown in Fig.1. The cubic crystal structure with five principal peaks corresponding to (2 0 0), (2 1 0), (2 1 1), (2 2 1) and (4 1 1) orientations. This XRD data is in good agreement with standard JCPDS card no.00-010-0616 and JCPDS card no. 00-010-0476 conforms cubical hauerite phase of MnS₂. Lattice constant (c) for cubical phase was determined from the relation in eq.1 [3].

$$\frac{1}{d_{hkl}^{2}} = \frac{4}{3} \left(\frac{h^{2} + hk + k^{2}}{a^{2}} \right) + \frac{l^{2}}{c^{2}}$$
(1)

From the position of the peak (2 0 0), determined lattice parameters a=b=c=6.09 A°, 17.4 nm is the average crystalline size of MnS₂ in the films. It was determined from line (2 0 0) by using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$



where, β is the FWHM, λ is the X-ray wavelength and θ is the Bragg's angle.



Fig.1. XRD pattern of MnS₂ thin films deposited on glass substrate.

2θ(degree)	FWHM in nm	h k l	d-spacing in (Å)
28.88	0.47	200	3.05
32.41	0.39	210	2.73
36.13	0.27	211	2.50
44.50	0.47	221	2.04
64.74	0.57	411	1.44

Using Scanning Electron Microscopy surface morphology was determined. Fig. 2 shows the SEM micrograph of MnS₂ films prepared on glass substrate for 24 h at room temperature by using simple chemical route. The film well covered and smooth all over glass substrate.



Fig.2. SEM images of MnS₂ thin films.

The films are firm and densely adhere to the surface. The grains are smaller with unequal in size and shapes. The particles are well adhering with unequal distribution the fine grain background.

IV.CONCLUSION

MnS2 thin films have been deposited sucessesfully on a glass substrate at room temperature by simple and cost effective chemical route method. From the XRD analysis, it was confirm that the film possesses a cubical structure of MnS2 of hauerite. The determined lattice parameters $a=b=c=6.09A^\circ$ were in a good match with the reported hauerite structured data. The SEM study showed smooth and well covered thin film on entire glass substrate.

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