Chalcogenide Letters Vol. 6, No. 10, October 2009, p. 541 – 547

STRUCTURAL ANALYSIS OF CBD γ-MnS THIN FILMS

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This paper presents the preparation of γ-MnS thin films from three different chemical baths having the chemicals manganese acetate, triethylamine, ammonium chloride, hydrazine hydrate and thioacetamide. The preparative parameters were optimized to obtain good quality MnS thin films. The reaction of formation of MnS was discussed in this paper. XRD analysis is employed to confirm the structure and nature of γ-MnS thin films. The calculated crystallite size ranges from 40-54 nm, indicating that the as-prepared MnS films are made up of nanocrystals. EDAX spectra enabled to identify the film as $Mn_{1.2}S_{0.8}$. SEM pictures showed the hollow spherical morphology of the prepared γ-MnS thin films. FTIR spectra of γ-MnS thin films have also been analyzed and discussed in this paper.

(Received September 4, 2009; accepted September 30, 2009)

Keywords: MnS, Chemical Bath Deposition , Thin Film; XRD, EXAFS

1. Introduction

Materials containing manganese are interesting because of their applications in many areas of modern technology. MnS is a wide gap [Eg~3.1eV] VIIB – VIA dilute magnetic semiconductor (DMS). MnS is used in solar cell applications as a window/buffer material [1] and also as blue green light emitters. MnS has been extensively studied because of their outstanding magneto-optical properties and an interesting combination of magnetism and semiconductivity. In DMS, the band electrons and holes strongly interact with the localized magnetic moments and cause a variety of interesting phenomena [2]. These materials could provide a new type of control of conduction and spin which is an important property of spintronics applications. The metastable form (γ- MnS thin films) can be easily prepared from an aqueous solution [3]. We present the preparation and structural analysis of γ- MnS thin films in this paper.

2. Experimental details

The deposition of MnS thin films is based on the reaction of Mn^{2+} and S^{2-} ions in deionized water solution. Chemicals used for the deposition of MnS thin films are manganese acetate, triethylamine, ammonium chloride, hydrazine hydrate and thioacetamide. For the preparation of MnS thin films, 10 ml (1mol l^{-1}) manganese acetate solution was taken in a 100ml beaker to which 1 ml triethylamine(98%) and 10 ml (1 M) NH_4Cl (1 mol l^{-1}) were added successively. After stirring for several minutes the solution becomes clear and homogenous. Then under continuous stirring, 0.2ml of hydrazine hydrate (80%) was mixed and followed by 10 ml of thioacetamide solution (1 mol l^{-1}). Deionized water was added to make the volume to 80ml. The bath temperature was fixed at an appropriate optimized temperature and then pre-treated substrates were vertically inserted into the beaker. After deposition for an optimized deposition time, the substrates were taken out, washed with deionized water and dried in air. The depositions were carried out in water bath at different temperatures and uniform films were obtained for the deposition temperature of

60- 70º C. The deposition time was varied from 3-7 hours and the optimized time range has been identified as 6-7 hours to get films of different thicknesses.

MnS film can be obtained from and aqueous baths containing Mn salt and a suitable complexing agent which allow us to control Mn^{2+} concentration and to have a soluble species of Mn^{2+} in the aqueous medium. The deposition process is based on the slow release of Mn^{2+} and S^{2-} ions in the solution which then condense on an ion by ion basis on the substrates that are suitability mounted in the solution. The deposition of MnS occurs when the ionic product of Mn^{2+} and S^{2-} exceeds the solubility product of the MnS. With the addition of TEA, Mn^{2+} can be complexed as [1]:

$$Mn(CH_3COOO)_3 + TEA \rightarrow (Mn(TEA))^{2+} + 3CH_3COO^- ; \quad (1)$$

Then the overall reaction of formation of MnS can be written as:

$$(Mn(TEA))^{2+} + CH_3CSNH_2 + 2OH^- \rightarrow MnS + TEA + CH_3CONH_2 + H_2O \quad (2)$$

A Shimadzu XRD-6000 x-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation (λ = 1.5406 Å) was used for the structural analysis of thin films of different thicknesses. The surface morphology of thin films was studied using a scanning electron microscope (JEOL-JSM-100). Energy dispersive X-ray analyser (LEICA.S44Oi) confirmed the composition of the constituents in γ-MnS thin films. The FTIR analysis of CBD γ - MnS was studied by FTIR spectrophotometer (FTIR-8400S).

3. Results and discussion

3.1 Structural studies

The x-ray diffraction patterns of CBD **γ**-MnS thin films of thickness 3620Å, 4170 Å and 5200 Å prepared from three chemical baths (Table 1) are shown in Fig. 1. The predicted peaks (002) (100) (101) (102) (110) (103) (112) (201) and (202) are reported as the identifying peaks for γ-MnS thin films as reported by JCPDS (4-626) and earlier reports [1,3-5]. The presence of these prominent peaks confirms the hexagonal γ-MnS (metastable state) with wurtzite phase of the as-grown MnS thin films. γ-MnS structure has been observed in thin films prepared from chemical bath deposition [1,3-5] and RF sputtering technique [6] whereas α–MnS (stable state) has been observed in thin films prepared from solvothermal synthesis [7]. The observed d (lattice spacing) and I (intensity) values of thin films prepared from three different chemicals baths are presented in Table 2.

Table. 1 Preparatory condition of films of three chemical baths

Chemical baths	Thickness(Å)	Temperature(˚C)	Time (Hrs)	pH
Bath 1	3620	70	4	
Bath 2	4170	70	6	5
Bath 3	5200	60	6	

Table. 2 XRD data of CBD γ-MnS thin films

Standard JCPDS (File no 4-626)		Observed						Plane (h k l)
		Bath 1		Bath 2		Bath 3		
d (Å)	Intensity	d (Å)	Intensity	d (Å)	Intensity	d (Å)	Intensity	
3.449	98	3.3897	84.7	3.3827	86.8	-	-	100
3.225	100	3.1747	100	3.1810	100	3.3727	93.7	002
3.041	75	-	-	2.8354	66	-	-	101
2.354	24	2.2518	58.6	2.1676	46.6	-	-	102
1.989	98	1.9749	64.4	-	-	-	-	110
1.823	60	1.9222	52.2	-	-	1.8408	53.6	103
1.723	9	-	-	-	-	-	-	200
1.693	61	-	-	-	-	1.68719	45	112
1.665	9	-	-	1.5781	42.3	-	-	201
1.520	2	-	-	1.5659	33.5	-	-	202

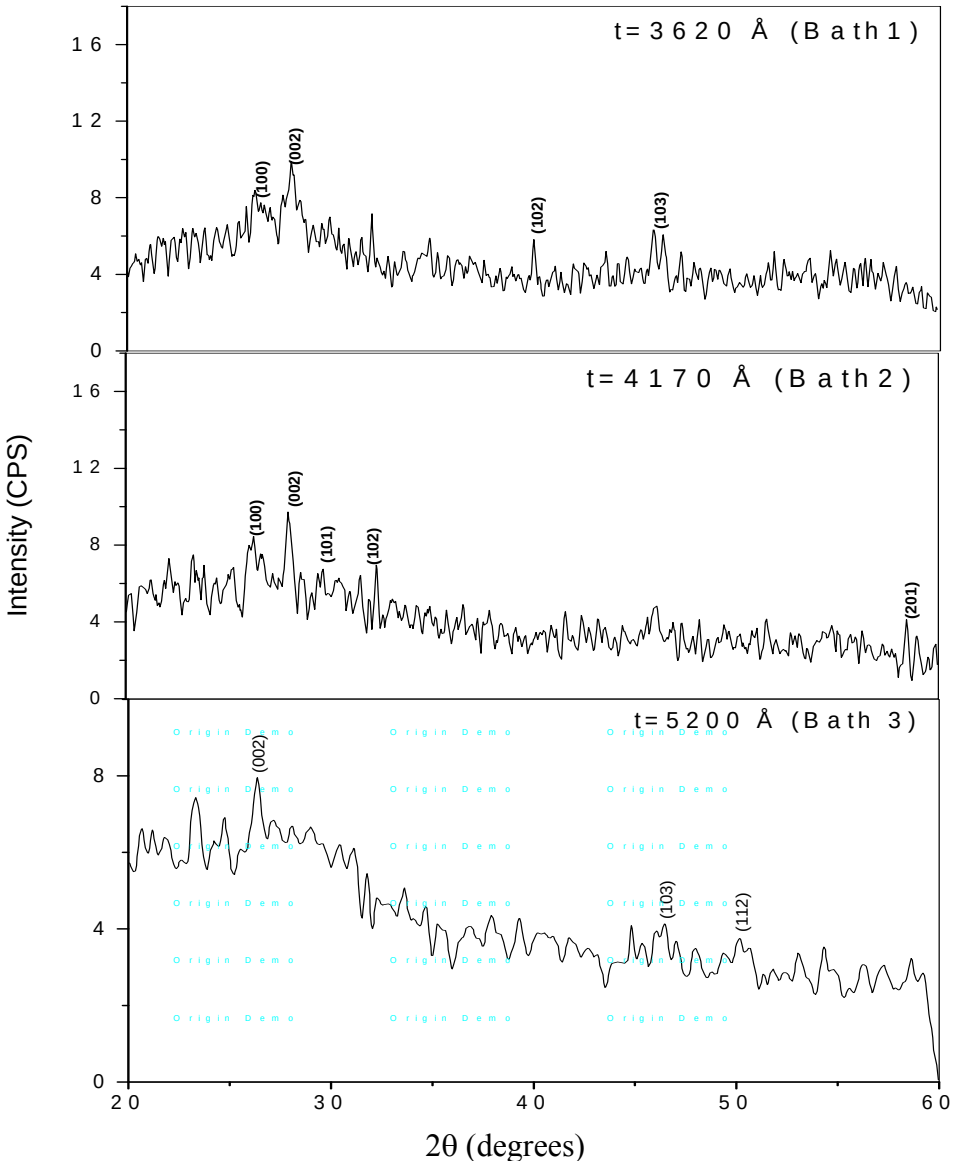

Fig. 1. X-ray diffractograms of CBD γ-MnS thin films of different thicknesses.

Table. 3 Confirmation of Better Orientated film

Chemical baths	Film Thickness (Å)	Peaks	Logering Factor	Better Orientation Factor	Preferential Orientation
Bath 1	3620	002 100	0.489 0.402	0.145	002
Bath 2	4170	002 100	0.344 0.288	0.079	002
Bath 3	5200	002 103	0.937 0.372	0.899	002

The absence of $Mn(OH)_2$ peaks in the x-ray diffraction is due to the use of the appropriate complex agent, hydrazine hydrate which limits the formation of metal hydroxide in the solution and favors the preparation of MnS thin films with the pure phase [4]. This is because the choice of the complex agent and its concentration determines to a certain extent the concentration of the free metal ions (Mn^{2+}), which in turn affects the rate of chemical reactions leading to the formation of the MnS thin films.

A method that evalutes the magnitude of the preferred orientation factor 'f' for a given plane relative to other planes in a material was employed [8]. According to this method, the preferred orientation factor f(002) of the 002 plane for the MnS thin film has been calculated by evaluating the fraction of (002) plane intensity over the sum of intensities of all peaks with in a given measuring 2θ range [20º–60º]. Similarly the orientation factor of the other peaks has been evaluated for all the films and their values are presented for MnS thin films of thickness 3620 Å as f (002) = 0.489, f (100) = 0.402, f (102) = 0.312, 3620 Å f (103) = 0.254. For MnS thin films of thickness 4170 Å, f (002) = 0.513, f(100) = 0.419, f (101) = 0.354, f (102) = 0.315, f (201) = 0.2689. For MnS thin films of thickness 5200 Å, f (002) = 0.937, f (102) = 0.372, f (112) = 0.221. Since f (002) is greater compared to other orientation factors, it can be concluded that MnS thin films have the preferential orientation along (002) plane.

A Lotgering method has been employed to evaluate the better orientation factor 'F' as follows [4],

$$F = \frac{(P-P_o)}{(1-P_o)} \tag{1}$$

where $P = \sum I(00l)/\sum I(hkl)$ and P_o is the P value for a non-oriented plane. P_o is calculated from the standard XRD data γ-MnS. The value of the better orientation factor is in the range of 0 and 1. As reported, large orientation factor F implies high alignment [2]. The lotgering factor (P) for the peak (002) is found to be large enough compared to that of the non-oriented peaks (P_o) in the films prepared from all the three chemical baths. This enables to conclude again that the preferential orientation is (002) in γ-MnS thin films. The increase of better orientation factor (F) with film thickness confirms that high thickness films have highly oriented preferential plane (002) (Table 3). It is interesting to note that lotgering factor also increases with film thickness irrespective of chemical baths. Therefore lotgering factor can also be employed as a tool to measure the better orientation of the preferential plane.

From the observed d-spacing and (hkl) planes, the lattice constants and hence the axial ratio, volume of the unit cell, crystallite size, dislocation density and strain are evaluated using the methods reported earlier [5] and the estimated values are reported in table 5. The determined

volumes of the unit cell of the prepared MnS films are in the range from 230 to 245 Å^3. The values of all the structural parameters determined for the films agreed well with those of the earlier reports and JCPDS data [40-1289] [5]. The calculated D_c values range from 40-54 nm, indicating that the as-prepared MnS films are made up of nanocrystals and are in good agreement with the previous report [2]. It is interesting to note that irrespective of the chemical bath the grain size improves and the defects like dislocation density and strain in the films decrease with film thickness. This is due to the improvement in crystallinity in the films with film thickness.

Table. 4 Determination of lattice parameters of γ-MnS thin films

Film Thickness (Å)	Lattice Constants (Å)				Axial ratio c/a	Volume of the Unit cell (Å^3) X 10^{-30}		Crystallite size D_c (nm)	Dislocation density (10^{14} lines/m^2)	Number of crystallites per unit area (10^{15}m^{-2})	Strain x 0^{-4}
	a		c								
	Observed	JCPDS	Observed	JCPDS		Observed	JCPDS				
3620	3.914		6.400		1.635	231.9		40.957	5.961	5.269	8.460
4170	3.906	3.979	6.362	6.447	1.628	229.6	241.0	46.792	4.567	4.070	7.405
5200	3.919		6.5453		1.645	245.2		54.417	3.377	3.227	6.367

3.2. EDAX Analysis

Fig 2 shows the EDAX result of MnS thin films of thickness 4170Å from bath 2. EDAX analysis confirms the composition of manganese and sulphur in MnS thin film with the composition $Mn_{1.2}S_{0.8}$. This result shows that the samples are rich in Mn. Mn rich MnS thin films (Mn:S = 3:2) have been obtained by the earlier workers from the reaction mixture having similar concentration and volume of Mn and S sources [1]. The presence of chlorine in the prepared thin films may be due ammonium chloride (NH_4Cl) in the reaction mixture. Strong Si and O signals were observed due to the glass substrates [5].

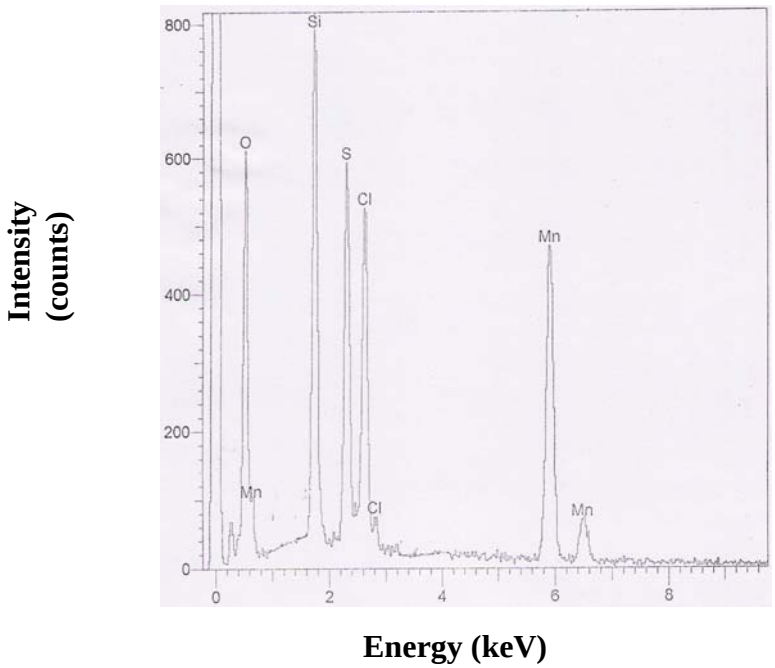

Fig. 2 EDAX spectra of CBD MnS thin films of thickness 4170 Å.

3.3 SEM Studies

The scanning electron micrographs of the deposited MnS thin films of thickness 5140 Å are shown in Fig.3 which shows that the film has rough surface with the presence of well defined nano-crystalline particles in a fine back ground. By improving the magnification further (x3K) the hollow spherical crystals can be clearly visualized in [Fig 3 (b)].

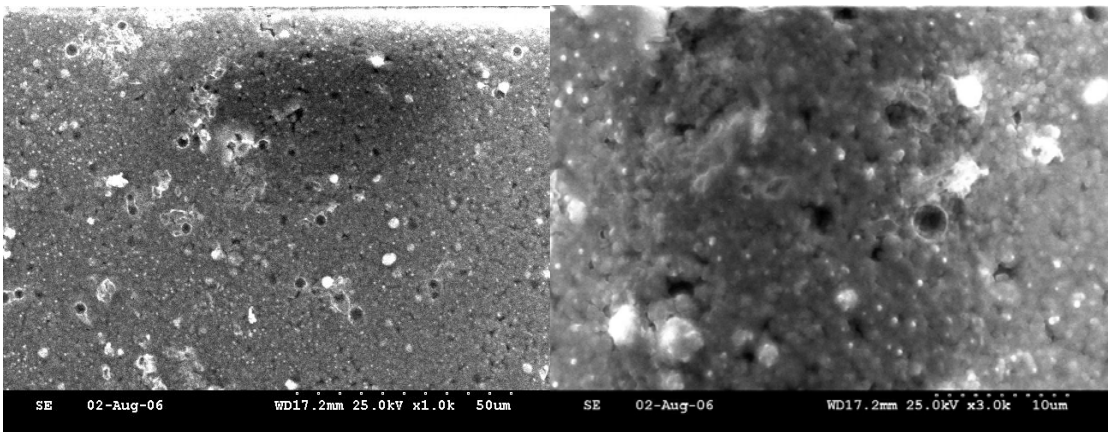

Fig. 3 SEM image of CBD γ-MnS of thickness 5140 Å for different magnification

3.4 FTIR analysis

Fig 4 presents the FTIR spectra of MnS thin film of thickness 5380Å. The spectra has been recorded in the region 400-4000cm^{-1}. The vibrational frequencies of the various chemical bonds in the films can be assigned from FTIR spectra interms of peak position. By the assignments of stretching and bending modes of vibration to the observed frequencies conformational preferences of the molecule can be identified. Since metal-sulfide stretching vibrations occur below 400cm^{-1}, this FTIR spectrum can not be used a tool to identify the chemical constituents. If the range has been widened, it is possible to confirm the chemical constituents quantitatively or qualitatively using FTIR spectrum.

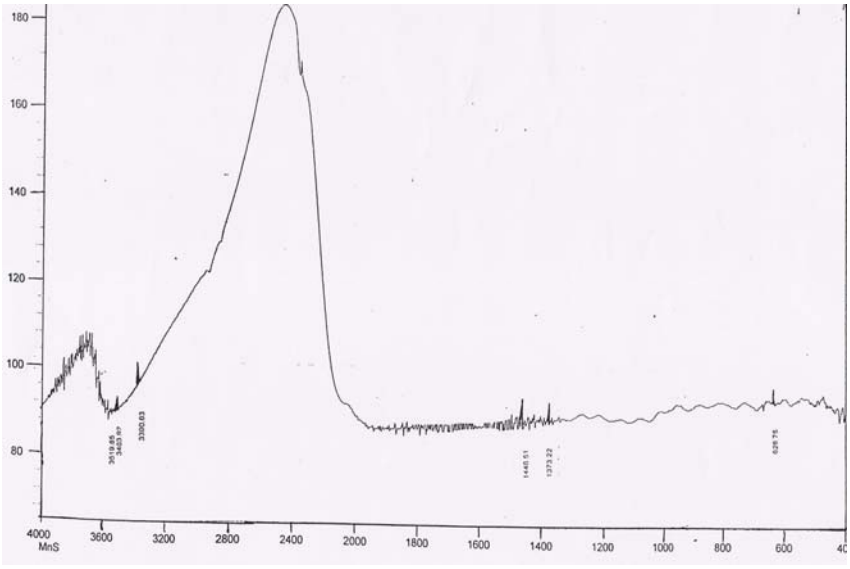

Fig. 4 FTIR Spectrum of CBD γ-MnS thin film of thickness 5380Å.

The broad band at 2000-3600cm^{-1} may be due to O–H bond compound type. Since all the solutions used in the reaction mixture are prepared in deionized water, O–H bond can be expected in the prepared film. The water (O–H) stretching vibration at 3390 cm^{-1} is lesser intense peak and water bending vibration at 1645 cm^{-1} have not been detected in MnS thin film as reported earlier [8]. This confirms that oxygen does not appear as water in MnS thin films. The two peaks at 3583 and 3458cm^{-1} due to hydroxy groups [9] are absent in MnS thin films. The absorbance band at 644.76 cm^{-1} is Mn–OH stretching peak [10]. The absorbance band at 1447 and 1373 cm^{-1} are due to HCO_2 as reported [11]. Thus FTIR spectrum enables to conclude the form of occurrence of oxygen in CBD MnS thin films as carbonate.

4. Conclusions

X-ray analysis of MnS thin films prepared from three chemical baths are found to have similar structural parameters. The chemical constituents and their compositions of the films have been estimated by the energy dispersive x-ray analysis. The deposited films are identified as $Mn_{1.2}S_{0.8.}$ The morphology of the deposited films has been found as highly oriented nanostructure composed of hollow spherical crystals. FTIR spectra enabled to realize the form of occurrence of oxygen in the prepared MnS thin films.

Acknowledgements

The authors are grateful to the Secretary, Principal, Dean and Head of the Department of Physics, Kongunadu Arts and Science College, Coimbatore for their excellent encouragement and support. One of the author Mrs.B.Kavitha, was grateful to express her thanks to Jawaharlal Nehru Memorial Fund for financial support.

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