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Preparation And Characterisation of Crystalline Manganese Sulphide Thin Films

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Abstract: *Pure Manganese sulphide thin films have been deposited on commercial glass substrates by chemical bath deposition method. Experimental results show that pre-treatment of the substrates by HF etching play an important role in the formation of crystalline films. The structure and morphology of the obtained manganese sulphide thin films were characterized for thickness, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX) and optical absorption spectroscopy. XRD measurements show that all the films are crystallize in the wurtzite phase.*
SEM studies confirm crystalline nature of films with grain size varying in the range between 1-2 µm. EDAX analysis shows that average ratio of atomic percentage of Mn:S is 1:1.The optical band gap of thin film is found to be 2.7 eV.

I. Introduction

Recently metal chalcogenide thin film materials have opened an intriguing area in the field of electronic applications. Dilute magnetic semiconductors (DMS) have received a challenging attention due to their proposed approach in fabrication of semiconducting devices which includes cellular phones (microwave transistors), compact disc (semiconductorlasers) and many other applications[1-5]. Depending upon the deposition parameters, the structural, electrical, microscopical and optical properties of these materials can be controlled in many ways [6-11].

Manganese sulphide is a wide band gap material (Eg= 2.7eV)semi magnetic semiconductor with potential interest in short wavelength optoelectronic applications such as solar selective coating, solar cells, sensors, DMS, photoconductors, optical mass memories [12-16].

Manganese sulphide have been prepared by different methods which includes chemical bath deposition method (CBD) [17], hydrothermalmethod [18-19], solvothermal method [20], radiofrequency sputtering method, thermal evaporation, microwave irradiation, molecular beam epitaxy [21-24].

Depending upon the optimized conditions, growth of film takes place by ion-by-ion condensation or cluster-by-cluster adsorption from the solution onto a substrate. Among these, CBD is most useful and less expensive for the deposition of ternary and quaternary thin films materials used in solar cells.

Manganese sulphide occurs in polymorphic forms: the α-MnS (Wurtzite). Both tetrahedrally co-ordinated β and γ forms can only exist in a low temperature range and will transform irreversibly to the octahedrally co-ordinate stable α-form at 100-400^{o}C [25-32].

In present investigation the depositions of MnS thin films have been prepared from an aqueous medium using manganese sulphide and thiourea as ion sources[33-35]. The preparative parameters have been optimized for getting good quality, welladherent, uniformly depositedMnS thin films.

II. Experimental

2.1 Preparation Of The Glass Substrate:

The deposition was carried out using commercial glass slides of dimension 75mm × 18 mm × 0.2mm. These glass slides were washed with detergent, cleaned and etched in (30%) HF for about 1-2 minutes. After etching these slides were cleaned with detergent, degreased with acetone, dried with the help of drier and immersed in deionised water before the deposition.

2.2 Deposition Of Mns

Deposition of MnS thin films is based on the release of Mn^{2+} ions and S^{2-} ions in the solution.All the chemicals used were of AR-Grade. 1.0 ml Manganesesulphate, 0.1 ml ammonia and 5.0 ml Thiourea solution were placed in 50 ml beaker. Deionised water was added to make the volume up to 40 ml. The pH of resulting solution was maintained to the pH = 10.5 ± 0.2 and bath temperature was fixed at an appropriate temperature. The pre – treated glass substrates were inserted vertically into the precursor and were allowed for 08 hoursof deposition time.

At two different bath temperatures, Manganese sulphide thin films were deposited as shown in table 1. The deposition process involved the reaction between positive and negative ions to form neutral atoms which are precipitated out of the solution with the help of complexing agent as ammonia.

III. Characterization Of Mns Thin Films

The film thickness was measured using a Dekta – 3030 profilometer. The structural and morphological studies of the MnS thin films were examined by X-ray diffraction (XRD), Scanning electron microscope (SEM), XRD patternswere recorded with Siemens D-500 diffractometer using a copper anode in a 2θ coupled geometry. The optical absorption measurements were made in the wavelength range 400- 1000 nm by using a Hitachi-3300 (Japan) UV-VIS- NIR double beam spectrophotometer at room temperature.The SEM analysis was performed with a stereoscan Cambridge (UK) MK-S instrument to take scanning electron microscope images, which was equipped with an EDAX analyzer to measure qualitatively the sample stoichiometry.

IV. Results And Discussion

4.1Growth Mechanism Of Mns Films

An aqueous bath containing Manganese salt, Thiourea and ammonia as complexingagent which allows the controlled release of the Mn^{2+}ions and S^{2-} ions in the solution which then condense on an ion by ion basis on the etched glass substrates that are suitably mounted in the solution. The deposition of MnSoccurswhen the ionic product of $Mn^{2+}$and S^{2-} exceeds the solubility product of the MnS.The reaction mechanism for MnS formation isshown below:

$$MnSO_4 + 2\ NH_4OH \leftrightarrow Mn^{2+} + (NH_4)_2SO_4 + 2\ OH^-$$

$$(NH_2)_2SC + 2\ OH^- \leftrightarrow CH_2N_2 + H_2O + HS^-$$

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

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

In CBD method the formation of thin films is possible by two reactions, notably:

a) adsorption and coagulation of colloids pre-formed in solution by homogenous reaction as well as,
b) ion-by-ion condensation at the surface of the substrates by heterogeneous reaction.

Practically, bath processes may occur. It is speculated that, in any case, the etching of the substrates results information of rough surface, which would provide either the nucleation sites for heterogeneous reaction or the adsorption sites for adsorption of colloids which are pre-formed in the solution.

Fig1.shows,the variation of film thickness with bath temperature in the range of 300k to 340k.

In initial stage, the film thickness increases rapidly, reaches to saturation with the deposition temperature. Such phenomenon can be explained by heterogeneous precipitation and homogenous precipitation which leads to the growth of film. Other one involves the desorption / dissolution of the pre-formed MnS film, which results in decrease in film thickness.

In initial time of deposition, the solution has high degree of supersaturation i.e.sufficient amount of source materials. The process of heterogeneous precipitation and homogenous precipitation plays an important role as compared to desorption or dissolution process, leading to the increase in film thickness. The source material are limited in a typical deposition bath because there is continuous homogenousprecipitation and heterogeneous precipitation as source material becomes less and less with time of deposition being prolonged, resulting in the decrease of film thickness. From this work it indicates that rise in bath temperature favors the heterogeneous precipitation which would produce more nuclei on the substrate, therefore promotes the growth of MnS films.

4.2 Structural And Optical Study

The structural properties were recorded using of MnS film, X-ray diffractogram of the film. XRD pattern of MnS deposited on glass substrate is shown in fig.2.XRD-patterns grown onto the etched glass substrates at different bath temperatures at 40^0C and 50^0C show three different structures i.e.α,βand γ forms. The films deposited at 50^0C consist of pure α - Mns phase. (Powder Diffraction file no. 40-1289).The optical absorption spectrum of MnS film deposited onto glass substrates wastaken in the wavelength range of 400-1000 nm. The optical studies show the films high absorption coefficient with direct band gap value, a plot of , $(\alpha h\upsilon)^2$vs. hυ is drawn and linear region is extraplotted with a photoenergy axis intercept indicative for the band gap[36,37]. The observed Eg value of MnS thin films is 2.7 eV.

4.3 Morphological And Compositional Study

The surface morphology of Manganese sulphide thin films was analyzed by using scanning electron microscope. SEM image of Manganese Sulphide film is shown in Fig.4. It is observed that nature of MnS deposited films are uniform, without cracks or pinholes and well adherent on glass substrates.The Photomicrographs reveals appreciable difference for variable bath temperature. The MnS thin films at bath temperature40^0C shows two different unstable forms, tetrahedral and needle. At higher temperature 50^0C there is single form which is crystalline in nature that indicates the increase in crystallinity of films. The calculated average grain size of Manganese Sulphide thin film is about 15-20µm.

Chemical composition of the constituents in film is confirmed by EDAX. The EDAX spectrum does not show deviation from the original composition. The EDAX spectra of MnS, shows the composition for Mn:S is 1:1. The EDAX of the MnS sample is shown in Fig.5.

V. Conclusions

Homogenous and uniform films of Manganese Sulphide were successfully deposited on HF-etched glass substrates using chemical bath deposition method. The film was formed by ion-by-ion growth mechanism. It was found that HF-etching and temperature are important parameter in Chemical bath deposition method. The crystallographic studies revealed the wurtzite type of structure. Optical studies revealed high optical absorption coefficient with Eg = 2.7 eV. The morphologies were found in metastable α – Mns form.The EDAX revealed the 1:1 stoichiometric ratio for MnS films.

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References

[1]. C.Gumus, A.Bayri, C.Ulutas, M.Karakaplan, Y.Ufuktepe. Journal of Optoeledronics and Advanced Materials 8(2006) 261.
[2]. Simmonds, Journal of Physics Today 48(1995) 26.
[3]. R.Fiederling, M.Keim, G.Reuscher, W.Ossau, G. Schmidt, A.Wang, L.W. Molenkamp, Nature 402 (1999) 787.
[4]. J.K.Furdyana, J.Appl.Phys.64 (1988) R 29
[5]. J.Kudernovsky, V.Drchal, J.Turek, L.Bergqvist, O.Eriksson, G.Bouzerar, L.Sandratskii, P.Bruno. J.Phys. Condens. Matter. 16(2004) 5571
[6]. C.Gumus, C.Ulutas, R.Esen, O.M.Ozkendir, Y.Ufuktepe, Thin Solid Films 492 (2005) 5.
[7]. L.Eckertava, Physics of Thin Films Processes, Plenum Press, New YorkNY (1986).
[8]. C.D.Lokhande, Mater. Chem.Phys. 27(1991)1.
[9]. R.N.Bhattaracharya. J.Electrochem.Soc.129 (1992) 332.
[10]. R.L.Greene, D.D.Sell, Phys.Rev.171 (1968) 600.
[11]. P.O.Brien, D.J.Otway, D.S. Boyle, Thin Solid Films 361 (2000)17.
[12]. H.M.Pathan, S.S.Kale, C.D.Lokhande, Sung–Hwan Han, Oh.Shim Joo, Materials Research Bulletin 42 (2007).
[13]. C.D.Lokhande, A.Ennaoui, P.S.Patil, M.Giersig, M.Muller, K. Diesner, H.Tributsch, Thin Solid Films 330 (1998) 70.
[14]. D.Fan, X.Yang, H.Wang, Y.Zhang, H.Yan, Physica B 337 (2007) 165.
[15]. B.Piriou, J.D.Ghys, S. Mochizuki, J.PhysicsCondens. Matters 6 (1994)7317.
[16]. R. Tappero, P. DArco, A.Lichanot, Chem. Phys. Lett. 273 (1997) 83.
[17]. S.N.Agbo, F.I.Ezema. Pacific Jour. of Sci. and Tech 8 (2007) 01.
[18]. Pingtang Zhao, Qiumei Zeng, Xianliang He, Hao Tang, Kaixun Huang, Jour. of Crystal growth 310 (2008) 4272.
[19]. Changhua An,GuienZhau, Yitai Qian, Jour. of crystal growth 252 (2003) 580.
[20]. SubhajitBiswas, Soumitra Kar, Subhadra chaudhuri, Jour.of crystal. Growth, 284 (2005) 135.
[21]. P.Pramanik, M.A.Akter, P.K.Basu, Thin Solid Film, 158 (1988) 275.
[22]. S.A.Mayen–Hernandez, S.T.Sandoval, R.C.Perez, O.J.Sandoval, B.S.Chao, G.T.Delagado, J.Cryst. Growth 256 (2003) 162.
[23]. I.Odor–Juarez, P.Jimenez, G.T.Delgado, R.C.Perez, O.J.Sandoval, B.Chan, S.J.Sandoval, Mater.Res. Bull. 37(2002)1749.
[24]. O.Goede, W.Heimbrodt. V.Weinhold, Phys. Stat.Sol. B. 136 (1986) 49.
[25]. O.Goede, W.Heimbrodt. V.Weinhold, E.Schnurer, H.G.Eberle, Phys. Stat. Sol. B 143(1947) 511.
[26]. S.B.Wang, K.W.Li, R.Zhai, H.Wang, Y.D.Hou, H.Yan, Mater. Chem.Phys. 91 (2005) 298.
[27]. B.J.Skromme, Y.Zhang, D.J.Smith, S.Sivananthan, Appl.Phys.67 1995) 90.
[28]. S.Sivananthan, L.Wang, R.Sporken, J.Chen, D.J.Smith, B.J.Skromme, Jour.Cryst.Growth 159 (1996) 94.
[29]. M.Okajima, T.Tohda, J.Cryst. Growth 117 (1992) 810.
[30]. L.David, C.Bradford, X.Tong, T.C.M. Graham, K.A.Prior, B.C. Cavenett, Jour.Cryst. Growth 251 (2003) 591.
[31]. O.Madelung, Landolt–Bornsten (L.B.newseries) Semiconductors; Physics of Non – tetrahedral Bonded Binary compounds III/ 17 g, Springer – Verlag(1984).
[32]. W.Gririat, J.K.Furdyna, J.Kossut, San Wiego (Eds) Semiconductors and Semimetals, 25, Academic Press, CA (1988).
[33]. Dong Bo. Fan, Hao Wang, Yong Cai Zhang, Jie Chang, Bo Wang, Hui Yan, Materials chemistry & physics 80 (2003)47.
[34]. R.L.Clendenen, H.G.Drichamer, J. chem, phys. 44 (1996)4223.
[35]. M.Kobayaski, T.Nakai, S.Mochizuki, N.Takayama, J.Phys.Chem.Solid 56(1995)341.
[36]. K. Kambas, Physica B 166 (1989) 103.
[37]. V.P.Munshinskii, V.I.Kobolev, Sov.Phys.Semicond.5 (1971)1104.

Figures:

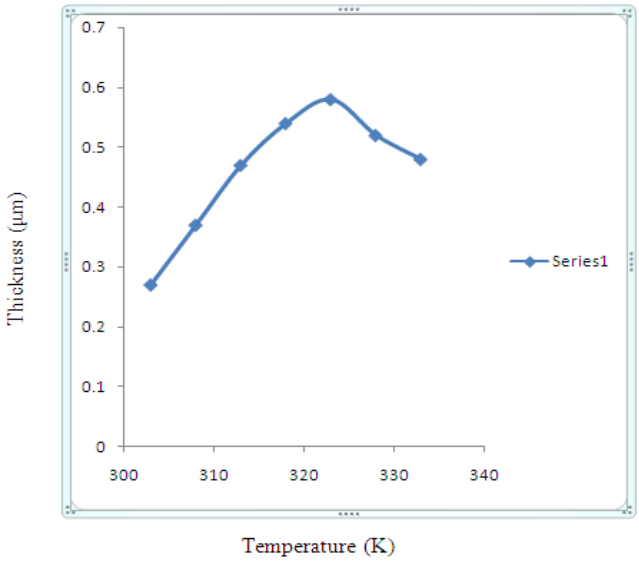

Fig No. 1 Variation of thickness vs. Temperature.

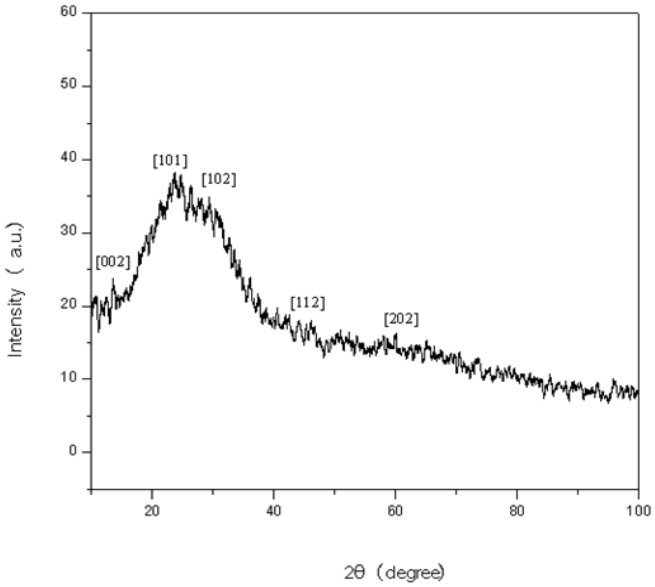

Fig. No- 2: XRD pattern of MnS thin

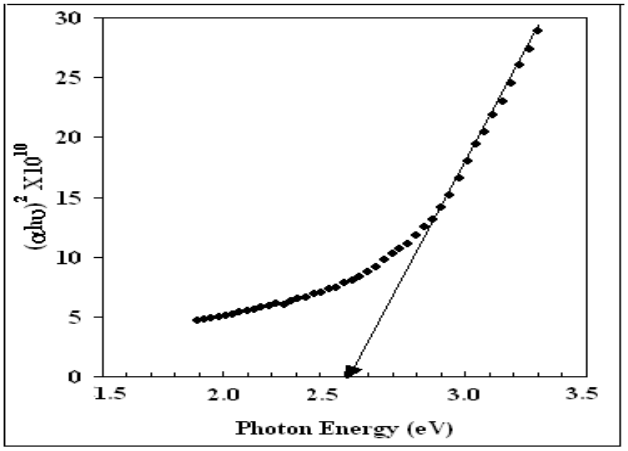

Fig. No- 3: Plots of $(\alpha h\upsilon)^2$ vs. photon energy.

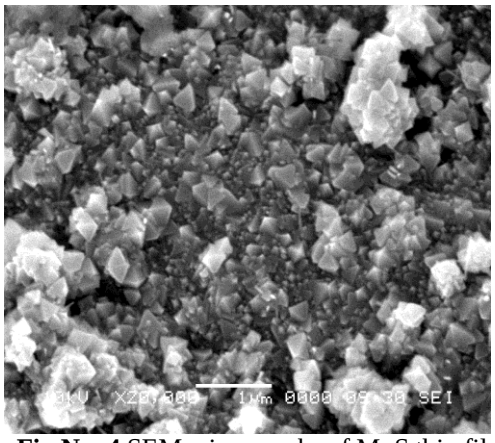

Fig.No. 4 SEM micrographs of MnS thin film.

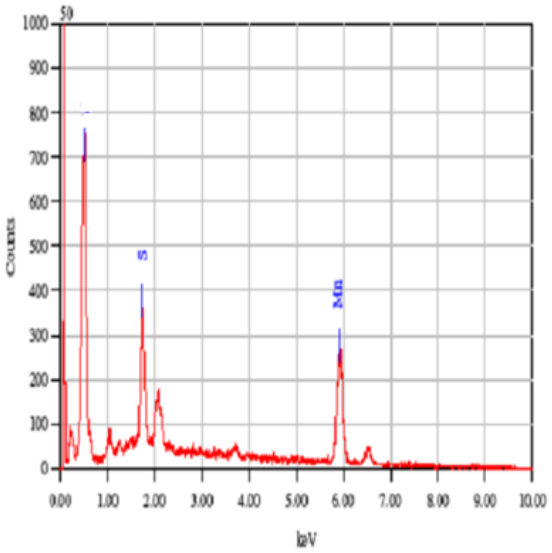

Fig . No. 5:EDAX pattern of MnS thin film.

Tables:

Table no.1:

Bath	**Time**	**1 M Manganese Sulphate**	**0.1 M Thiourea**	**NH_3**	**H_2O**
MnS 4	20 hrs	1ml	5ml	1ml	50ml
MnS 5	20 hrs	1ml	5ml	1ml	50ml

Table no.2: Structural and morphological data of MnS thin film:

Film	d-values(A^0)		Planes	Grain Size(A^0)	
	Observed	ASTM	hkl	XRD	SEM
MnS	3.324	3.225	002	140	148
	3.077	3.041	101		
	2.492	2.354	102		
	1.697	1.693	112		
	1.529	1.520	202		