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Metastable MnS films prepared by the addition of EDTA using chemical bath deposition technique

T. Dhandayuthapani[1], M. Girish[2], R. Sivakumar[1]*, C. Sanjeeviraja[3] and R. Gopalakrishnan[4]

[1]Directorate of Distance Education, Alagappa University, Karaikudi, India.
[2]Dept of Physics, Alagappa University, Karaikudi, India.
[3]Dept of Physics, AlagappaChettiar College of Engineering and Technology, Karaikudi, India.
[4]Department of Physics, Anna University, Chennai, India.

Abstract : In this work, first time we report on metastable manganese sulfide (MnS) thin films prepared by chemical bath deposition using ethylenediamine tetra acetic acid (EDTA) as a chelating agent. X-ray diffraction study shows the presence of both β and γ – MnS phases (metastable) in the films. Photoluminescence study confirms the optical quality of films and the band edge emission was observed at 360 nm. Micro-Raman study revealed the enhancement in crystallization of the films due to the effect of molar ratio of precursor solutions. Surface morphological study shows the formation of nanograin with almost uniform size. The paramagnetic nature of MnS film was confirmed by the M-H plot.
Key words: CBD method, MnS films, micro-Raman study, surface morphology

Introduction

Manganese sulfide (MnS) is a p-type wide band gap ($E_g \approx 3.7$eV) dilute magnetic semiconductor (DMS) having diverse applications in lithium sulfur batteries, spintronics, and electroluminescent displays owing to its unique magneto-optical properties[1]. Generally, MnScrystallizes in three polymorphic forms, the stable green colored rocksalt α-MnS, which exists in nature as alabandite, two pink colored metastable phases, zinc blende (β-MnS) and the wurzite (γ-MnS), which usually occur at low temperature. Both tetrahedrally coordinated metastable zinc blende and wurziteMnS will transform into octahedrally coordinated rocksalt α-MnS at high temperature (100-350^{o}C) or at high pressure. Metastable MnS thin films exhibit unique chemical and physical properties, which are suitable for any technological applications. However, the preparation of metastable MnS thin film possesses considerable challenge as they are prone to oxidation; suffer from thermal instability, and contamination because of their high chemical reactivity. Among the various techniques reported[2,3] for metastable MnS thin film preparation, the chemical bath deposition (CBD) is a simplest approach, which offers high quality films. In the CBD method, the complexing/chelating agent plays a vital role to get uniform MnS films. Earlier triethanolamine[4] (TEA) and TEA and trisodium citrate as complexing agents for the deposition of MnS films[5,6]. In general, the purpose of complexing agents is to ensure the slow release of Mn^{2+} ions during the MnS film preparation. However, the earlier reports showed that the addition of TEA may

result in a very low release of Mn^{2+} ions when using the initial lower concentration of Mn and/or S precursor solutions, which in turn result the formation of non-homogeneous and discontinuous MnSfilm.It is worth to mention that the ethylenediamine tetra acetic acid (EDTA) is a strong chelating agent to enhance the stable complexes between metal ions and to dissociate at low rate[7]. In this work, first time we have successfully prepared homogeneous metastable MnS thin films by chemical bath deposition technique using EDTA as a chelating agent.The structural, surface morphological, optical, vibrational, and magnetic properties of the deposited films were studied and reported.

Experimental

Aqueous solutions of 0.5 M manganese acetate [$Mn(CH_3COO)_2$] (Mn^{2+} source) and 0.5 M thiourea [$CS(NH_2)_2$] (S^{2-} source) (Mn:S = 1:1) was prepared. Later on, 0.25 M EDTA was added with the precursor solution. The pH of the solution was maintained at 10 by adding the ammonia drop wise into the solution. The resultant solution was mixed with a magnetic stirrer and the solution becomes turbid and turns to grey color. The degreased glass substrates were vertically inclined in the growth solution and the solution was placed in the CBD bath. The temperature of growth solution was maintained at 60^{o}C all over the deposition and the deposition was carried out for 24 hours. The coated substrates are rinsed with deionized water and dried in air.The MnS films were also prepared by changing the concentration of sulfur source with constant manganese source (Mn:S = 1:2 and 1:3). The strong chelation of EDTA slows down the release of Mn^{2+} ions and enhances the ion by ion deposition mechanism, which in turn produce the homogeneous and well adherent films. The structural property of MnS thin films were studied by x-ray diffraction (XRD) using CuK_α (λ = 0.154nm) radiation source (X'pert Pro PANalytical) over 2θ scan range of 25-70°. Surface morphology of the films was studied by using scanning electron microscopy (SEM; JEOL; JSM-6390LV). Micro-Raman measurements were performed using a backscattering geometry. The spectra were recorded using the 514.5 nm line of Ar^{+}-ion laser with a 100 mW power. The photoluminescence (PL) study was performed using a fluorescence spectrophotometer (Varian Cary Eclipse). The magnetic property of MnS sample was measured using the vibrating sample magnetometer (VSM; Lakshore 7410) and its hysteresis loop was recorded at 300 K with an applied magnetic field sweeping from -15,000 to 15,000 Oe.For VSM measurement, a few milligram of powder was used from the sample prepared at 1:3 molar ratio.

Results and Discussion

Structural and surface morphological properties

Figure 1 shows the XRD patterns of MnS films deposited at various molar ratios. The onset of crystallization was observed from the XRD pattern of the film deposited at 1:1 molar ratio. The increase in intensity of XRD peaks with increasing molar ratio (1:2 and 1:3) revealed the enhancement in crystallinity of MnS films. The diffraction peaks along (211), (102), (110), (103), (004),and (202) orientations were indexed to the hexagonal wurzite (γ-MnS) phase (JCPDS File No.:89-4089; 65-3333). The peaks along (111) and (200) directions are corresponding to the zinc blende (β-MnS) (JCPDS File No.: 40-1288) structure. This revealed the formation of metastable MnS films in the present work. The peak width narrowing with respect to increase in molar ratio is presumably associated with the size quantization, as the crystal size increases with excess of sulfur which promotes nucleation and growth. The average crystallite size of (1:1), (1:2), and (1:3) molar ratio deposited MnS films are 34 nm, 46 nm, and 64 nm, respectively. In addition, it is evident from XRD results that the use of EDTA as a complexing agent has significantly improved the crystallinity of MnS thin films when compared with the previous reports of MnS thin film prepared using TEA and Trisodium citrate[4-6].

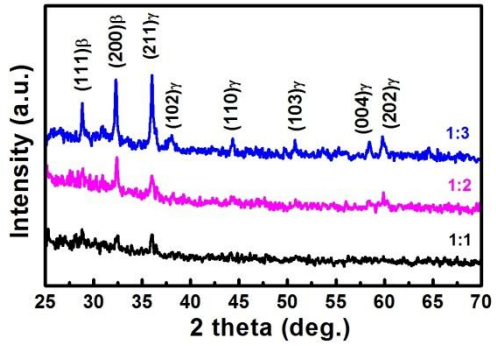

Figure 1. X-ray diffraction patterns of MnS thin films

Figure 2 shows the scanning electron microscopic (SEM) images of MnS thin film deposited at various concentrations of thiourea. In all the three cases agglomerated nanoparticle morphology was observed. However, the film deposited at 1:1 molar ratio is having discontinuous structure. On the other hand, the films deposited with excess of thiourea(1:2 and 1:3)offers theaggregated nanoparticles covered over the entire substrate. This shows that the excess of thiourea promotes nucleation and further growth, which enhance the crystallization of films as observed from the XRD result. As mentioned above, most of the reports showthe amorphous and non homogeneousMnS film formation when using the TEA and/or trisodium citrate complexing agents[4-6]. Instead, the present study results the addition of EDTA leads to metastable homogeneous film formation by reducing the fast release of Mn^{2+} ions, in addition to that EDTA reduces the oxygen incorporation in toMnS films. Similar observation was madefor chemical bath deposited CdS and $Zn_xCd_{1-x}S$ films[7,8]. So the addition of EDTA enhances the ion by ion deposition mechanism which is presumably a crucial factor in obtaining homogeneous and well adherent MnS thin films[9].

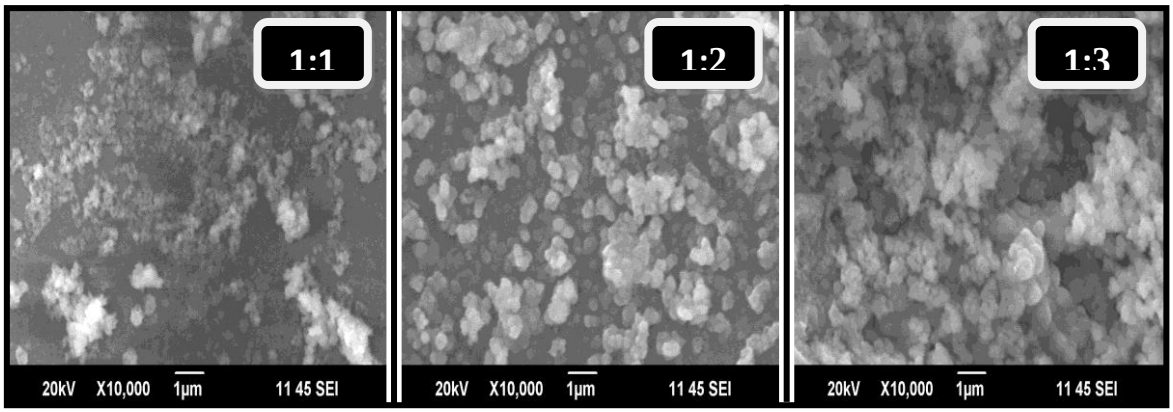

Figure 2. The SEM images of MnS thin films deposited at various concentrations.

Photoluminescencestudy

Figure 3 shows the photoluminescence spectra of MnS thin films when excited at 310 nm. The band edge emission was observed at 360 nm (3.4 eV). The other four peaks (377, 410, 460, and 494 nm) are due to the Mn^{2+} d-d transitions of $^6A_1(S) \rightarrow {}^4E(^4D)$(377 nm), $^6A_1(S) \rightarrow {}^4T_2(^4D)$(410 nm), $^6A_1(S) \rightarrow {}^4A_1, {}^4E{}^4G$(460nm), and $^6A_1(S) \rightarrow {}^4T_2(^4G)$(494 nm). This observation is consistent with the reported results[10,11]. The MnS thin film exhibits UV light emission at 377 nm and blue light emission at 410 nm. This shows that the optical property of MnS thin films can be tailored by changing the sulfur source concentration, which suitable for optoelectronic applications such as light emitters.

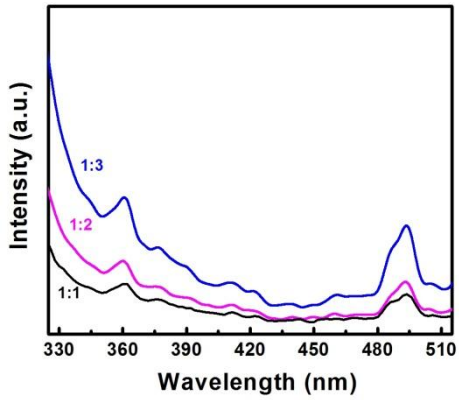

Figure 3. Photoluminescence spectra of MnS thin films

Vibrational property

Micro-Raman spectra of MnS thin films are shown in Fig. 4. The broad peaks observed at 318 cm^{-1} and 369 $cm^{-1}$are corresponding to the transverse optical phonon and longitudinal optical phonon modes of vibrations, respectively[1]. In addition, we have observed a strong resonance peak at ~ 658 cm^{-1}, which is a strong photoluminescence band as earlier reported[12]. The intensity of Raman peaks increased with increasing molar

ratio, which revealed the enhancement in crystallinity of films. This inference is corroborated by our XRD measurement.

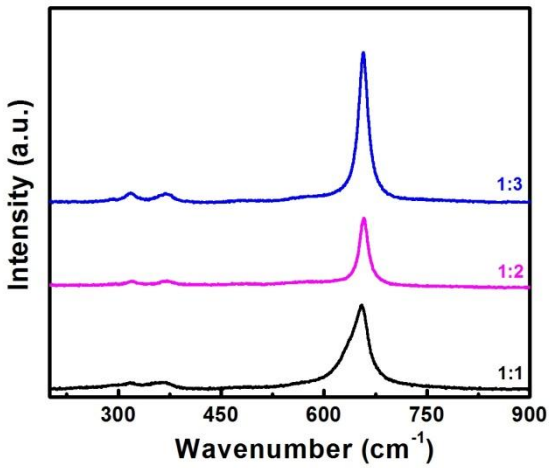

Figure 4. Micro-Raman spectra of MnS thin films

Magnetic property

Manganese sulfide is antiferromagnetic below Neel temperature (150K) and paramagnetic at room temperature[13].The magnetic property of MnS film deposited at 1:3 ratio was studied by VSM at room temperature (300K) as shown in Fig. 5. The hysteresis loop (M-H) of MnS thin film deposited at (1:3) does not reach saturation even at maximum applied magnetic field indicating that it has paramagnetic behavior.

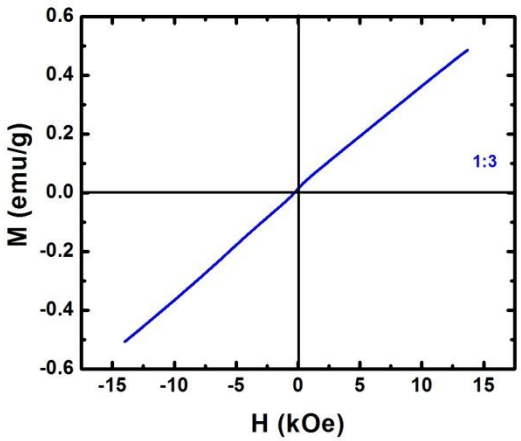

Figure 5. (M-H) plot of MnS thin film deposited with (1:3) molar ratio.

Conclusion

The metastable MnS thin films by the addition of EDTA were successfully prepared using chemical bath deposition technique. XRD result showed the molar concentration induced enhancement in crystallization of the films with mixed β and γ – MnS phases. This was further confirmed by the micro-Raman measurement. Photoluminescence study revealed the band edge emission at 360 nm. The paramagnetic nature of MnS film was confirmed by the M-H plot.

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