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Tuning the morphology of metastable MnS films by simple chemical bath deposition technique

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ABSTRACT

In the present investigation, we have prepared the spherical particles, almond-like, and cauliflower-like morphological structures of metastable MnS films on glass substrate by chemical bath deposition technique at low temperature without using any complexing or chelating agent. The morphological change of MnS films with molar ratio may be due to the oriented aggregation of adjacent particles. The compositional purity of deposited film was confirmed by the EDAX study. X-ray diffraction and micro-Raman studies confirm the sulfur source concentration induced enhancement in the crystallization of films with metastable MnS phase (zinc-blende β-MnS, and wurtzite γ-MnS). The shift in PL emission peak with molar ratio may be due to the change in optical energy band gap of the MnS, which was further confirmed by the optical absorbance study. The paramagnetic behavior of the sample was confirmed by the *M–H* plot.

1. Introduction

In recent years, manganese based diluted magnetic semiconductors (DMS) have attracted considerable attention and remains one of the most researched topics due to their unique magneto-optical properties and potential application in the area of spintronics [1]. In DMS, the band electrons and holes strongly interact with the localized magnetic moments and cause a variety of interesting phenomena. Manganese sulfide (MnS) is a *p*-type wide band gap ($E_g \approx 3.7$ eV) diluted magnetic semiconductor that has potential applications in short wavelength optoelectronic devices, photoconductors and optical mass memories [2–4]. Manganese sulfide crystallizes in three distinct phases; the stable green (α-MnS) with rocksalt type structure which exists in nature, and two pink/orange metastable tetrahedral structures, zinc-blende type (β-MnS), and wurtzite type (γ-MnS) which does not exist in nature. Both the metastable phases β-MnS and γ-MnS exist only at low temperature and transforms to α-MnS at high temperature (120–400 °C) or at high pressure [3]. α-MnS has practical applications in the areas of spintronics, lithium sulfur batteries and microwave absorption [5], whereas β-MnS has applications in electroluminescent displays and light emitters, and γ-MnS has applications in lithium sulfur batteries [6].

The metastable materials may have unique optical [3], electrochemical [6], and magnetic [2] properties, which are suitable for both basic and applied research. However, these properties of metastable MnS nanostructures/thin films depend highly on preparation techniques [7]. For the preparation of MnS nanostructures, the hydrothermal or solvothermal method is so far mostly used. For instance, Mi et al. [8] have synthesized the dandelion like MnS nanostructure with enhanced catalytic performance by hydrothermal method. Yang et al. [4] have prepared MnS nanocubes by solvothermal method. On the other hand, manganese sulfide thin films have been prepared by various techniques such as chemical vapor deposition [9], molecular beam epitaxy [10], RF sputtering [11], etc. However, these preparation techniques have many complex processes, require sophisticated equipment and rigorous experimental conditions. Therefore, at present, the need for developing a simple, inexpensive, and efficient method to prepare the metastable MnS films with significant nanostructure morphology in laboratory environment at low temperature with desired physical and chemical properties, high quality, and high repeatability is a matter of intense research for wide applications. Chemical bath deposition (CBD) is a simple, cost effective and low temperature solution processing technique, which can be used to deposit large

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area MnS thin films on any kind of substrates. The advantage of CBD technique is that the properties of deposited films can be tuned by simply changing various growth parameters such as precursors, pH of the solution, concentration of the precursors, bath temperature, and bath time [12].

Generally, manganese sulfide thin films were prepared by CBD using manganese acetate as manganese (Mn^{2+}) source and thioacetamide as sulfur (S^{2-}) source. Most of the reports used trisodium citrate and triethanolamine as complexing agents for the preparation of MnS thin film [12–14]. For instance, Lokhande et al. [12] used triethanolamine (TEA) and Gumus et al. [13] and Fan et al. [14] have used TEA and trisodium citrate as complexing agents for the deposition of MnS films. Generally, complexing agents are used to ensure the slow release of Mn^{2+} ions during the MnS film preparation. However, Lokhande et al. [12] concluded 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. This will result in a non-homogeneous and discontinuous MnS film formation. It may be mentioned that thiourea is one of the alternative organosulfur compounds, which can be used as a sulfur source for the preparation of semiconducting sulfide films [15]. In addition, thiourea plays multirole during the synthesis of metal sulfide nanostructures as a sulfur source and structure directing agent. Though several reports are available for the deposition of metal sulfide thin films using thiourea as a sulfur source [15,16], the report on the role of thiourea as a structure directing agent for the morphology tuning of metal sulfide thin films are scarce [17]. In the present work, for the first time we have successfully prepared homogeneous and metastable MnS thin films on glass substrate with diverse morphological nature (spherical nanoparticle, almond-like, and cauliflower-like structures) without any complexing agent by chemical bath deposition technique using manganese acetate as a manganese source and thiourea as a sulfur source. The morphology of MnS films are tuned by changing the concentration of thiourea (structure directing agent). The plausible growth mechanism for the formation of different morphologies of MnS films is discussed. In addition, the structural, vibrational, optical, and magnetic properties of the films are studied and discussed in detail. The possible correlations among the data are presented.

2. Experimental details

2.1. Film preparation

Manganese sulfide (MnS) thin films were prepared on corning 7059 microscopic glass substrates using chemical bath deposition technique. Substrate cleaning plays a vital role in the deposition of thin films especially by CBD technique. Prior to the deposition, the glass substrates were kept in hot chromic acid for several hours to remove organic impurities from the substrate surface, followed by a thorough cleaning with deionized water. Further, the glass substrates were ultrasonically cleaned with 2-propanol, acetone and de-ionized water, 10 min each and finally dried in hot air oven. The chemicals used for the MnS film preparation were AR grade. Aqueous solutions of manganese acetate [$Mn(CH_3COOH)_2$] was used as manganese (Mn^{2+}) source, thiourea [$SC(NH_2)_2$] was used as sulfur (S^{2-}) source and ammonium hydroxide (NH_4OH) was used as buffer (to control the pH of the solution) for the deposition of MnS films.

The precursor solution was prepared (Mn:S = 1:1 ratio) by dissolving the aqueous solutions of 10 mL of 0.5 mol/L [$Mn(CH_3COOH)_2$] and 10 mL of 0.5 mol/L $SC(NH_2)_2$. Later on, ammonium hydroxide was added drop wise into the solution to maintain its pH at 10. The resultant solution was mixed with a magnetic stirrer to get a clear homogeneous solution. Now, the cleaned glass substrates were placed vertically in the growth solution and solution was kept in the CBD bath. Fig. 1 shows the schematic illustration of simple chemical bath deposition setup used in the present work. The temperature of growth solution was maintained at 60 °C and the deposition was carried out for 24 h. In order to maintain uniform temperature in the entire precursor solution throughout the experiment, the growth solution was kept inside the oil bath, as shown in Fig. 1. The coated substrates were rinsed with deionized water and dried in air. The MnS thin films were also prepared by changing the concentration of sulfur source with constant manganese source concentration (Mn:S = 1:2 and 1:3 ratios). All the films are homogeneous and well adherent to the substrates. In the preparation of MnS, the ratio of Mn to S precursor is expected to play a significant role. Therefore, we varied the thiourea concentration to study its effect on the resulting product. The thickness of films deposited at 1:1, 1:2, and 1:3 molar ratios are 0.9, 1.0, and 1.4 μm, respectively, as measured by stylus profilometer (Mitytoyo, SJ-301).

2.2. Mechanism for film growth

In general, the formation of thin films in chemical bath deposition method involves two basic mechanisms such as ion by ion deposition mechanism (through heterogeneous reaction on the surface of the substrate) and cluster by cluster mechanism (through homogeneous reaction in the bulk solution), as proposed by 'O' Brien and McAleese [18]. In CBD method, the deposition of MnS occurs when the manganese and sulfide ions ionic product is greater than the solubility product of MnS.

$$Mn^{2+} + S^{2-} \leftrightarrow MnS \quad \text{(ion by ion process)} \tag{1}$$

As mentioned earlier, for the deposition of MnS film in an aqueous alkaline medium, the S^{2-} ions are obtained by decomposing thiourea according to the following reactions:

$$SC(NH_2)_2 + OH^- \leftrightarrow SH^- + H_2O + H_2CN_2 \quad \text{(thiourea decomposition)} \tag{2}$$

$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O \tag{3}$$

However, the rate of release of S^{2-} ion mainly depend on the pH of bath solution. The NH_4OH was used as buffer to fix the pH (10) of the solution and ammonia controls the concentration of Mn^{2+} in the bath solution according to the reactions given below:

$$Mn(CH_3COOH)_2 \leftrightarrow Mn^{2+} + 2(CH_3COO)^- \quad \text{(manganese acetate dissociation)} \tag{4}$$

$$NH_4OH \leftrightarrow NH_3 + H_2O \quad \text{(ammonia decomposition)} \tag{5}$$

$$Mn^{2+} + 4NH_3 \leftrightarrow Mn(NH_3)_4{}^{2+} \quad \text{(metallic ion complexation)} \tag{6}$$

Finally, the MnS film was formed as given in Eq. (1). In CBD technique, the bath temperature and growth time play a vital role to get better crystalline nature, morphology, and optical properties, etc. In this work, the optimized growth temperature is 60 °C and growth time is 24 h.

2.3. Characterization

The structural property of MnS thin films was studied by X-ray diffraction (XRD) using Cu-Kα (λ = 0.154 nm) radiation source (X'pert Pro PANalytical; X'Celerator detector) over a 2θ scan range of 20–80° (scan rate: 0.047°/s). Micro-Raman measurements were performed at room temperature using Raman spectrometer