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Effect of Solution Concentration on MnS_2 Thin Films Deposited in a Chemical Bath

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ABSTRACT

Manganese sulfide (MnS_2) thin films were deposited from aqueous solutions at room temperature on indium tin oxide glass substrates by the chemical bath deposition method. The method employed was cheap, simple and did not require any special set-up process. The chemical bath contained manganese sulphate, thiourea and triethanolamine solutions. The effect of various solution concentrations on crystalline films was determined. The structure, morphology and optical absorption of the films were analysed using X-ray diffraction, atomic force microscopy and UV/Vis spectrophotometry. Formation of a cubic structure with preferential orientation along the (210) plane was confirmed from structural analysis. From atomic force microscopy images, the thin films prepared at higher concentration showed complete coverage of material over the substrate compared to the films prepared at lower concentration. The band gap energies of films ranged from 3.5 to 3.8 eV, depending upon the solution concentration.
Keywords: chemical bath deposition, thin film, solar cells, semiconductor

INTRODUCTION

In the past decade, extensive research has been devoted to growing various kinds of binary (Larramendi *et al.,* 2001; Ubale *et al.,* 2007; Ravichandran and Philominathan, 2009) and ternary (Sonawane *et al.,* 2004; Khefacha *et al.,* 2004; Anuar *et al.,* 2009) semiconductor materials. They have potential use in solar cells, optoelectronic devices, photoconductors and infrared detector devices. Manganese sulphide thin films with a wide direct band gap, which are cheap and possess semiconducting properties, have attracted the attention of many researchers. Several physical and chemical techniques are available for the growth of manganese sulphide thin films, including radio-frequency sputtering (Oidor-Juarez *et al.,* 2002), hydrothermal (Zhang *et al.,* 2002), SILAR (Pathan *et al.,* 2007) and chemical bath deposition (Lokhande *et al.,* 1998; Fan *et al.,* 2003; Gumus *et al.,* 2005). Among them, chemical bath deposition is the most promising technique for film synthesis, since it is one of the simplest and cheapest methods. The chemical bath deposition method is based on the reaction between dissolved manganese ions and a sulfur-containing organic compound (thiourea) in an alkaline water solution. Triethanolamine is used

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as the complexing agent for depositing manganese sulphide thin films. The complexing agent as a component of the chemical bath eliminates spontaneous precipitation by slowing down the release of the metallic ions on dissociation, thereby resulting in slow precipitation of the compound (Agbo and Ezema, 2007).

The current work, reported for the first time on growing nanostructured MnS_2 thin films using the chemical bath deposition technique at room temperature. The influence of various solution concentrations on the crystalline structure, morphology and optical properties of the films were revealed by X-ray diffraction, atomic force microscopy and UV-Vis spectrophotometer, respectively.

MATERIALS AND METHODS

Sample preparation

All the chemicals used for the deposition were analytical grade. The chemicals were manganese sulphate ($MnSO_4.4H_2O$) as the manganese source, thiourea [$CS(NH_2)_2$] as the sulfur source, triethanolamine [$(HOC_2H_4)_3N$] as the complexing agent, ammonia/ammonium chloride (NH_3/NH_4Cl) (pH=10.55) as the buffer solution and hydrochloric acid (HCl). All solutions were prepared in deionised water (Alpha-Q Millipore). The indium tin oxide glass substrates were degreased in ethanol for 10 min and then ultrasonically cleaned with distilled water for another 15 min before deposition of films. Deposition of MnS_2 thin films was carried out at room temperature (25°C) using the following procedure: 10 ml of manganese sulphate solution was placed in a 50 mL beaker. Then, 2 mL of concentrated triethanolamine (TEA) was added to the beaker. Under continuous stirring, 10 mL of thiourea solution was mixed in, followed by ammonia/ammonium chloride solution. The final mixture had pH 10. The clean indium tin oxide glass was placed in the beaker, supported vertically on the wall of the beaker. In order to determine the best conditions for the deposition process, the films were deposited at different solution concentrations, ranging from 0.5 to 2 M of manganese sulphate and thiourea. During deposition, the beaker was kept undisturbed. After completion of film deposition (48 h), the glass substrates were removed, washed several times with distilled water and dried naturally in desiccators. Then, these films (as-deposited thin films) were annealed at 150°C for 30 min in nitrogen atmosphere and kept for further analysis.

Characterization method

Structural analysis of the films used an X-ray diffractometer (Philips PM 11730 diffractometer with CuK_α λ=1.5418 Å radiation) in the 2θ range 20-60°. An atomic force microscope (Quesant Instrument Corporation, Q-Scope 250) was used to examine the surface morphology of the thin films, operated in contact mode with an Si_3N_4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using commercial software. Optical absorption measurement was carried out in the wavelength range from 300 to 800 nm using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway, while the uncoated glass substrate was put across the reference path. The absorption data were manipulated for the determination of the band gap energy (E_g).

RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction (XRD) patterns of manganese sulphide thin films deposited at various solution concentrations after annealing at 150°C for 30 min under nitrogen atmosphere. The as-deposited thin films obtained were characterized using XRD analysis. However,

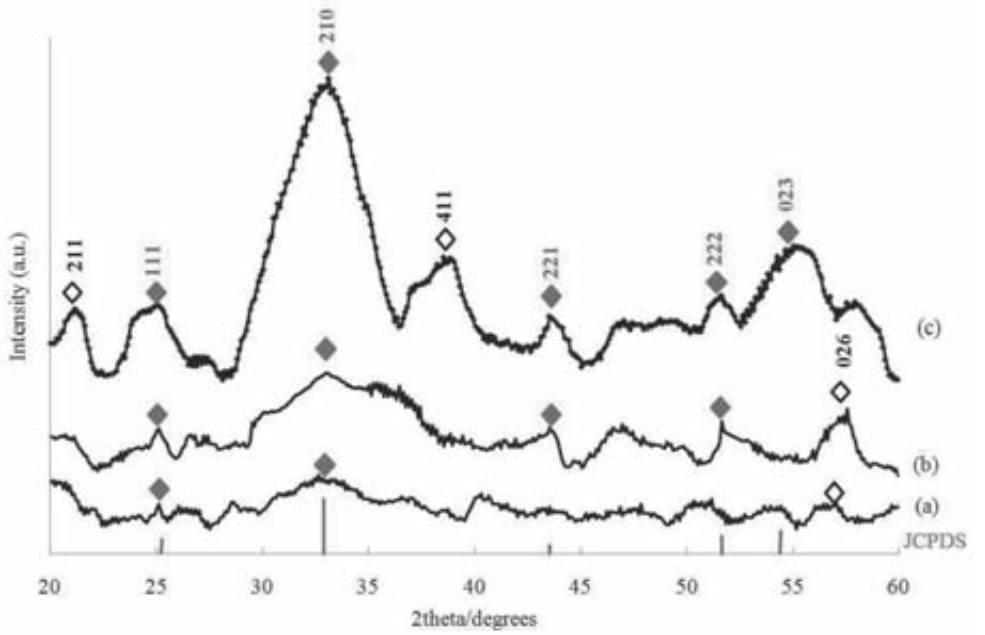

Figure 1 X-ray diffraction patterns of MnS_2 thin film deposited at various solution concentrations of manganese sulphate and thiourea: (a) 0.5 M; (b) 1 M; and (c) 2 M. (MnS_2, % $In_{1.875}O_3Sn_{0.125}$).

no informative data were obtained from the XRD analysis. This could have been due to the deposition of a very thin layer of the material that could not be analyzed by XRD. Surface treatment of the samples was chosen as a method to improve the crystallinity of the as-deposited thin films. One of the most commonly used surface treatment methods is annealing. In this process, the films are placed in a quartz tube and heated in a furnace at the required temperature. In the current study, the annealing process was carried out at 150°C. The temperature was controlled by a single set point temperature controller. Exposure at high temperature is known to affect the crystal structure of the films. During the annealing process, nitrogen was maintained at a constant flow rate to ensure similar conditions to those in the experimental set up.

The thin films prepared at 0.5 M of manganese sulphate and thiourea solutions (Figure 1a) show two peaks corresponding to the (111) and (210) planes of MnS_2 films. These films showed very weak and broad peaks, which meant that the crystallinity was very poor. According to the XRD patterns, when the concentration of manganese sulphate and thiourea was increased to 1M (Figure 1b) and 2 M (Figure 1c), there were four and finally five manganese sulphide characteristic peaks detected, respectively. These peaks were in good agreement with data from the Joint Committee on Powder Diffraction Standards (JCPDS, reference No.: 00-065-1844) for MnS_2 (Hastings *et al.,* 1959) (Table 1). The lattice parameters of the cubic structure were equal to a=b=c=6.097Å. On the other hand, as the solution concentration increased from 0.5 to 2 M, the intensity of the MnS_2 peak (210) increased and this peak became narrower, indicating an improvement in the crystallinity. This indicated that the grain size of the thin films increased with an increase in the solution concentration. This result was consistent with the observations from the AFM results. Based on the XRD patterns, no manganese peaks, sulfur peaks or unassigned

Table 1 Comparison of the JCPDS *d*-spacing data for MnS_2 thin film with experimentally observed values for samples deposited under different solution concentrations.

Solution concentration	2θ (°)	Relative intensity of diffraction peaks (%)	*hkl*	*d*-spacing (Å)	
				Observed value	JCPDS value
0.5 M	25.2	22	111	3.51	3.52
	32.5	100	210	2.74	2.73
1 M	25.2	19	111	3.51	3.52
	32.5	100	210	2.74	2.73
	44.2	21	221	2.02	2.03
	51.6	20	222	1.77	1.76
2 M	25.2	31	111	3.51	3.52
	32.5	100	210	2.74	2.73
	44.2	10	221	2.02	2.03
	51.6	11	222	1.77	1.76
	54.0	33	023	1.68	1.69

peaks were observed, indicating that the MnS_2 thin films obtained were pure without any impurities. However, the appearance of three other peaks, corresponding to the (211), (411) and (026) planes, matched well with the indium tin oxide peaks (JCPDS reference No.: 01-089-4597). The presence of indium tin oxide peaks came from the substrates during the deposition process. In Figure 1, the peaks marked with solid diamonds are associated with reflections of the cubic structure of MnS_2 and those marked with open diamonds indicate the cubic structure of indium tin oxide (Nadaud *et al.,* 1998).

The surface morphology, thickness and roughness were examined by recording atomic force microscopy (AFM) images. Root mean square (RMS) roughness (defined as the standard deviation of the surface height profile from the average height), is the most commonly reported measurement of surface roughness (Jiang *et al.,* 2005). Figure 2 shows the AFM images (20×20 μm) of MnS_2 thin films prepared under various solution concentrations onto indium tin oxide glass substrate. Thin films deposited at 0.5 M of manganese sulphate and thiourea showed incomplete coverage of materials over the surface of the substrate. The process of thin film deposition on a substrate depends mainly on the formation of nucleation sites and the subsequent growth of the films from these centres. The root mean square roughness and thickness of these thin films was 90 and 1015 nm, respectively. When the solution concentration was increased to 1 M, the surface of the films started to grow thicker (1430 nm) and also an increase in surface roughness (110 nm) was observed. The material was found to cover the surface of the substrate completely (Figure 2b). The small grains (average size) were almost similar to each other. However, a few larger grains were observed with a grain size approximately 1 to 3 μm larger than the smaller grains. On the contrary, the distribution of grain size was more uniform for the films deposited at 2 M of manganese sulphate and thiourea. These thin films were dense and free of pores and cracks as shown in Figure 2c. In addition, these thin films had a larger average

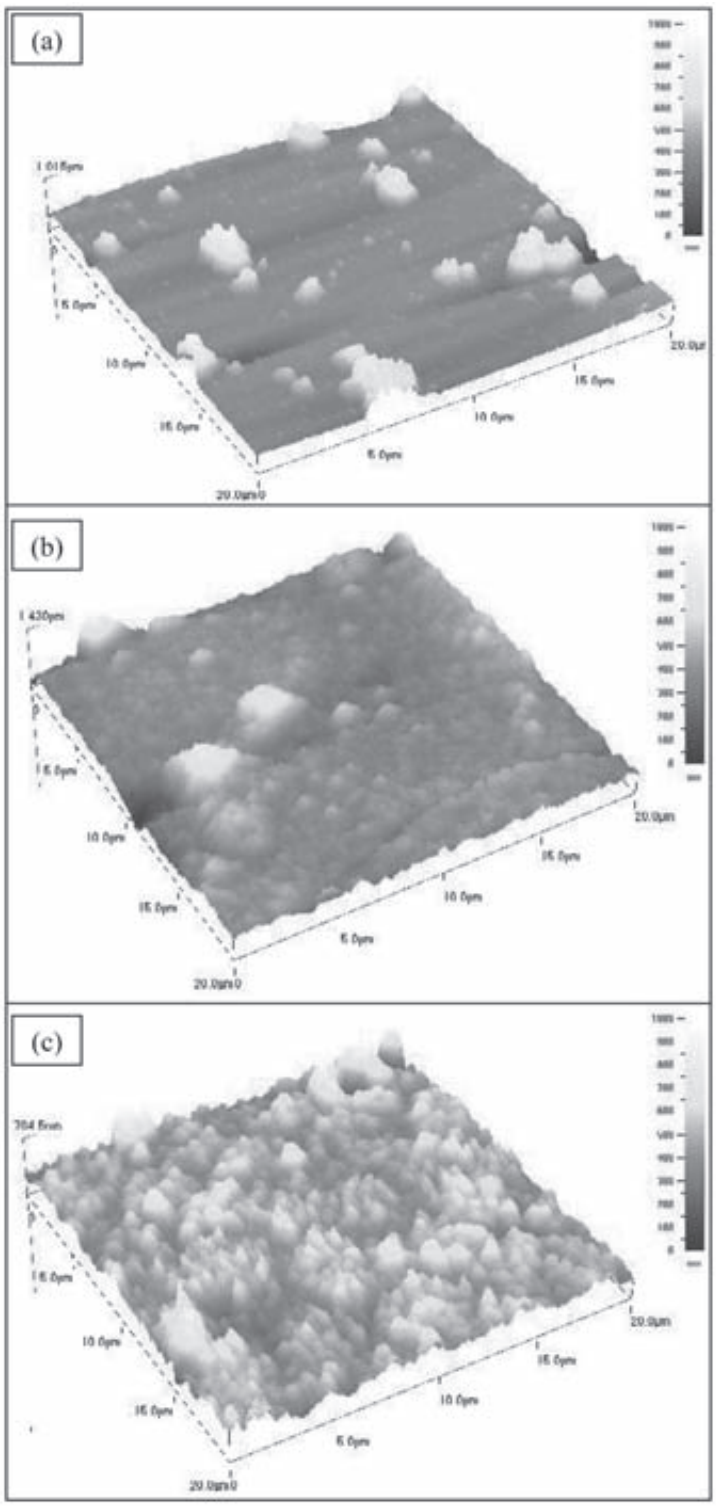

Figure 2 Atomic force microscopy images of MnS_2 thin films deposited at various solution concentrations of manganese sulphate and thiourea: (a) 0.5 M; (b) 1 M; and (c) 2 M.

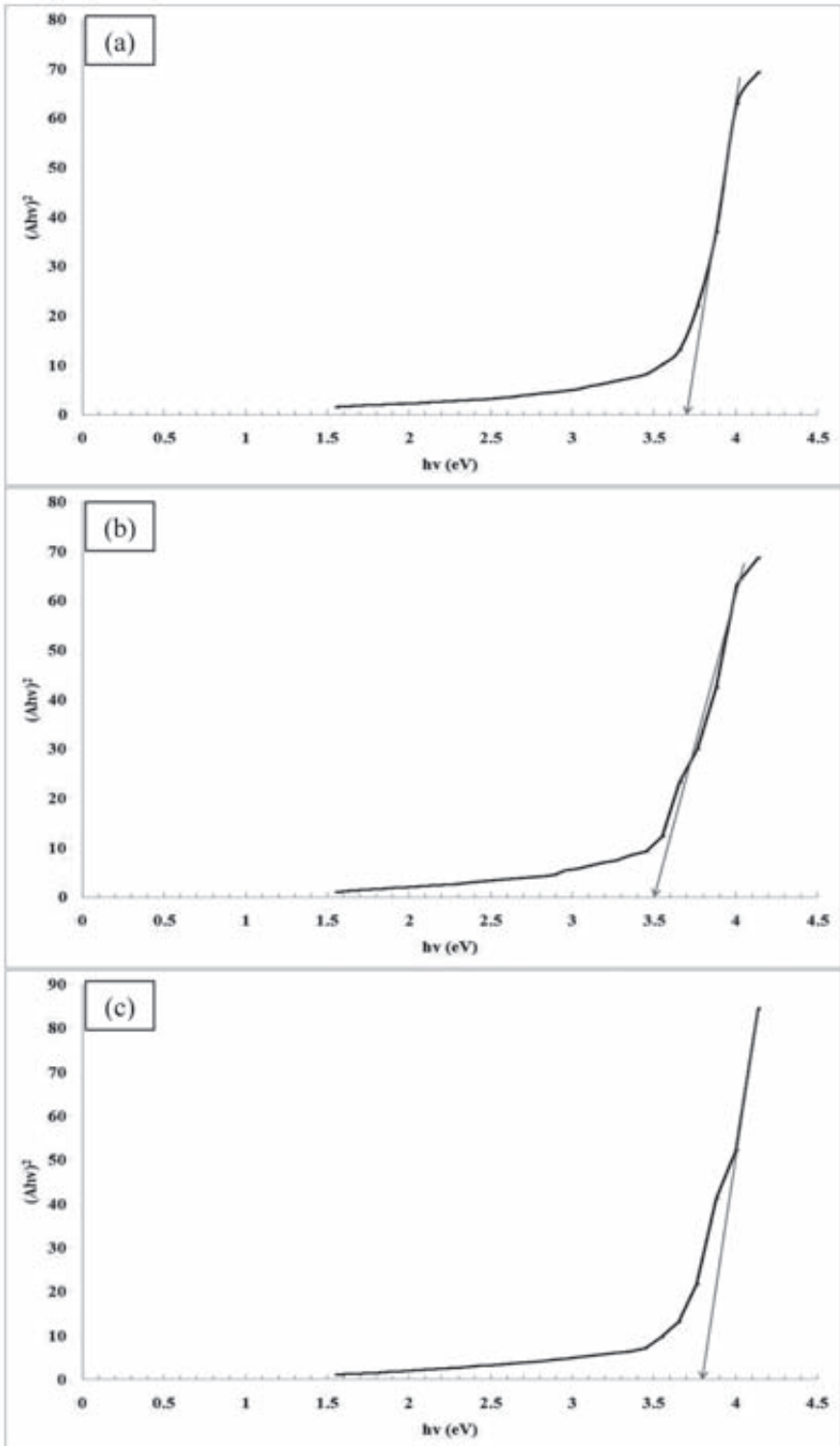

Figure 3 Plot of $(Ahv)^2$ versus hv for MnS_2 thin films deposited at various solution concentrations of manganese sulphate and thiourea: (a) 0.5 M; (b) 1 M; and (c) 2 M.

grain size compared with the films deposited using 1M of manganese sulphate and thiourea. Comparing all the AFM images, it was clear that the roughness (75 nm) and thickness (705 nm) values decreased in films deposited at higher concentration (2 M).

Optical absorption analysis of the MnS_2 thin films was carried out at room temperature by placing an uncoated glass substrate in the reference beam. The optical spectra of thin films deposited using a chemical bath have been recorded in the wavelength range 300-800 nm. In order to determine the band gap of thin films, the equation of Stern (1977) was used (Equation 1):

$$A = \frac{[k(hv - E_g)^{n/2}]}{hv} \quad (1)$$

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively.

A plot of $(Ahv)^2$ versus hv of MnS_2 thin films prepared under various solution concentrations is shown in Figure 3. The linear nature of the plot indicates the existence of direct transition (Lokhande *et al.,* 1997). The band gap energy was obtained by extrapolating the linear portion of $(Ahv)^{2/n}$ versus $hì$ to the energy axis at $(Ahv)^{2/n} = 0$. The band gap energy initially decreased (3.7 to 3.5 eV) with an increase in the solution concentration from 0.5 to 1 M. Subsequently, the band gap energy increased to 3.8 eV, as the solution concentration was further increased to 2 M. Therefore, the solution concentration had some influence on the band gap value of the films. These band gap values were close to those of manganese sulphide thin films prepared using the chemical bath deposition technique (Gumus *et al.,* 2007) and radio frequency sputtering (Oidor-Juarez *et al.,* 2002).

CONCLUSION

Manganese sulphide thin films were grown successfully by the chemical bath deposition technique using manganese sulphate, thiourea and triethanolamine solutions. Different structural and morphological changes were observed for the films deposited under various solution concentrations. According to XRD analysis, as the solution concentration was increased to 2 M, the total peaks attributable to MnS_2 and the intensity of the (210) peak increased gradually. Based on the AFM images, the grains in these films appeared very homogeneous and covered the substrate surface completely. The band gap values of films ranged from 3.5 to 3.8 eV, depending upon the solution concentration.

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