Growth And Characterization Of Manganese Sulphide (MnS) Thin Films.

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Abstract: *The growth and characterization of MnS thin films using electrodeposition technique. Manganese sulphide thin films have been deposited onto well cleaned glass (ITO) as our substrate. The absorbance was measured using Janway 6405 UV – VIS model of the spectrophotometer in the wavelength range of 500nm-1500nm. Manganese sulphide thin films were investigated at 300k. Optical absorbance study showed that manganese sulphide films are in the range of 0.422-0.140. Manganese sulphide films were of indirect band gap type semiconductor, the resistivity and thickness decreases as the pH and conductivity of the films increases. The micrograph revealed a polycrystalline nature and the deposited films were found to be non-homogeneous. The structural parameters such as interplannar distance (d), lattice constant (a), grain size (D), dislocation density and microstrain have been evaluated. The grain size is calculated for all films. XRD analysis showed that manganese sulphide thin films, so deposited, exhibit polycrystalline in nature in a cubic structure with preferred orientation along (111) plane.*

Keywords: Thin Film, Electrodeposition, MnS

1.0 INTRODUCTION

Thin films have received a great deal of attention because of their potential application in the area of electronic and optoelectronic devices. Recent research has focused on the synthesis of metal chalcogenide thin films which include tin sulphide [1], manganese sulphide [2], copper sulphide [3], cadmium sulphide [4], zinc sulphide [5], lead sulphide [6], and these materials are of practical interest because of very useful optical, mechanical and electrical properties [7]. Thin film semiconductors of metal-metal sulphides can be deposited on metals, glass and polymer substrates that are immersed in solutions containing metal complex ions and a source of sulphide [8]. The metal-metal chalcogenides are increasingly studied in the search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells [9]. These materials have been known to be potential candidates for photo-electrochemical solar cells, extensive research has been devoted to prepare various kinds of semiconductor thin films manganese sulphide thin films have been used in variety of applications such as solar cells, sensor, photoconductors, optical mass memories and solar selective coatings [10]. According to theoretical prediction and subsequent experimental verification, Methods of thin films processing can be divided into two major groups: those carried out in gas phases (dry process) and in liquid phases (wet process). The dry process includes techniques such as vacuum evaporation [11] chemical vapor deposition (CVD) sputtering, spray-pyrolysis [12]. Electrodeposition is used to prepare MnS thin film. Among the various methods electrodeposition technique provides a simple root of synthesizing thin films because of its simplicity, low-cost experimental setup from an economical point of view [13-14]. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. CVD techniques, without exceptional, require high vacuum and or temperature because it is necessary to produce gaseous precursor molecules or atoms. Besides the high energy needed for the film processing, emission of gaseous waste materials is another serious problem with these technique.

This research paper reports on the growth and characterization of the electrical, morphological and optical properties of electrodeposited manganese sulphide thin films. The optical properties investigated include the absorbance (A), transmittance (T) and reflectance (R) and the band gap energy.

2.0 MATERIALS AND METHOD

The chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in distilled water. The manganese sulphide thin films were prepared using aqueous solutions of manganese sulphate (MnSO4, Na_2SO_4 and K_2SO_4) acted as a source of Mn^{2+} and S^{2-} ions, respectively. The H_2SO_4 was used to acidify the solution. The indium doped tin oxide (ITO) glass was used as the substrate for the deposition of MnS thin films. ITO glass was degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 5 min and air dried. Deposition of MnS thin films was carried out using 15ml of manganese sulphate, 10 ml of Na_2SO_4 solution, 5ml of K_2SO_4 solution and 2ml of H_2SO_4. The pH of the solution was 10.7. The ultrasonically cleaned indium doped tin oxide (ITO) glass substrate was immersed vertically into the solution for electrodeposition process. The films growth was carried out at 300k. The films were deposited in various deposition compositions. During deposition process, the deposited films were tested for adhesion by subjecting it to a steady stream of distilled water. Optical absorbance study was carried out using Janway 6405 UV – VIS model of the spectrophotometer. The coated (ITO) with MnS was placed across the sample radiation pathway while the uncoated indium doped tin oxide

(ITO) glass was placed on the reference path and other solid state properties were calculated. The electrical (I/V) was obtained using four point probe (Model T345) and the resistivity and conductivity were calculated for various thickness.

RESULTS AND DISCUSIONS

3.1 Electrical analysis of MnS thin films

The resistivity and conductivity of all samples lies in the range 10^6 and $10^{-7}(\Omega m)^{-1}$. Electrical studies were carried out to determine the resistivity and conductivity and the effect of pH on material. The studies are carried out at room temperature by using four probe method (ModelT345). From the table 1 shows the calculated results for the sheet resistivity and electrical conductivity with their corresponding pH and thickness. The results showed that MnS films resistivity and thickness decreases as the pH and conductivity of the films increases. The high conductivity of the deposited films makes the material suitable for mass production of solar cells and other electronics devices. It was observed that the resistivity of the MnS thin films decreased and electrical conductivity was observed increased with increasing thickness. The increasing electrical conductivity with pH shown that MnS material deposited on the substrates is semiconducting.

Table 1: Electrical properties of MnS thin films

SAMPLES	pH	THICKNESS, t (nm)	RESISTIVITY, ℓ (Ωm)	CONDUCTIVITY, σ $(\Omega m)^{-1}$
MSA	10.7	221	2.652×10^6	3.770×10^{-7}
MSB	11	198	2.432×10^6	4.111×10^{-7}
MSC	11.4	195	2.232×10^6	4.480×10^{-7}
MSD	11.9	193	2.123×10^6	4.710×10^{-7}
MSE	12	189	2.101×10^6	4.759×10^{-7}

3.2 Surface Morphological Study Of MnS Thin Films

The morphology of the MnS films examined using electrodeposition technique was mainly affected by the deposition parameter such as pH. Scanning electron microscopy (SEM) micrograph allows us to obtain information about the morphology of sample surface. Figure 1 and 2 indicates the scanning electron microscopy micrograph of the MnS films deposited at pH10.7 and 11. This SEM micrograph reveals that the obtained films are rather dense and uniform. The size distribution of the grains seems to be broad, with the maximum size reaching 10kV. The uniform films were obtained at lower pH such as pH 10.7 While, the films formation were found to be regular as the pH further increased to 11. The micrograph revealed a polycrystalline nature and the deposited films were found to be non-homogeneous

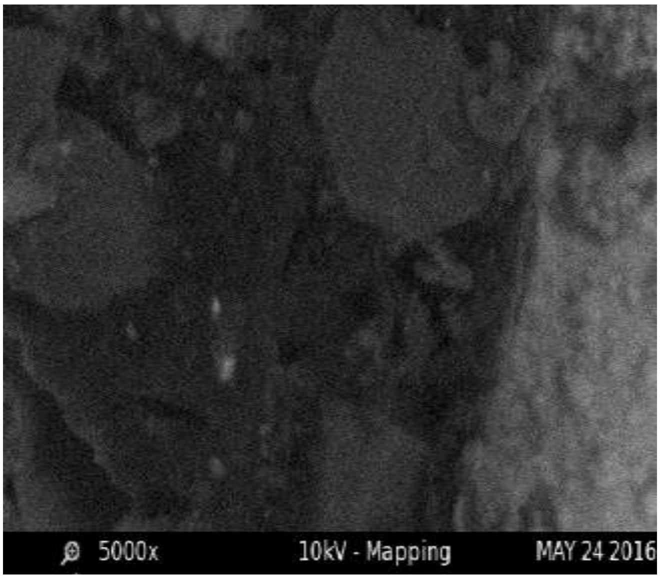

Fig. 1: Micrograph of MnS at pH 10.7 (Sample MSA)

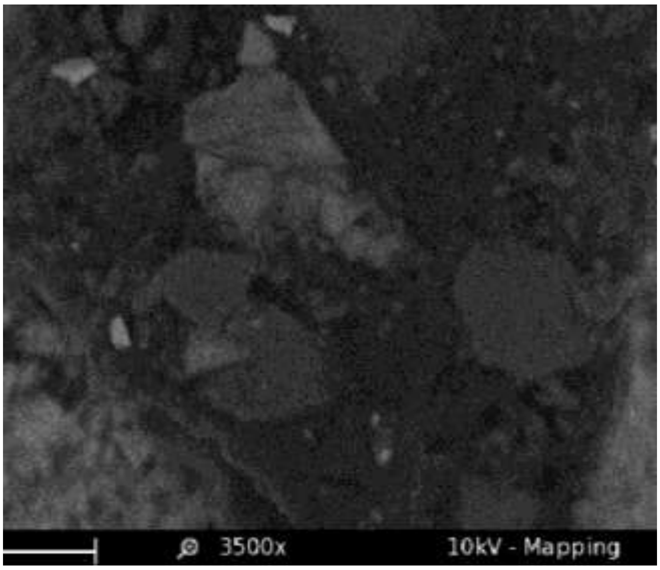

Fig. 2: Micrograph of MnS at pH 11 (Sample MSB)

3.3 Structural analysis of MnS thin films

XRD analysis in Figure 3 revealed that the MnS thin films, so deposited, exhibit polycrystalline in nature in a cubic structure with preferred orientation along (111) plane. The lattice constant was given in the X-ray diffraction analysis is found to be a = 5.6Å. The crystallite size was determined by means of the X-ray line broadening method using Scherer equation [6]

$$D = \frac{0.94\lambda}{\beta Cos\theta} \quad (1)$$

$$\delta = \frac{1}{D^2} \text{ lines/m}^2 \quad (2)$$

Where λ is the wavelength of CuKal radiation (λ = 1.5406 Å), is the full width of half $\boldsymbol{\beta}$ maximum FWHM of the (hkl) peak of the diffracting angle hkl 2θ. The average grain size D, the dislocation density δ is calculated using the following relation [7]

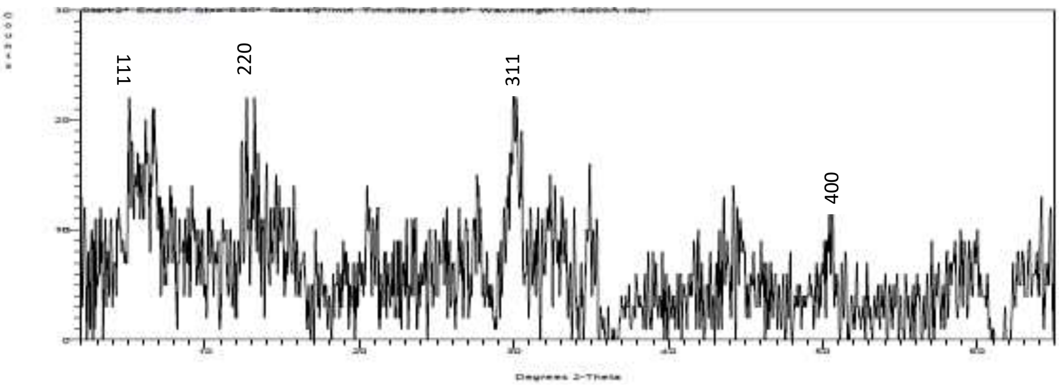

Figure 3: XRD pattern of MnS thin films

Table 1: Structural parameters of MnS thin films

Thickness	**2θ (degree)**	**d (spacing) Å**	**(β) FWHM**	**(hkl)**	**Lattice (a) Å**	**Grain Size(D) nm**	**density (δ) x10^{13} lines/m^2**	**Micro Strain (ε) x10^{-3}**
	13.13	3.111	0.1300	111	5.6	3.006	0.0211	2.400
221nm	15.14	3.094	0.1220	220		2.235	0.0209	3.000
	21.23	3.076	0.1310	311		3.534	0.0400	2.830
	24.14	3.012	0.1230	400		2.008	0.0343	4.123

3.4 Optical Analysis of MnS thin films

Figure 4 shows the plot of absorbance versus wavelength deposited at various pH; it was observed that the sample deposited at pH 11.9 absorb more compare to the sample deposited at pH 12 with lowest absorbance value. It is well showed that sample (MSD) will be a good material in solar cells production and also in the electronic industries

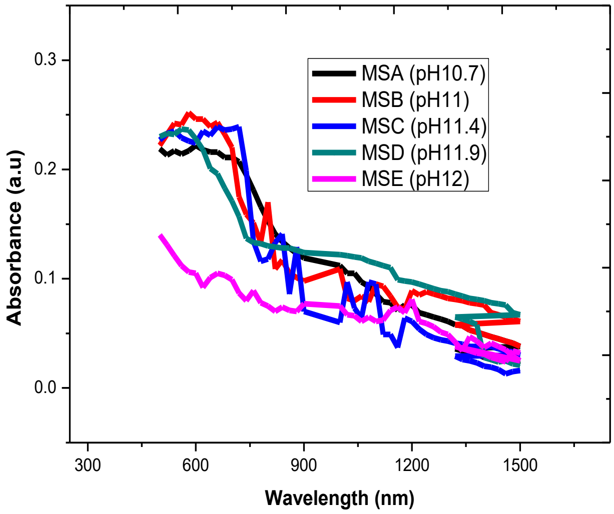

Figure 4: Plot of optical absorbance versus Wavelength

Figure 5 shows the plot of transmittance versus wavelength deposited at various pH; it was observed that the sample deposited at pH 10.7 transmit more compare to the sample deposited at pH 11.9 with lowest transmittance value. It is well showed that sample (MSA) will be a good material in solar cells production and also in the electronic industries.

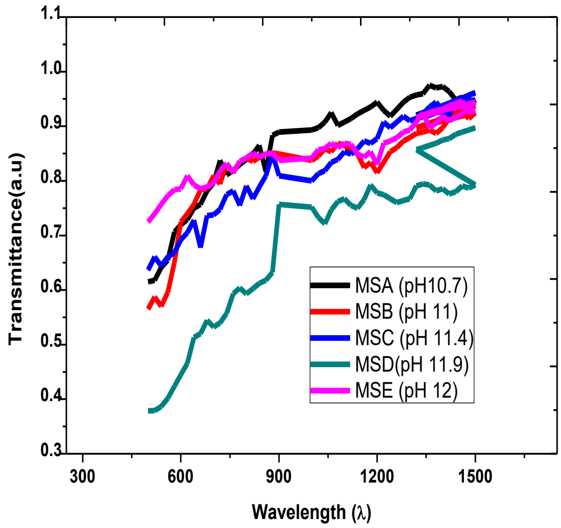

Figure 5: Plot of transmittance versus Wavelength

Figure 6 shows the plot of reflectance versus wavelength deposited at various pH; it was observed that the sample deposited at pH 11.9 reflect more compare to the sample deposited at pH 10.7 with lowest reflectance value. It is well showed that sample (MSD) will be a good material in solar cells production and also in the electronic industries. The films as deposited is nice glazing material for maintaining cool interior in buildings in warm climate regions while still keeping the rooms well illuminated. To ensure that the thermal radiation from the warm glazing to the interior is inhibited and the thermal energy dissipated in the glazing due to reflection is predominantly transferred to the exterior by enhanced convective heat transfer of the glazing to the exterior. It is suggested that reflectance in the spectral region should be strengthened while encouraging low thermal emittance.

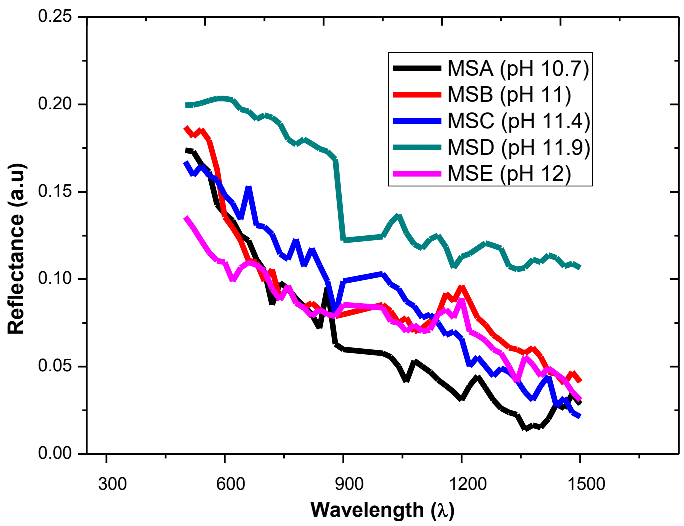

Figure 6: Plot of reflectance versus Wavelength

Figure 7 shown band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern relationship of near-edge absorption:

$$A = \frac{[k(hv-E_g)^{\frac{n}{2}}]}{hv} \qquad (3)$$

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 band gap, E_g , could be obtained from a straight line plot of $(Ahv)^{2/n}$ as a function of hv. Extrapolation of the line to the base line, where the value of $(Ahv)^{2/n}$ is zero, will give E_g. The $(Ahv)^{1/2}$ versus hv plot is a straight line indicating that the energy band gap of MnS is indirect and intercept on the hv axis yield a band gap of 1.7eV-2.3eV for the film prepared using electrodeposition technique

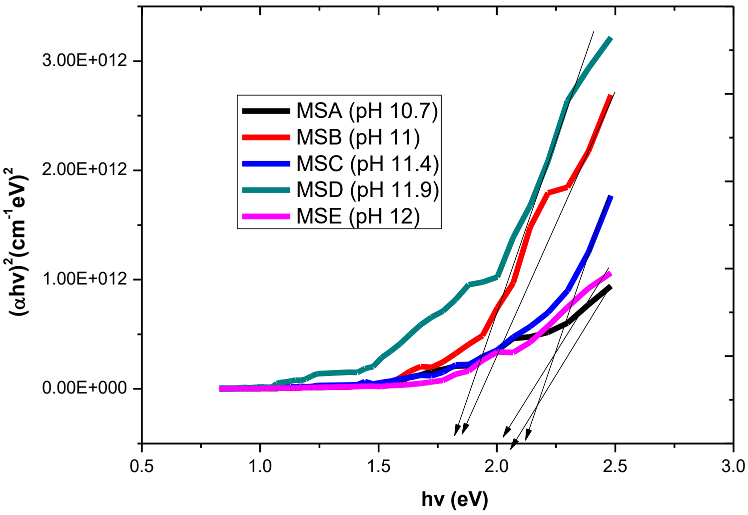

Figure 7: Plot of absorption coefficient square versus photon energy

Conclusions

Electrodeposition techniques have been used to grown MnS thin films in this research paper. It was observed that the thickness of the material as deposited depend on deposition pH. The resistivity and thickness decreases as the pH and conductivity of the films increases.

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