Analysis of Chemically Deposited MnS Thin Films

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ABSTRACT

The chemical bath deposition technique was used to deposit thin films of manganese sulphide (MnS) on glass substrates. The bath composition included manganese sulphate ($MnSO_4.H_2O$) which was the source of the Mn^{2+}, aqueous ammonia, distilled water and thiourea $[(NH_2)_2SC]$ which supplied the S^{2-} ion. Spectrophotometric analyses of the films were carried out for the following optical properties: absorbance, transmittance, reflectance, extinction coefficient, refractive index, absorption coefficient, and optical conductivity. The films showed absorbance ranging from 0.10-0.79 in the UV-VIS-NIR regions. The maximum percentage reflectance and transmittance are respectively 20.3% and 79.4% within the same region. The band gap ranges from 2.10 to 2.50 eV. The possible areas of application of the films are also highlighted based on the optical and solid state properties of the film.

(Keywords: chemical bath deposition, MnS. manganese sulphide, thin films, optical properties, solar application)

INTRODUCTION

Chemical Bath Deposition technique has been used extensively for the deposition of the thin films of sulphides and selenides (Eze and Okeke, 1997; Ndukwe, 1992), oxides (Ezema and Okeke, 2003; Chopra and Das, 1983) and ternary compounds (Ezekoye and Okeke, 2005; Okoli *et al*, 2006). The choice of this method arises from its low cost, ease of handling, and possibility of application on a large surface; hence it is most suitable for adaptation in developing countries where facilities for other highly expensive and technically advanced techniques such as Chemical Vapour Deposition, Spray Pyrolysis, Electro-Chemical Deposition, Molecular Beam Epitaxy, RF Sputtering, etc. are not easy to come by.

The basic principle involved in the synthesis of thin films by the chemical bath method is the controlled precipitation of the desired compound from a solution of its constituents. This requires that the ionic product must exceed the solubility product (Barnes and Czeeny, 1931) thus the formation of thin films on the substrate by ion-by-ion condensation. The complexing agent as a component of the bath eliminates spontaneous precipitation by slowing down the release of the metallic ions on dissociation thereby resulting in slow precipitation of the compound. After deposition, the film is characterized in order to determine its optical, electrical and solid state properties and the results indicate areas of likely application.

Thin films of manganese sulphide have been deposited and characterized (Nnabuchi, 2006) by the reaction of solutions of manganese chloride ($MnCl_2.4H_2O$), sodium thiosulphate, distilled water, and ethylene diamine tetra acetic acid (EDTA) which served as the complexing agent. This study however, reports on the preparation and optical characterization of MnS thin films deposited on glass substrates by the same method, but different bath compositions and ambient conditions. The MnS thin films were synthesized from the solution of manganese sulphate, distilled water, thiourea, and ammonia.

METHODS AND MATERIALS

Manganese sulphide thin films were deposited by the chemical bath method. Glass slides were used as substrates. These substrates were cleaned using commercial detergent and distilled water and afterwards dried in open air. The bath was composed of manganese sulphate, which was the source of Mn^{2+}; thiourea, which supplied the S^{2-}; and ammonia, which served as the complexing agent. The bath solutions were made up to 50mL by adding distilled water and were allowed 24h of deposition time.

Three samples of the MnS thin films were deposited at different bath parameters as presented in Table 1. The deposition process involved the reaction of the positive and negative ions to form neutral atoms which are precipitated out of the solution and deposited as thin films. The films, which are orange to light brown in colour, were removed from the bath after a 24h dip time and were washed in distilled water before air drying. The reaction equations for the film deposition are as shown below:

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

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

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

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

Table 1: Deposition Parameters of the MnS Thin Films.

Bath	Time (hr.)	Temp (k)	$MnSO_4.H_2O$		$(NH_2)_2SC$		NH_3	H_2O
			Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	Vol. (ml)	Vol. (ml)
MnS 4	24	300	1.0	2.0	0.1	5.0	2.0	41.0
MnS 5	24	300	1.0	2.0	0.1	5.0	1.0	42.0
MnS 8	24	300	1.0	1.0	0.1	5.0	1.0	43.0

After the films were deposited, they were characterized using a UNICAM® SP8-100 double beam UV spectrophotometer. The absorbance-transmittance-reflectance spectra of the films were obtained in the UV-VIS-NIR regions by means of PYE UNICAM® SP8-100 double beam spectrophotometer with uncoated glass slide as reference.

The optical properties investigated include the absorbance, transmittance, and reflectance, which were used to calculate the other properties such as refractive index, extinction coefficient, dielectric constant, and optical conductivity. These optical properties and the band gap of the films were deduced from mathematical expressions relating them which were obtained from earlier reports (Pankove, 1971; Ezema and Okeke, 2002, 2003).

RESULTS AND DISCUSSION

The spectral absorbance of the three samples of manganese sulphide film prepared at 300K is shown in Figure 1. It indicates that the film has low absorbance in the UV region which decreased with increasing wavelength towards the NIR regions. The film generally exhibited poor absorbance throughout the UV-VIS-NIR regions.

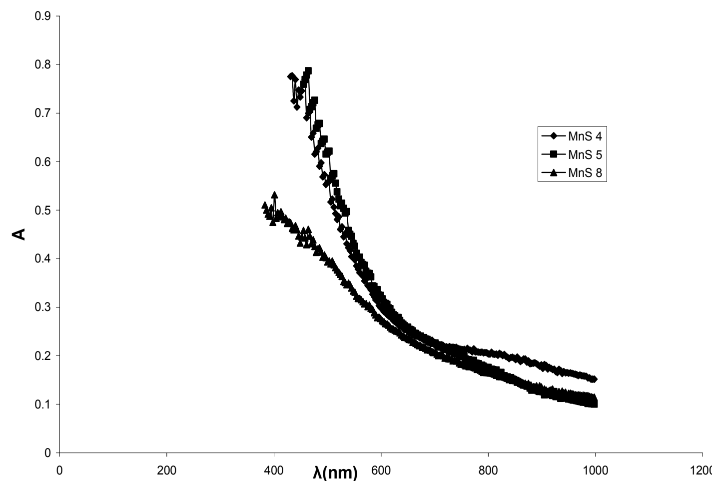

Figure 1: Spectral Absorbance of the MnS Thin Film.

Figures 2 and 3 are the transmittance and reflectance spectra of the MnS thin films, respectively. The films show high transmittance in the ultraviolet, visible, and infra red regions of the electromagnetic spectrum. Conversely, the reflectance of the films is found to be low (8-20%) within the same region. These high transmittance and low reflectance properties make the films good materials for antireflection coatings and for solar thermal applications in flat-plate collectors, house heating for solar chick brooding, etc.

Figure 4 relates the extinction coefficient (k) of the film samples to the photon energy and Figure 5 shows the plot of refractive index against photon energy.

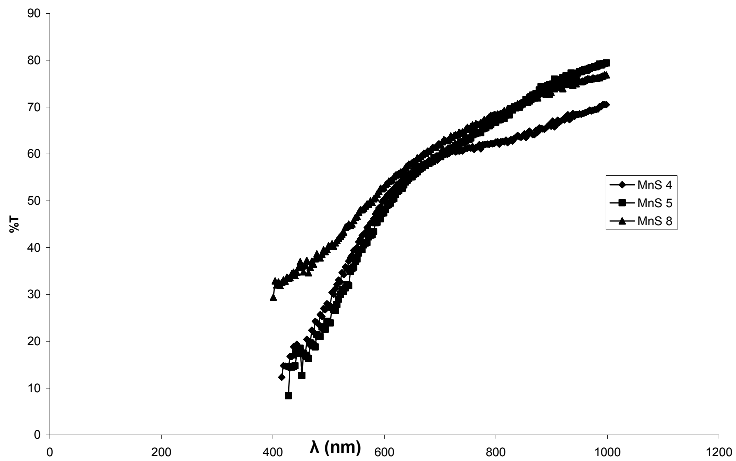

Figure 2: Spectral Transmittance for the MnS Thin Film.

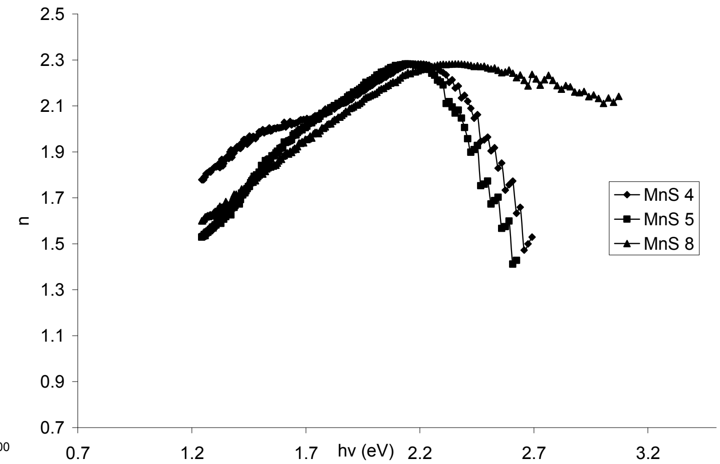

Figure 5: Plot of n Against hv for MnS Thin Film.

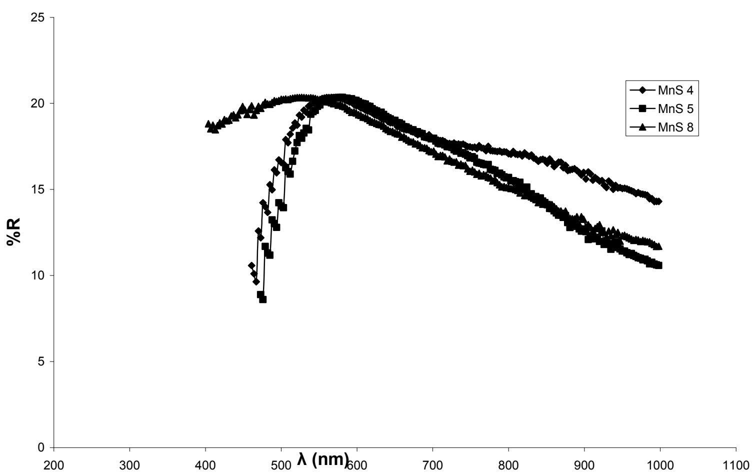

Figure 3: Spectral Reflectance of the MnS Thin Film.

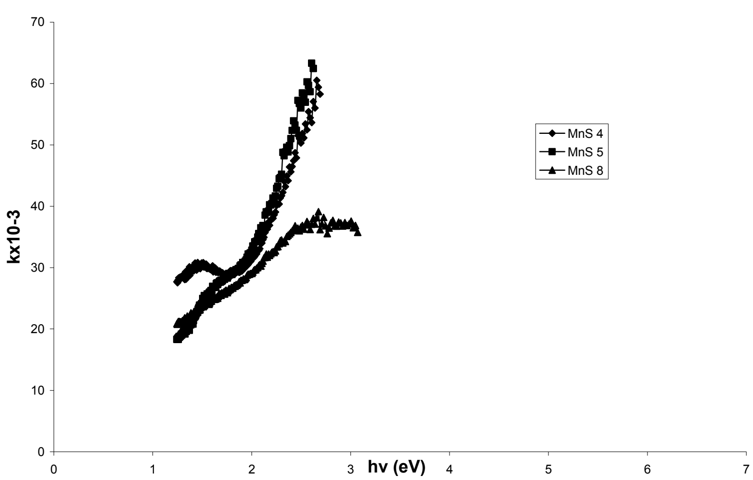

Figure 4: Plot of k Against hv for MnS Thin Film.

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The minimum value of k is 1.83 x 10^{-2} and the maximum is 6.33 x 10^{-2} observed at the photon energy of 1.24eV and 2.61eV respectively. The range of the refractive index is 1.4 -2.3 with peak value recorded at the photo energy of 2.38eV.

Plots of optical conductivity against hv are shown in Figure 6. It has maximum values that ranged between 0.58 x $10^{14}S^{-1}$ and 0.60 x $10^{14}S^{-}$ and minimum values between 0.08 x $10^{14}S^{-}$ and 0.15 x $10^{14}S^{-}$

Figures 7 and 8 indicate the plot of real and imaginary parts of dielectric constant verses photon energy for the films respectively.

The real part of the dielectric constant (ε_r) increases sharply as the photon energy increases to attain a maximum value of 5.2 at photon energy of 2.1eV before decreasing sharply again. The imaginary part (ε_i) also increases sharply within the same range of photon energy.

In Figure 9, the band gap is shown to range from 2.1eV to 2.5eV. This result is within the range of earlier result (Nnabuchi, 2006).

Table 1 shows the deposition conditions of the MnS thin films. Figure 10 shows the photomicrographs of the MnS thin films created during this study.

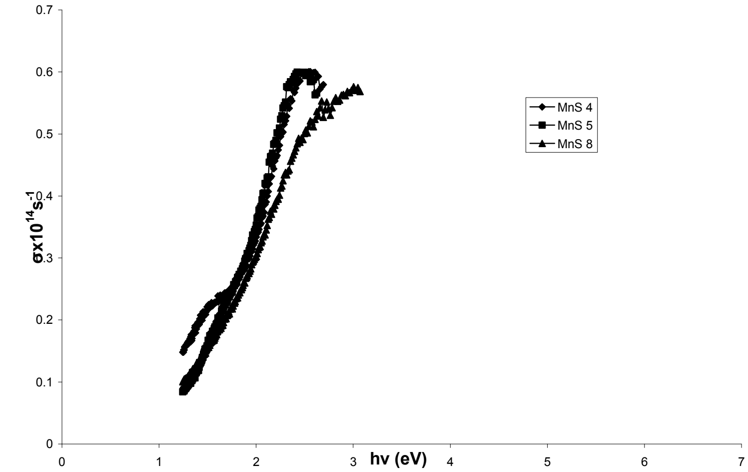


Figure 6: Graph of σ Against hv.

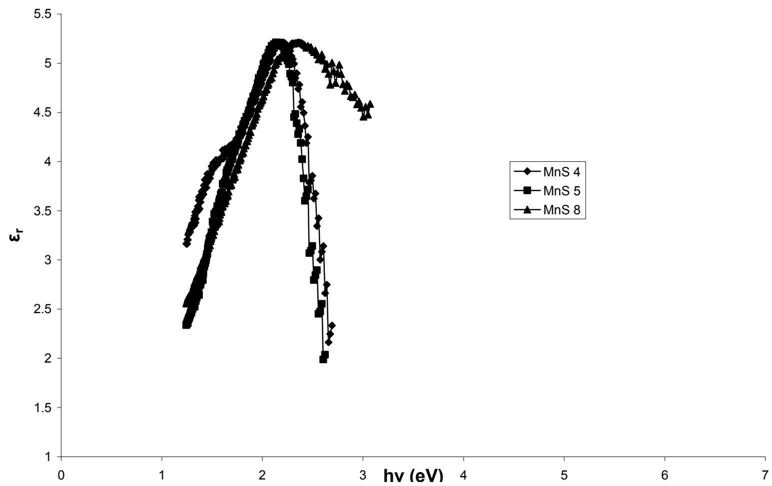


Figure 7: Plot of $\mathcal{E}_r$ Against hv for the MnS Thin Film.

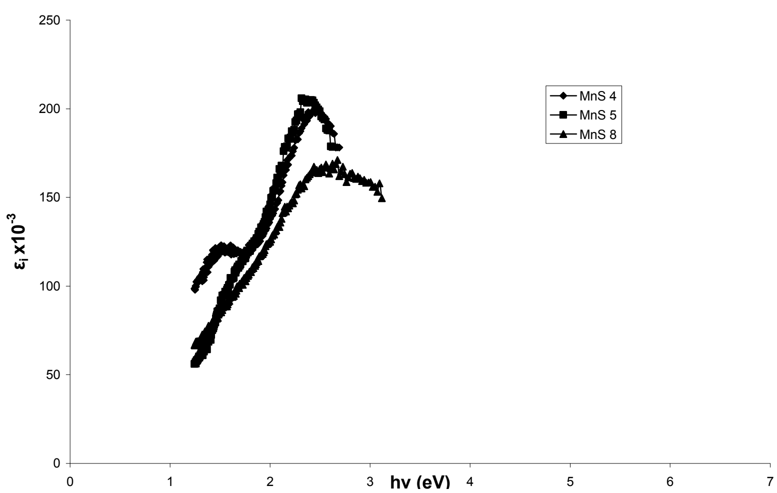


Figure 8: Plot of $\mathcal{E}_i$ Against hv for the MnS Thin Film.

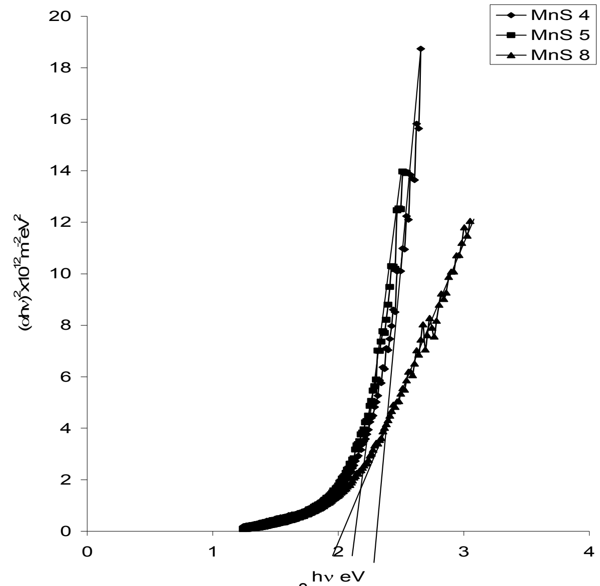
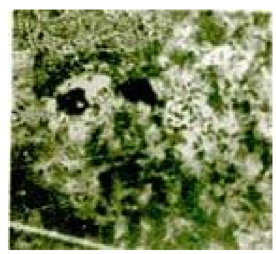


Figure 9: Plots $(\alpha h\nu)^2$ Against hv for MnS Thin Films.



(A)

(B)

(C)

Figure 10: Photomicrographs of the MnS Thin Films. A) MnS 4; B) MnS 5; C) MnS 8

CONCLUSION

Thin films of MnS have been deposited on glass substrates by the chemical bath deposition method using manganese sulphate, thiourea, ammonia, and distilled water. The optical properties of the films within the UV-NIR indicate that the films can find application in solar thermal technology, particularly in antireflection coating.

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