*Research Journal of Physical Sciences* ISSN 2320–4796
Vol. 2**(2),** 1-8, May **(2014)** *Res. J. Physical Sci.*

# Spectral Analysis of Amorphous Thin Films of MnS Obtained Chemically by Varying Solution Concentrations

**Usoh C.I.[1] and Okujagu C.U.[2]**
[1]Department of Physics, Alvan Ikoku Federal College of Education, Owerri, NIGERIA
[2]Department of Physics, Faculty of Physical Sciences and Information Technology. College of Natural and Applied Sciences, University of Port Harcourt, NIGERIA

**Available online at: www.isca.in**
Received 2nd April 2014, revised 27th April 2014, accepted 2nd May 2014

## Abstract

*Binary thin films of Manganese Sulphide (MnS) were chemically grown on glass substrates at 300k by varying molar concentrations of solution. The structure, morphology, optical properties, elemental composition and thickness of the grown films were analyzed using x-ray diffractometer, scanning electron microscope, Uv-Vis spectro photometric analysis, Rutherford Backscattering Spectrometry and surface profiler. From the study, all the as-deposited films showed amorphous nature with no prominent peaks. Transmittance was found to increase with decrease in solution concentration while absorbance showed the inverse. A peak transmittance of 76.88% was obtained for film with least solution concentration while peak absorbance of 93.40% was obtained for film with highest solution concentration. The energy gap which ranged between 2.99ev-3.30ev, showed increase with solution concentration and thickness. Possible areas of application based on their properties have been discussed.*

**Keywords:** Thin film, amorphous, concentrations, manganese sulphide, solution.

## Introduction

The optical properties of metal chalcogenide semiconductors have attracted the attention of researchers in the past decade because of their potential use in different areas of technology. MnS which belong to this group of materials has interesting properties such as direct wide band gap [3.1eV], exhibition of combination of magnetism and semi conductivity (dilute magnetic semiconductor)[1], abundance in nature and absence of toxicity[2]. Manganese Sulphide finds application in devices such as solar cell[1],as selective coatings, photoconductors, sensors[3] and anti-reflection coatings[4]. Thin film materials exhibit crystalline or amorphous nature depending on their deposition conditions. Films with amorphous nature also have optical properties that are of potential applications in various areas of technology[5]. MnS has been prepared by different techniques which include radio-frequency[6], SILAR[7], hydrothermal[8] and chemical bath deposition (CBD) technique[1-2,4,9]. Of all the techniques mentioned, chemical bath method is the most attractive for the fabrication of thin films because of the ease with which films can be grown with non-sophisticated equipment and materials; convenience for large area deposition, while at the same time giving results that are comparable with other sophisticated techniques. In this technique, it is important that the chemical reaction is controlled in order to achieve good deposition. This is achieved by using a complexing agent which slows down the reaction. MnS has been deposited by varying both concentrations of precursors of metal ion and Sulphide ion[10]. We report the spectral analysis of MnS thin films fabricated by varying molar concentrations of only the Sulphide ion source. In this work, the source of $Mn^{2+}$ was manganese sulphate while the source of sulphide ion, $S^{2-}$ was thiourea. Ammonia solution served as the complexing agent. Optical, structural, morphological studies; the elemental constituents and thickness of the grown films were investigated using UV-VIS spectrophotometric analysis, X-ray diffractometer, Scanning electron microscopy, Rutherford Back Scattering Spectrometry and Surface profiler.

## Materials and Methods

Using CBD technique manganese sulphide thin films were deposited on glass substrates with varying concentrations of thiourea at room temperature. Substrates were firstly degreased by soaking them in acqua-regia for 48hrs[11], after which they were thoroughly washed with detergent and water. After drying, they were kept in a desiccator for subsequent use.

The growth of MnS films on substrates is based on the gradual release of the metal ion ($M^{2+}$) and sulphide ion ($S^{2-}$) in an alkaline medium and condensation of the ions on a substrate that is suitably placed in the reaction bath. Formation of thin film of MnS is only possible if the product of $M^{2+}$ and $S^{2-}$ is greater than the solubility product constant ($K_{sp}$) of the compound (MnS). Deposition of MnS was carried out in a reaction bath which contained manganese sulphate as source of $Mn^{2+}$, thiourea which supplied $S^{2-}$ and ammonia which served as the complexing agent. The complexing agent slows down the reaction so that fast precipitation is avoided. The bath solution was made up to 50mls by adding distilled water and stirring to

ensure uniform deposition. A pH meter was used to keep the pH at 9. Previously degreased microscopic glass slides were immersed vertically in the bath and deposition took place at room temperature with different molar concentrations of thiourea (0.5m, 0.2m, 0.05m) at a period of 24hrs. At the end of this period, the coated glass slides were removed from the bath, rinsed with distilled water and allowed to dry for characterization. Three samples were prepared at varying bath concentrations as shown on table-1.
The chemical equations governing the reaction for the growth of MnS films are shown below:

$$MnSO_4 + 2H_4OH^- \rightarrow Mn^{2+} + (NH_4)_2SO_4 + 2OH^- \quad \ldots\ldots 1$$

$$(NH_2)_2SC + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \quad \ldots\ldots 2$$

$$HS + OH^- \rightarrow S^{2-} + H_2O \quad \ldots\ldots 3$$

$$Mn^{2+} + S^{2-} \rightarrow MnS \downarrow \quad \ldots\ldots 4$$

The deposited films were characterized using Rutherford BackScattering Spectrometry (RBS) for the elemental constituents and TM 3000 Tabletop Microscope (HITACHI) for scanning electron microscopy. For the structural investigation, an X-ray diffractometer (PANALYTICAL) with CuKα (1.54Å) operating at 40mA and 45kv at scanning range of $20^0$-$90^0$ was used while Avantes double beam spectrophotometer, model 2048 Ava soft 7.1 was used for the absorbance-transmittance-reflectance measurement between the wavelength range 370nm to 900nm, with uncoated glass slide as reference. The thickness was however measured with a Veeco Dektak 150 stylus surface profiler. The optical conductivity ($\sigma_{op}$) and constants such as the refractive index (n) and extinction coefficient (k) were calculated from the absorbance, transmittance and reflectance according to the mathematical relations given by Pankove J.T.[12] and Tanusevski A.[13].

## Results and Discussion

Figure-1 shows X-ray diffraction patterns for MnS thin films deposited with different molar concentrations of thiourea. The samples for all the concentrations showed no prominent peaks showing that they were amorphous. Practically there is no difference in structure seen in all the films. Similar report has been given by Pathan H.[7] for MnS prepared by SILAR and also by Lokhande C.D. et.al.[1] for CBD-MnS thin films on glass substrates, at room temperature. Non-crystallinity of the films could be attributed to low temperature used during deposition.

**Table-1**
**Preparation Parameters for MnS thin films**

| Sample | Deposition time (hrs) | $MnSO_4$ mol(M) | $MnSO_4$ vol(ml) | Thiourea mol(M) | Thiourea vol (ml) | Ammonia soln mol(M) | Ammonia soln vol (ml) | Distilled water(ml) | pH |
|---|---|---|---|---|---|---|---|---|---|
| M1 | 24 | 1.0 | 2.0 | 0.5 | 10 | 4 | 2 | 36 | 9 |
| M2 | 24 | 1.0 | 2.0 | 0.2 | 10 | 4 | 2 | 36 | |
| M3 | 24 | 1.0 | 2.0 | 0.05 | 10 | 4 | 2 | 36 | |

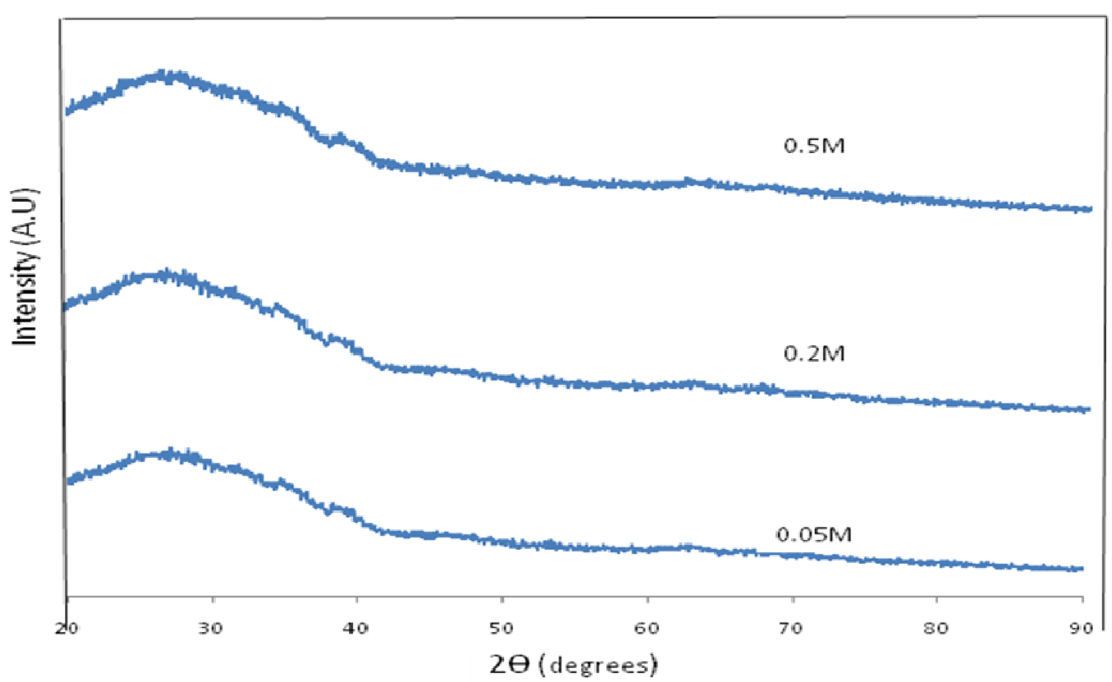


**Figure-1**
**X-ray patterns of amorphous MnS films grown with varying solution concentrations**

**Table-2**
**Composition of MnS and substrate from RBS analysis**

| MnS | Mn | S | O | Si | Na | Fe | Al | Ca |
|---|---|---|---|---|---|---|---|---|
| Sample | 71.00% | 29.00% | - | - | - | - | - | - |
| Substrate | - | - | 56.00% | 28.00% | 12.60% | 0.52% | 0.53% | 1.83% |

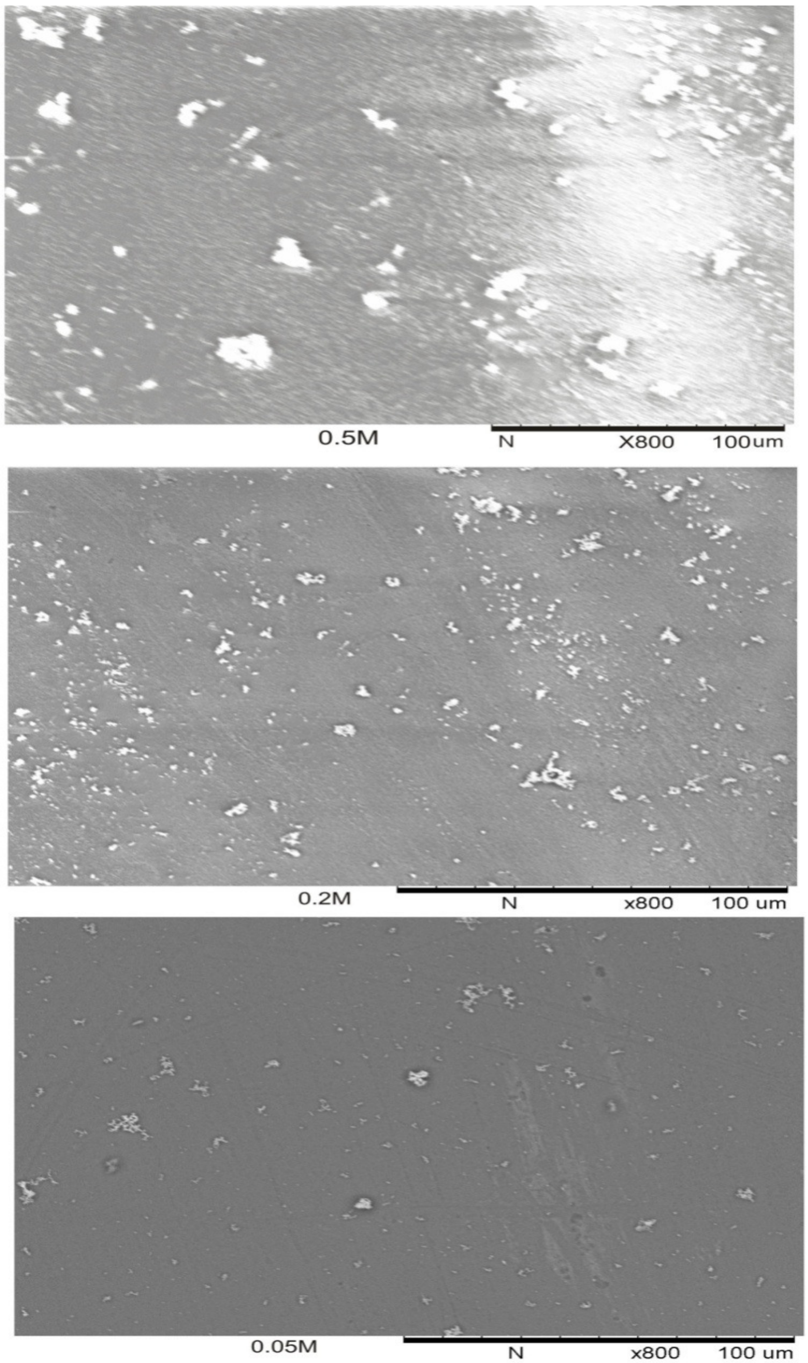


**Figure-2**
**SEM images of amorphous MnS thin films deposited with varying solution concentrations**

The surfaces in all the films are not homogeneous and contain irregular features. Film $M_1$ with 0.5M concentration showed many irregular agglomerated features with surface roughness, confirming amorphousness of the deposited MnS thin films.

The result of Rutherford BackScattering Spectrometry (RBS) for the elemental constituents of MnS films, is shown in table-2 while figure-3 displays the RBS spectrum, which contains a plot of the number of helium ions that were backscattered against their different energies. The average atomic percentage of Mn and S is 71%:29%. The result shows that there are no impurities in the deposited films. The presence of $O_2$, Si, Na, Fe, Al, Ca, are due to glass substrate.

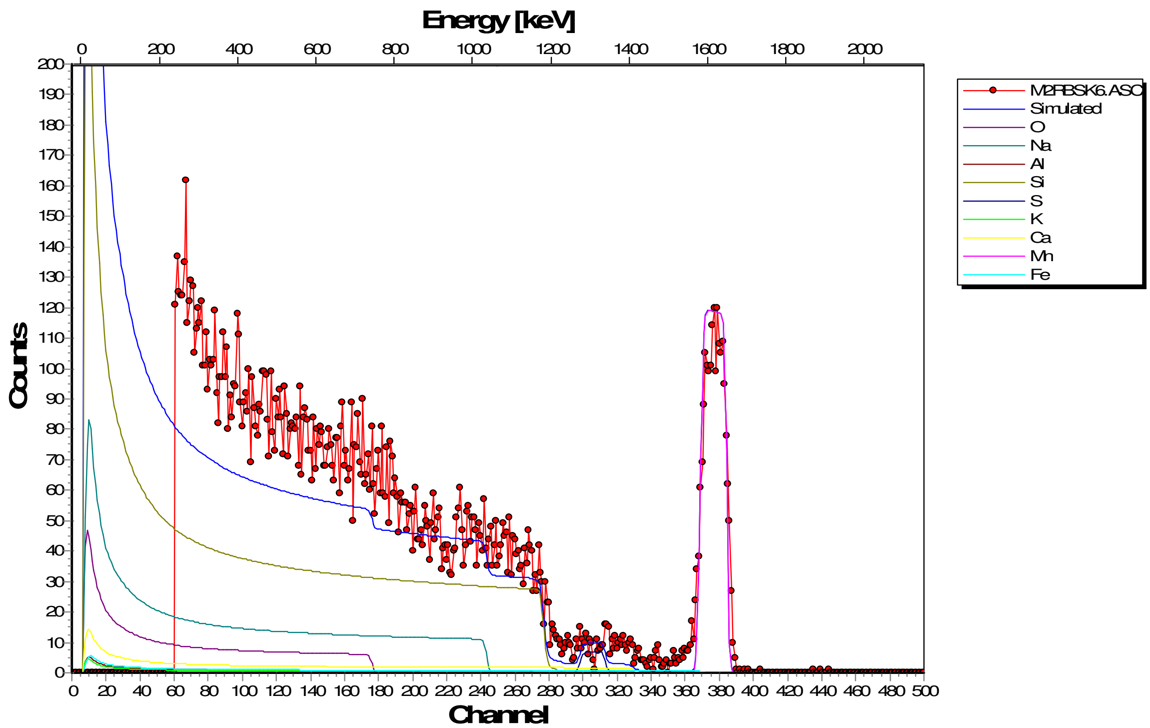


**Figure-3**
**RBS analysis for MnS thin films**

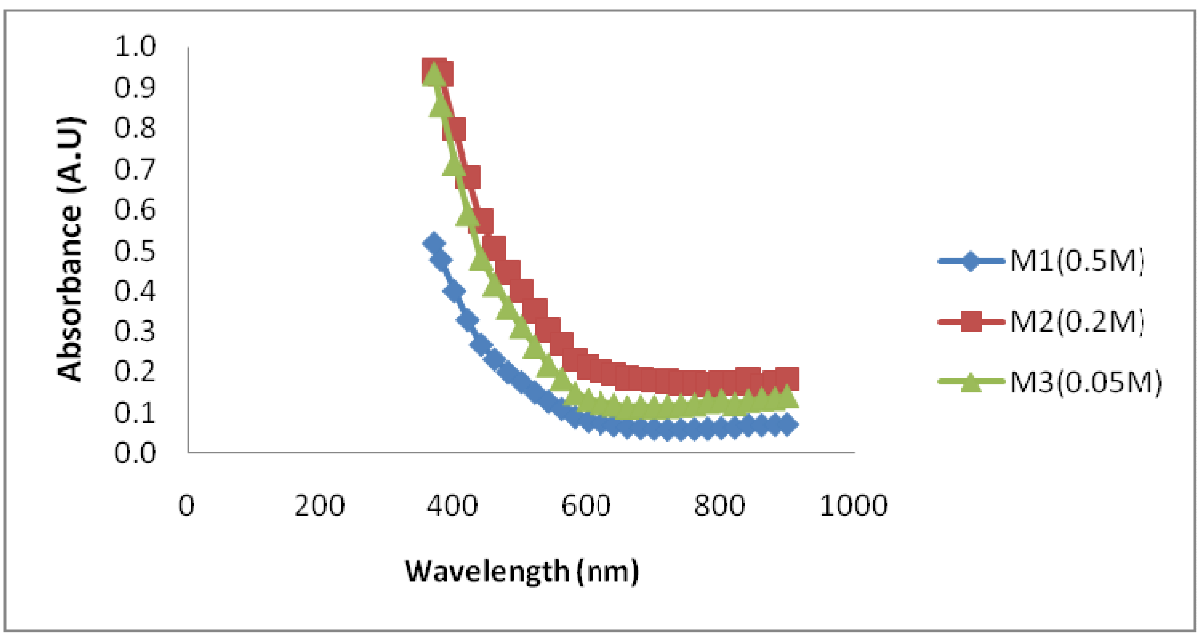


**Figure-4**
**Absorption Spectra of amorphous MnS films with varying solution concentrations**

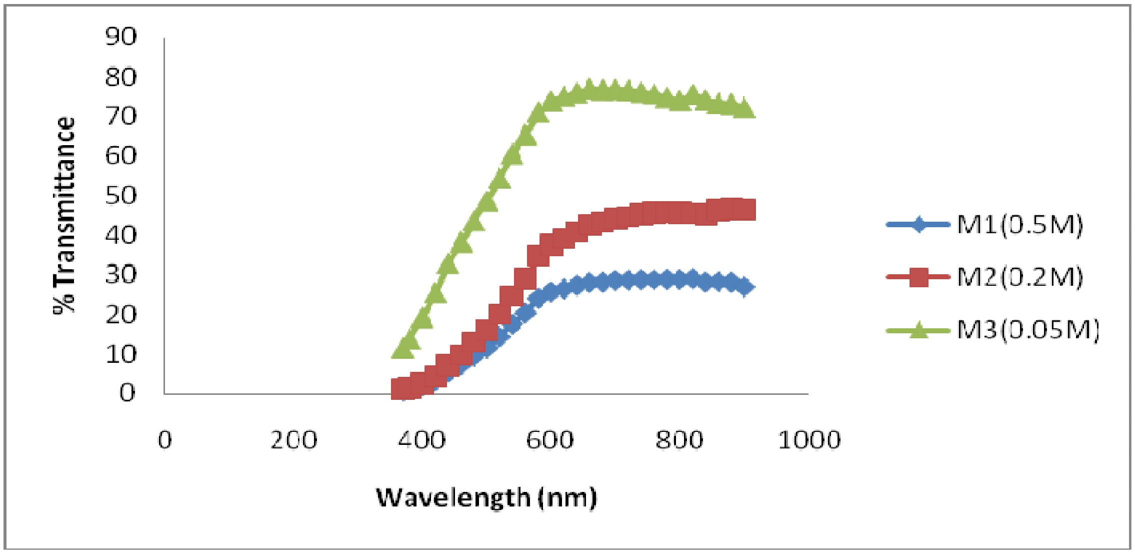


**Figure-5**
**Transmittance spectra of amorphous MnS films with varying solution concentrations**

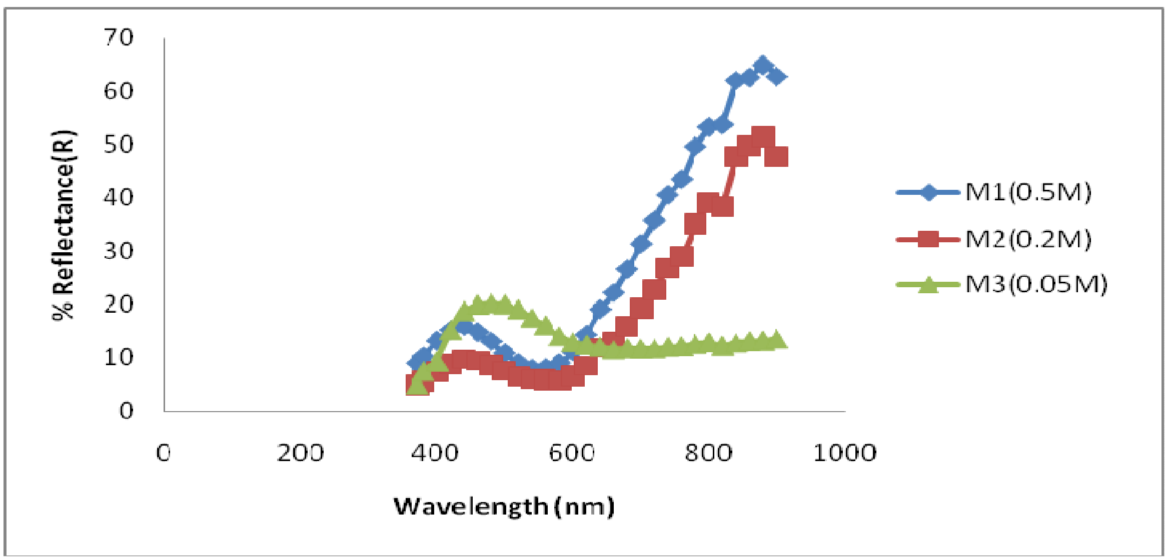


**Figure-6**
**Reflectance Spectra of amorphous MnS films with varying solution concentrations**

The spectral analysis of the absorption spectra in figure-4 indicate that absorbance increased with increase in sulphide ion concentration which also led to increase in thickness of deposited MnS films. Film $M_1$, with highest concentration showed highest absorbance peak of 93.4%. This is so because with thicker films more atoms are present in the film which means more states will be available for the photons to be absorbed Adeh H. et.al.[15]. All the films had their highest absorption in the Uv region of the electromagnetic spectrum. Furthermore, the transmittance spectra in figure-5 showed a decrease in transmittance with increase in concentration of sulphide ion ($S^2$). Increasing $S^-$ ion concentration means increasing film thickness, hence increasing the absorption. Film with least concentration has highest peak transmittance of 76.88% and could serve as transparent conducting materials in optoelectronic devices such as solar cells and light emitting diodes. Reflectance for the three samples in figure-6 was minimum in the Uv and rose to maximum values. Here also reflectance increased as concentration of sulphide ion increased with maximum value of 62.28% at 820nm. Films $M_1$ and $M_2$ had high reflectance values when compared to $M_3$. This implies that the optical properties of the films are functions of solution concentration. Films $M_1$ and $M_2$ with high reflectance could find application in the manufacture of highly reflectance mirrors, car head lamps, halogen lamps and desktop scanners while $M_3$ with relatively very low reflectance could serve as anti-reflection coatings.

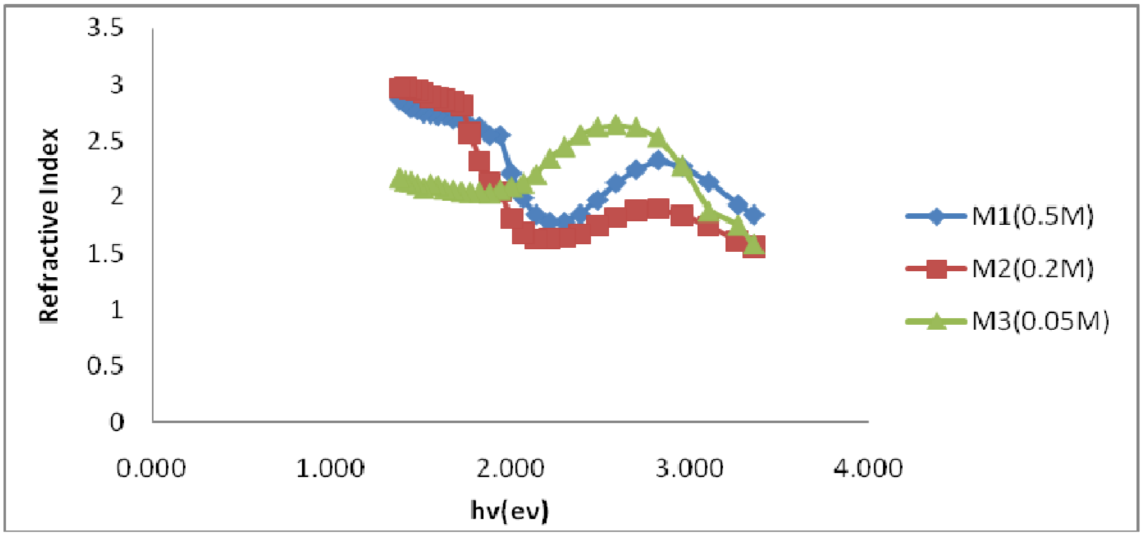


**Figure-7**
**Plot of refractive index versus hν for MnS films with varying solution concentrations**

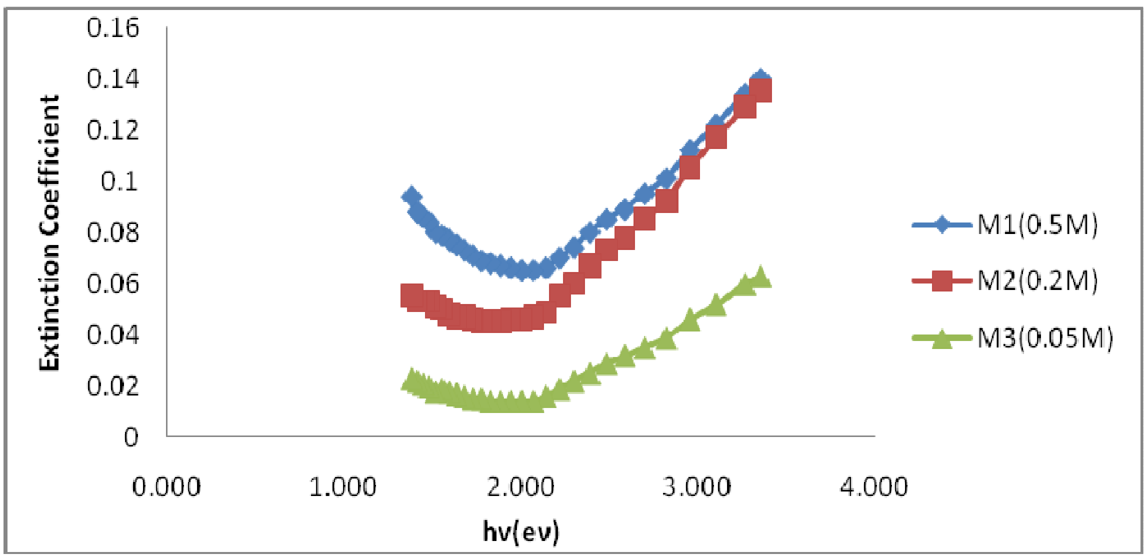


**Figure-8**
**Plot of extinction coefficient versus hν for MnS films with varying solution concentrations**

The plot of refractive index against hν for MnS films is shown in figure-7. The average values of n range between 1.38 and 2.18 with highest peak recorded at photon energy of 1.38 eV. It was noted that least value of n was recorded for the sample that had the least molar solution concentration. The values obtained are comparable with previous results 1.4-2.30 obtained by Agbo S.N. and Ezema F.I.[4], 1.92 obtained by Gumus C. et.al.[9] for chemically deposited MnS and 2.03 for radio frequency sputtered MnS obtained by Oidor-Juarez I. et.al.[6].

Extinction coefficient curves displayed in figure-8 show great dependence on concentration of solution. Its values increased with increasing sulphide ions. Peak values obtained for k ranged between 0.063 and 1.40 at photon energy of 3.35eV

The effect of varying solution concentration is also pronounced on the curves of optical conductivity versus hν in figure-8. $\sigma_{op}$ increased with increase in concentration of thiourea. It has maximum values that ranged between 0.811 x $10^{14}S^{-1}$ and 2.019 x $10^{14}S^{-1}$ at the higher energy region and minimum values between 0.126 x $10^{14}S^{-1}$ and 0.467 x $10^{14}S^{-1}$ at lower energy region.

The direct energy gap of deposited MnS was studied with the aid of the mathematical, expression given by Stern F.[14].

$$\alpha = \frac{[A(h\nu - Eg)]^{1/2}}{h\nu} \quad \ldots\ldots\ldots\ldots \quad 1$$

where; α is the absorption coefficient, hν is the incident photon energy, A is a constant and $E_g$ is the band gap energy.

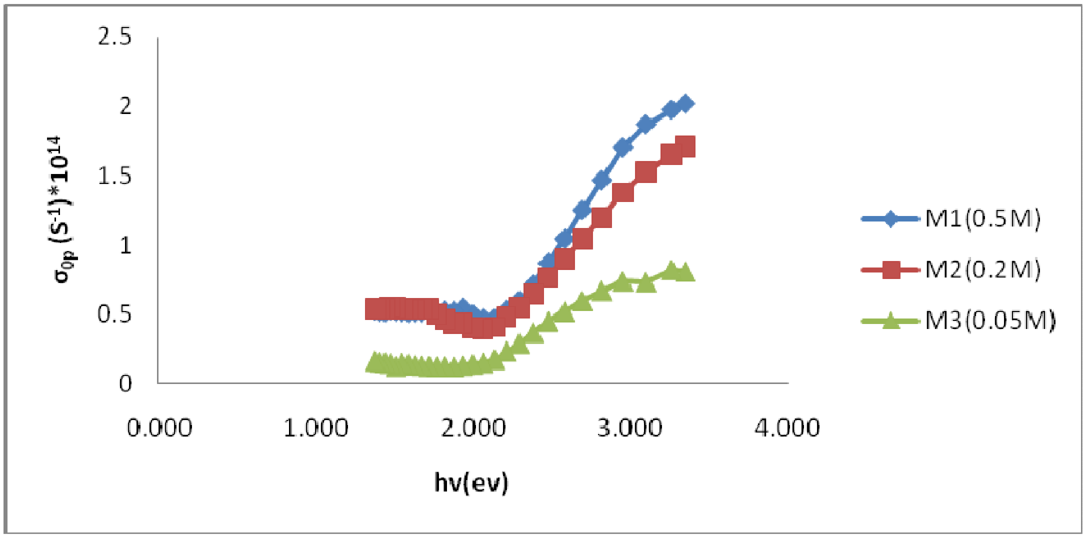


**Figure-9**
**Plot of optical conductivity $\sigma_{op}$ against hv for MnS with varying solution concentrations**

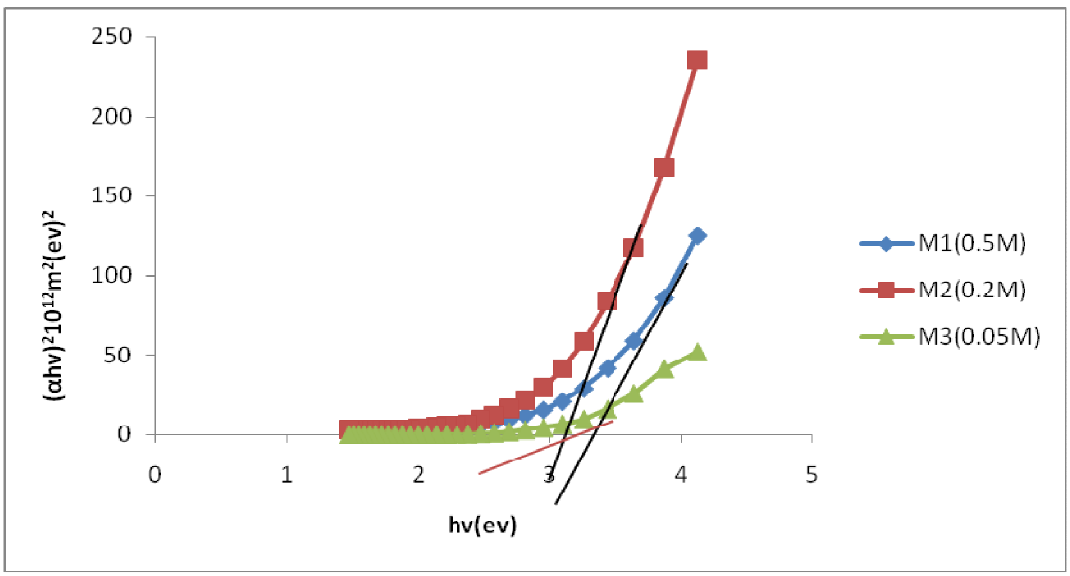


**Figure-10**
**Optical band gap for amorphous MnS with varying solution concentrations**

**Table-3**
**Band gap dependence on solution concentration of amorphous MnS thin films**

| sample | Deposition time (hrs) | Thickness (µm) | Thiourea mol (M) | Band gap $E_g$ (ev) |
|---|---|---|---|---|
| $M_1$ | 24 | 0.15 | 0.50 | 3.30 |
| $M_2$ | 24 | 0.10 | 0.20 | 3.10 |
| $M_3$ | 24 | 0.07 | 0.05 | 2.99 |

The direct optical band gap were calculated by extrapolating the straight line part of the graph of $(\alpha h\nu)^2$ vs hν (figure-10) on the energy axis to $(\alpha h\nu)^2 = 0$. The figure shows that the films have direct band gap which are displayed on table-3. They are in the range of 2.99eV-3.30eV and were found to increase with increasing concentration of $S^{2-}$ ion (0.05M-0.5M). Therefore the solution concentration had some effect on the optical band gap of the films. This is in line with previous report of Anuar kassim [10] on increase of band gap with solution concentration which implies that the band gap of the films are thickness dependent. Thickness obtained range between 0.07µm and 0.15µm. The obtained values are comparable with values 3.70eV to 3.5eV reported by Anuar kassim [10], 3.02eV by[1] and 3.25eV by Pramanik P.[16].

## Conclusion

Manganese Sulphide (MnS) thin films have been deposited at room temperature by employing Chemical bath deposition method. The X-ray diffraction and morphological studies reveal that the films were amorphous with no prominent peaks even after varying the solution concentration. However, the spectral analysis showed that the optical properties are dependent on solution concentration. Transmittance increased as concentration reduced while absorbance increased with concentration of solution. The energy gap in the range 2.99ev-3.30ev was found to increase with concentration of solution which is also thickness dependent. From their optical properties, amorphous MnS could be used as transparent conducting materials in solar cells. Films with high reflectance could find application in the manufacture of highly reflectance mirrors, desktop scanners and halogen lamps.

## References

**1.** Lokhande C.D., Ennaoui A., Patil P. S., Giersig M., Muller M., Diesner K. and Tributsh H., Process and Characterization of chemical bath deposited Manganese Sulphide (Mns) thin films, *Thin solid Films*, **330**, 70-75 **(1998)**

**2.** Anuar-kassim, Abdui Halim Abdullah, Ho Soon and Saravaran Nagalingem, Influence of deposition time in the properties of chemical bath deposited Manganese Sulphide thin films, *Avances en Quimica,* **8(3)**, 141-145 **(2010)**

**3.** Sreekantha Reddy D., Raja Raddy D., Reddy B., Mallikarjuna Reddy A., Gunasekhar K. and Sreedhere Reddy P., Annealing effect on physical properties of thermally evaporated MnS nanocrystalline films, *J. Optoelectron. Adv. Mat*. **9**, 2019-2022 **(2007)**

**4.** Agbo S.N. and Ezema F.I., Analysis of Chemically Deposited MnS thin Films, *The Pacific J. Sci. and Technol*, **8(1)**, 1-5 **(2007)**

**5.** Guneri E. and Kariper A., Optica properties of amorphous, CuS thin films deposited chemically at different pH values, *J. Alloys and Comp.*, **515**, 20-26 **(2012)**

**6.** Oidor-Juarez I., Garcia-Jimenez P., Torres- Delgado G., Castanedo- Perez B., Jimenez-Sandoval O., Chao B. and Jimeneze-sandoval S., Substrate temperature effects on the growth and properties of $\gamma$-MnS thin films grown by rf sputtering, *Mater. Res. Bull*., **37**, 1749- 1754 **(2002)**

**7.** Pathan H., Kale S.S., Lokhande C.D., Sung-Hwan Han and Oh-Shim Joo, Preparation and characterization of amorphous Manganese Sulfide thin films by SILAR, *Mater. Res. Bull.,* **42(6)**, 1565-1569 **(2007)**

**8.** Zhang Y., Wang H., Wang B., Yan H. and Yoshimura M., Low temperature hydrothermal synthesis of pure metastable Y-Manganese Sulfide (Mns) crystallites, *J. Cryst. Growth*, **243**, 214 -217 **(2002)**

**9.** Gumus C., Ulutas C. and Ufuktep Y., Optical and Structural properties of manganese sulfide thin films, *Optical Materials,* **29**, 1183-1187 **(2009)**

**10.** Anuar kassim, Tan wee, Ho soon Min, Abduz Halim Abdullah, Ahmed Haziq Jusoh and Saravanan, Nagaligam, Effect of solution Concentration on MnS thin films deposited in a chemical bath, *Kasetsart J. (Nat. Sci),* **44**, 446- 453 **(2010)**

**11.** Okujagu C.U., Growth and Characterization of thin film selective surfaces and their applications, Doctoral thesis, University of Nigeria, Nsukka, **(1992)**

**12.** Pankove J.T., Optical Processes in semiconductors, Prentice–Hall, New Jeresey, **58,** 88 **(1971)**

**13.** Tanusevski A., Optical and photoelectric properties of SnS thin films prepared by chemical bath deposition, *Semicon. Sci. Technol*, **18**, 501-505 **(2003)**

**14.** Stern F., Elementary theory of the Optical properties of solids, *solid state Physics* **15**, 299-408 **(1963)**

**15.** Adeh H., Omiran Al- Khajatt, Mustafa D. Jaafer., Annealing Effect on the structural and optical properties of CuS thin Film Prepared by chemical bath deposition, *J. of kufa-phy.*, **5(1)**, 79-90 **(2013)**

**16.** Pramanik P., Akher A. and Basu P.K., A Solution Growth Technique for deposition of MnS thin Films, *Thin solid films*, **158(2)**, 2027-2035 **(1988)**