



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

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Available online at: www.isca.in

Received 2nd April 2014, revised 27th April 2014, accepted 2nd May 2014

Abstract

A second order non linear semi organic optical crystal 2- amino 5- nitro pyridinium nitrate (2A5NPN) was grown by slow evaporation technique and characterized by microhardness, dielectric and photoconductivity studies. Hardness values were measured using Vickers hardness tester. The study of dielectric measurement was done by HIOKI HITESTER instrument. The photoconductivity of grown crystal was elucidated by using KEITHLEY 485 picometer.

Keywords: Microhardness, dielectric, photoconductivity, pyridinium, single crystals.

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 toxicity². Manganese Sulphide finds application in devices such as solar cell¹, as selective coatings, photoconductors, sensors³ and anti-reflection coatings⁴. 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 technology⁵. MnS has been prepared by different techniques which include radio-frequency⁶, SILAR⁷, hydrothermal⁸ 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 ion¹⁰. 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

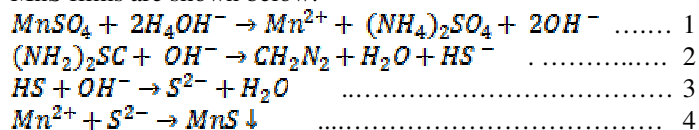
spectrophotometric analysis, X-ray diffractometer, Scanning electron microscopy, Rutherford Back Scattering Spectrometry and Surface profiler.

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 aqua-regia for 48hrs¹¹, 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:



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 CuK α (1.54Å) operating at 40mA and 45kv at scanning range of 20⁰-90⁰ 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 (σ_{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		Thiourea		Ammonia soln		Distilled water(ml)	pH 9
		mol(M)	vol(ml)	mol(M)	vol (ml)	mol(M)	vol (ml)		
M1	24	1.0	2.0	0.5	10	4	2	36	
M2	24	1.0	2.0	0.2	10	4	2	36	
M3	24	1.0	2.0	0.05	10	4	2	36	

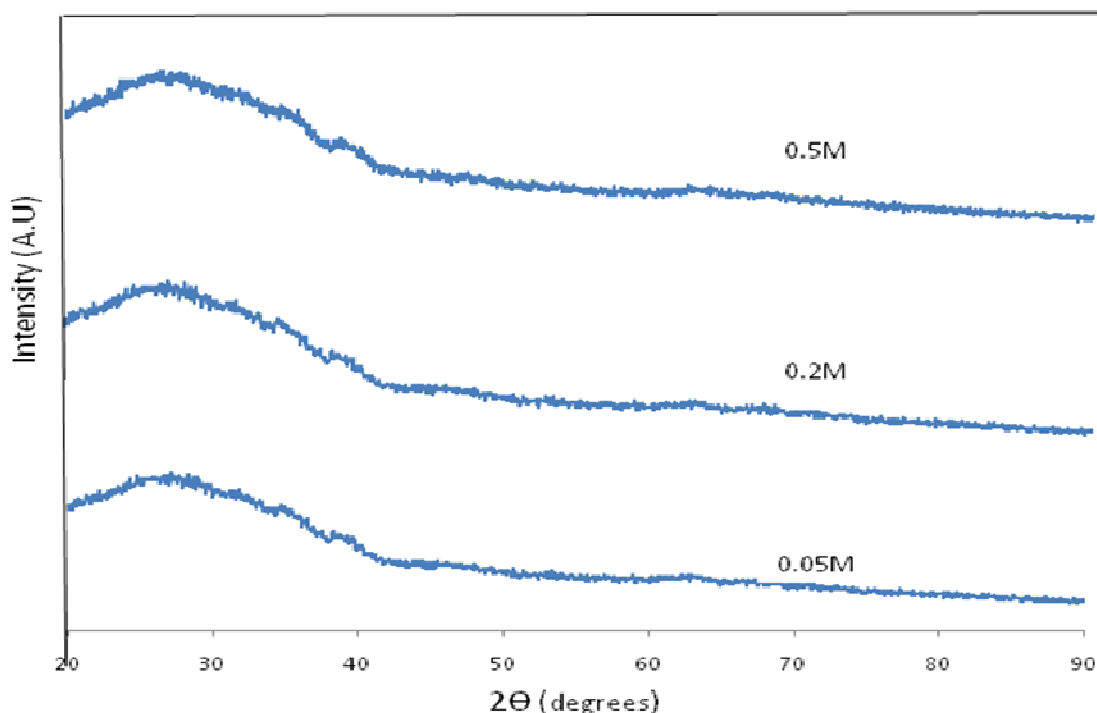


Figure-1
X-ray patterns of amorphous MnS films grown with varying solution concentrations

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%

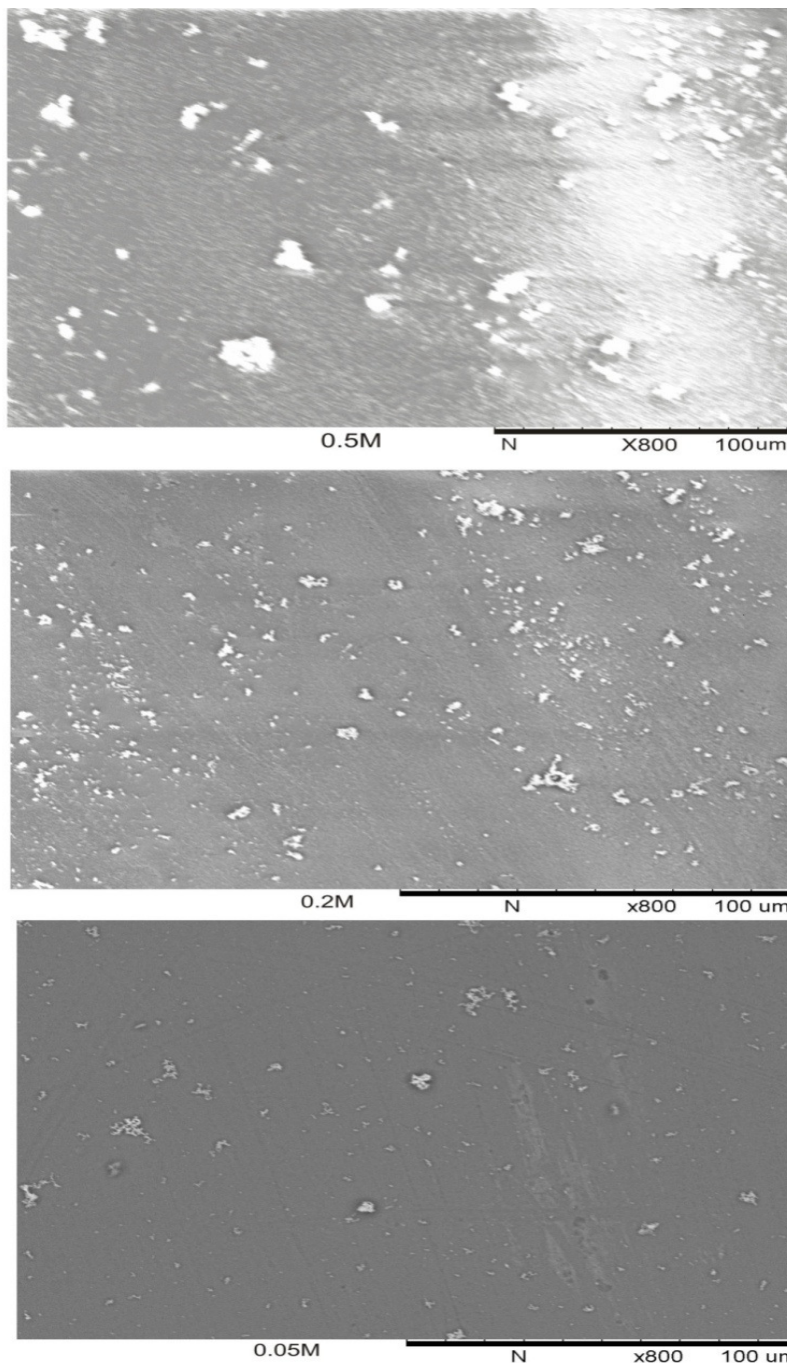


Figure-2
SEM images of amorphous MnS thin films deposited with varying solution concentrations

The surfaces in all the films are not homogeneous and contain irregular features. Film M₁ 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 O₂, Si, Na, Fe, Al, Ca, are due to glass substrate.

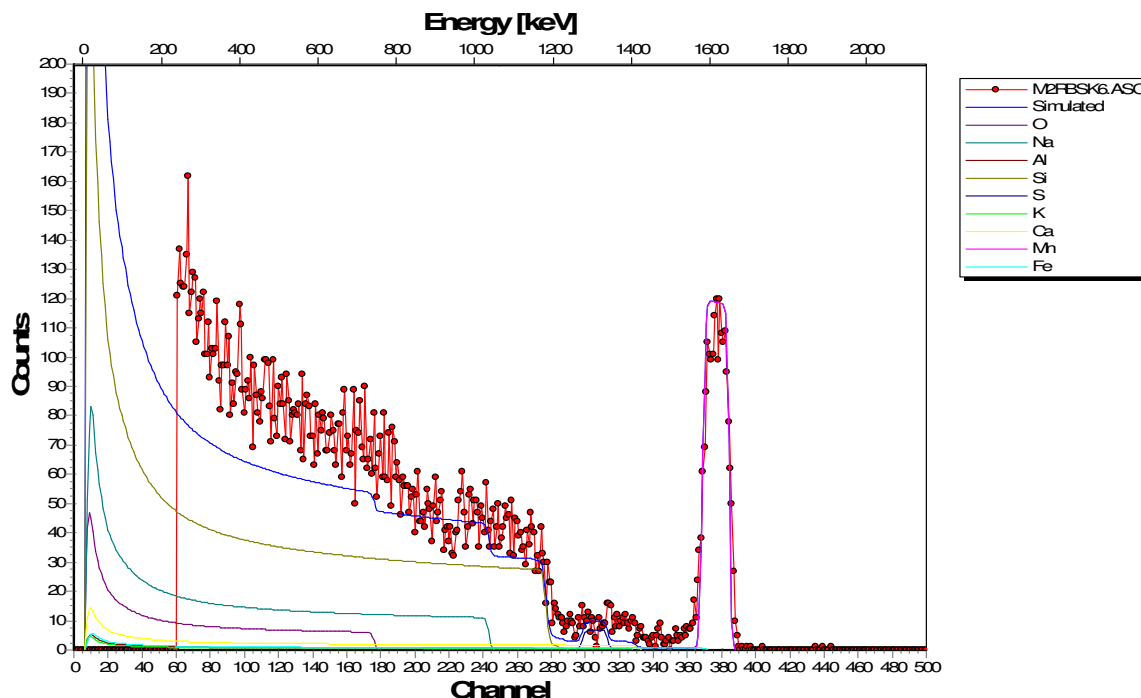


Figure-3
RBS analysis for MnS thin films

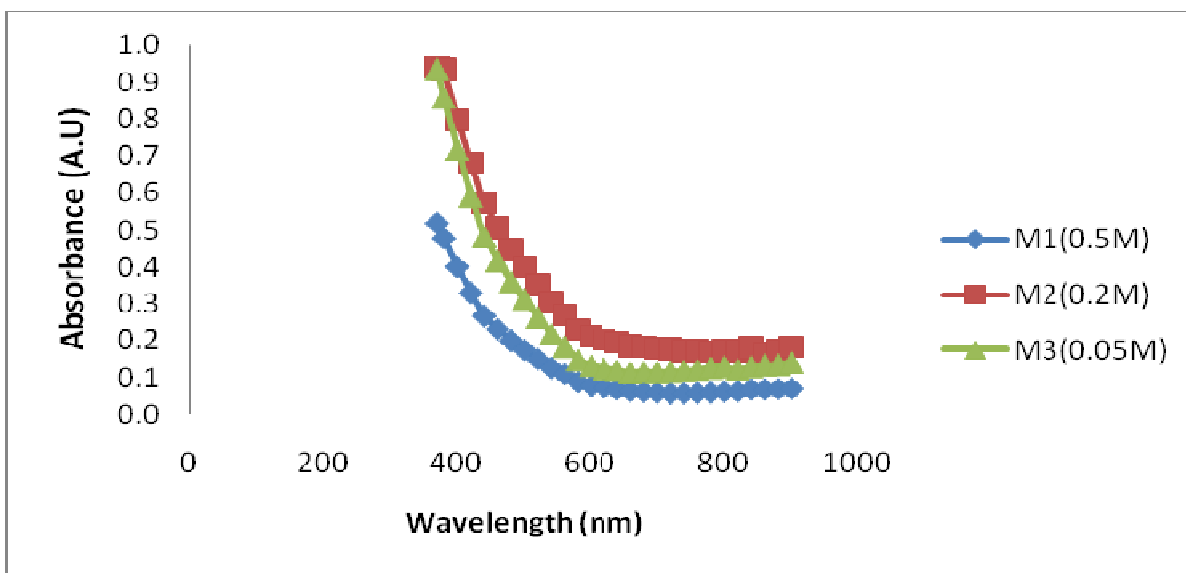


Figure-4
Absorption Spectra of amorphous MnS films with varying solution concentrations

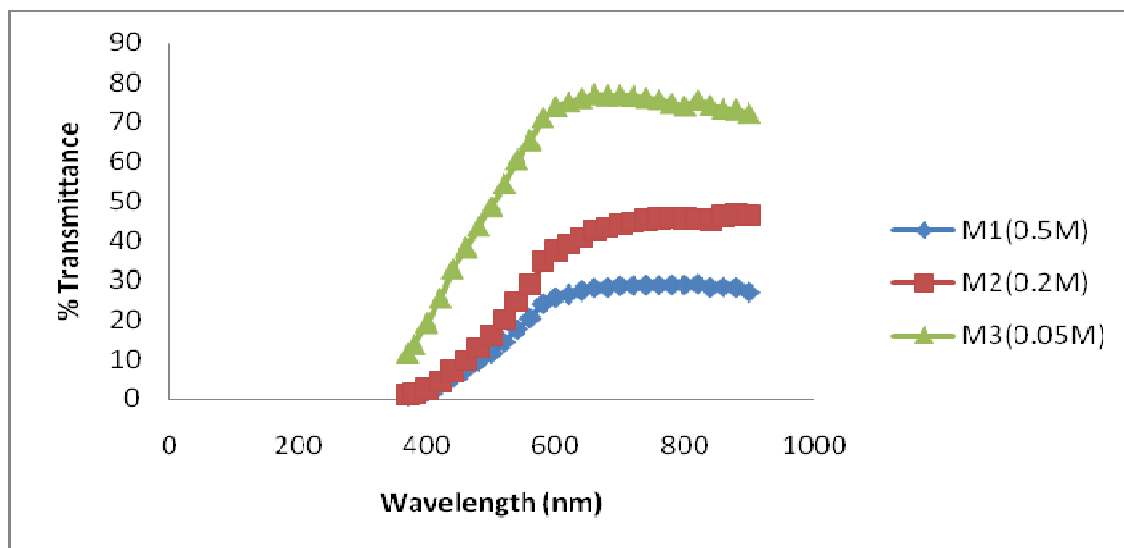


Figure-5
Transmittance spectra of amorphous MnS films with varying solution concentrations

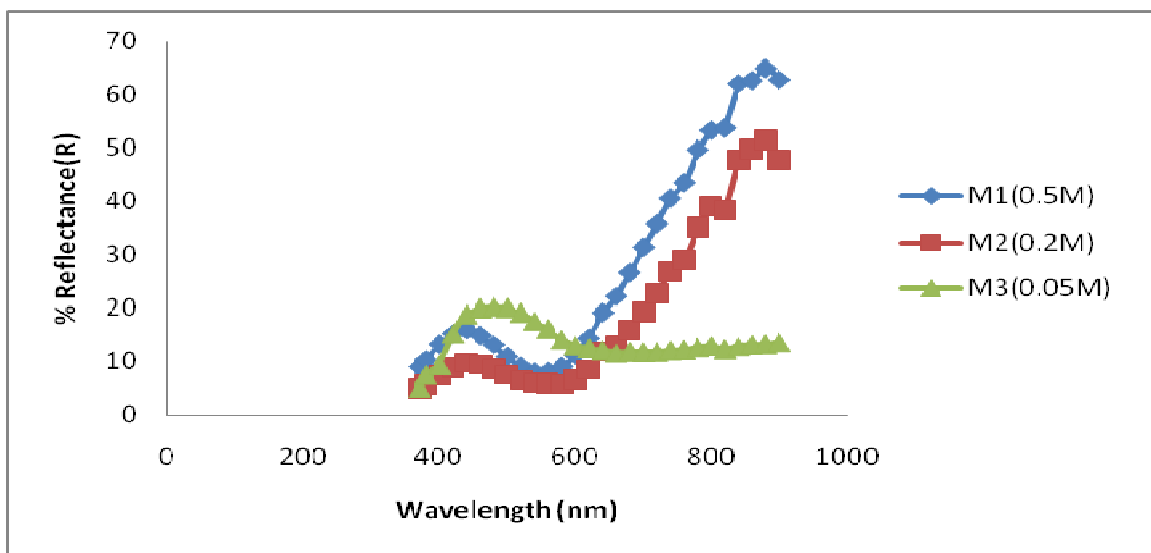


Figure-6
Reflectance Spectra of amorphous MnS films with varying solution concentrations

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^{2-} 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.

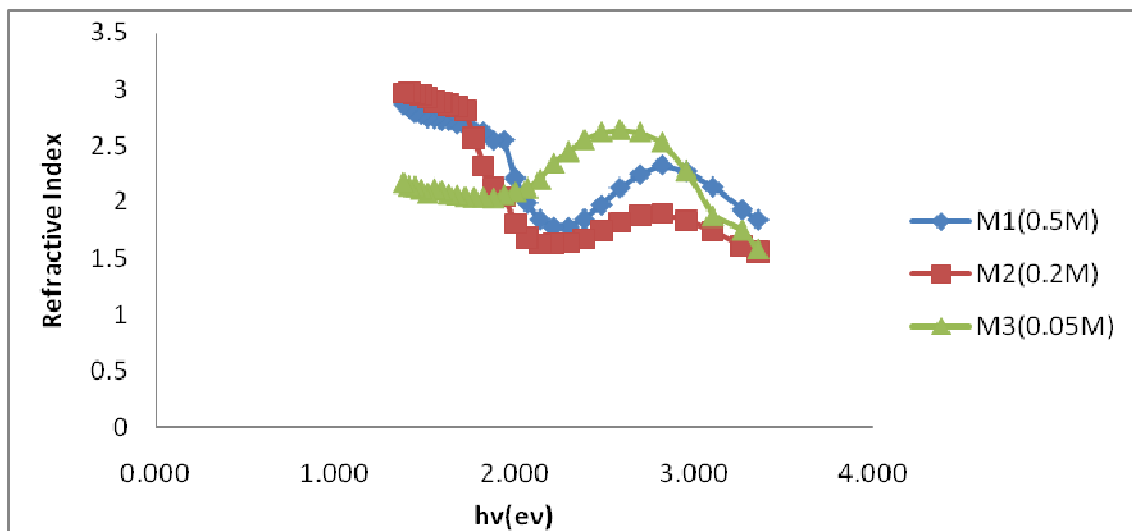


Figure-7
Plot of refractive index versus hv for MnS films with varying solution concentrations

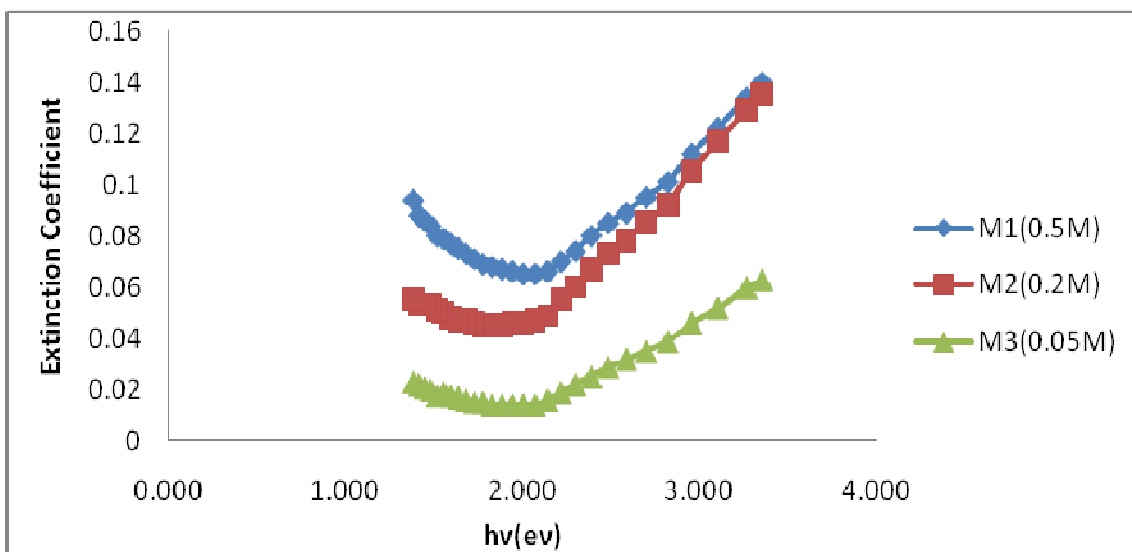


Figure-8
Plot of extinction coefficient versus hv for MnS films with varying solution concentrations

The plot of refractive index against $h\nu$ 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 $h\nu$ in figure-8. σ_{op} increased with increase in concentration of thiourea. It has maximum values that ranged between $0.811 \times 10^{14} S^{-1}$ and $2.019 \times 10^{14} S^{-1}$ at the higher energy region and minimum values between $0.126 \times 10^{14} S^{-1}$ and $0.467 \times 10^{14} S^{-1}$ 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.

$$\alpha = \frac{[A(h\nu - E_g)]^{1/2}}{h\nu} \dots\dots\dots 1$$

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

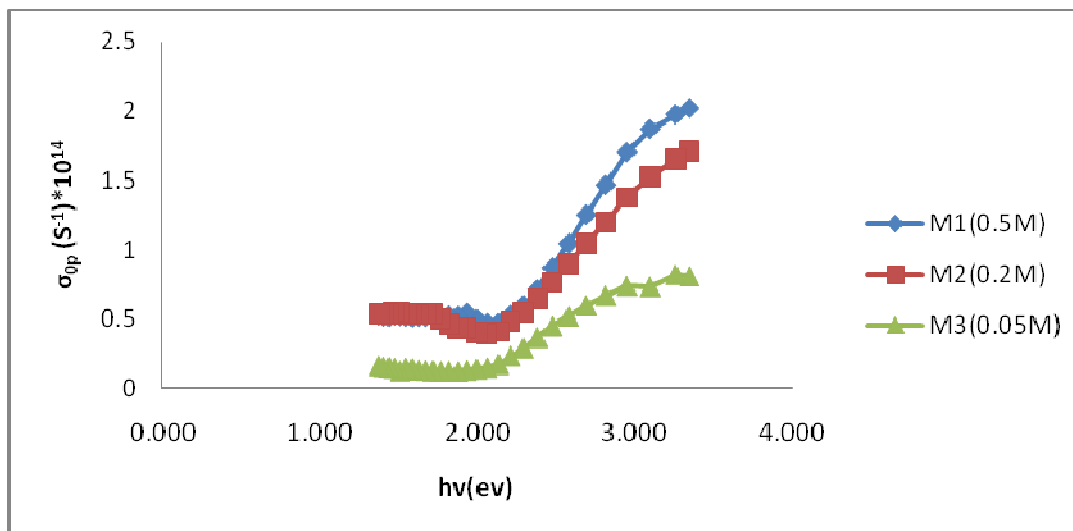


Figure-9
Plot of optical conductivity σ_{op} against $h\nu$ for MnS with varying solution concentrations

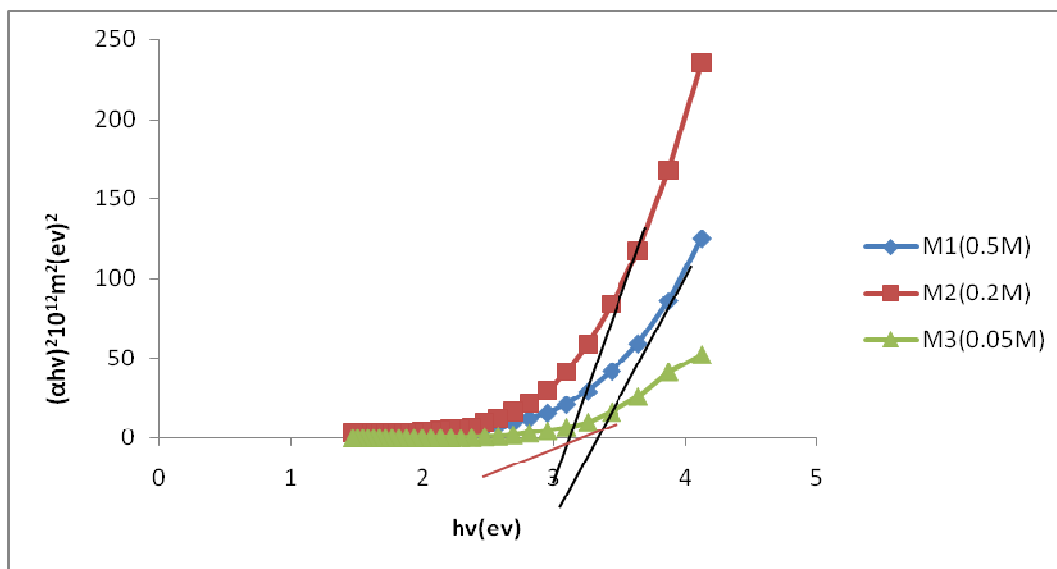


Figure-10
Optical band gap for amorphous MnS with varying solution concentrations

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 $h\nu$ (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 kassim¹⁰ on increase of band gap with solution concentration which implies that the band gap of the films are thickness dependent. Thickness obtained range between 0.07 μm and 0.15 μm . The obtained values are comparable with values 3.70eV to 3.5eV reported by Anuar kassim¹⁰, 3.02eV by¹ 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.

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