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RESEARCH ARTICLE

Study of the Optical, Electrical, Structural and Morphological Properties of Electrodeposited Lead Manganese Sulphide (PbMnS) Thin Film Semiconductors for Possible Device Applications

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ABSTRACT

Semiconductor thin films of lead manganese sulphide (PbMnS) have been successfully deposited on florinated tin oxide (FTO) conductive glass substrate using an electrodeposition method. Lead acetate ($Pb(CH_3COO)_2$), manganese sulphate ($MnSO_4.H_2O$) and thiourea (CH_4N_2S) were the precursor used for lead (Pb^{2+}), manganese (Mn^{2+}) and sulphur (S^{2-}) sources respectively. The concentration of manganese (Mn^{2+}) was varied while keeping the concentrations of Pb^{2+} and S^{2-} constant at 0.2 M and 0.1 M respectively. The deposited films were annealed at temperature of 250 ^oC and subjected for optical, electrical, structural and morphological characterizations. The results of the characterizations showed that the deposited thin films of PbMnS have high absorbance, high absorption coefficient throughout VIS and NIR regions. The band gap energy of the films is tuned to the order of 1.9 eV to 2.0 eV and tends to constant as concentration of Mn^{2+} increased. The electrical properties (electrical resistivity and conductivity) of the films are dependent on the concentration of Mn^{2+} and film thickness. The range of values of the electrical properties is found to be within the range of values for semiconductor materials. The XRD analysis revealed that the deposited thin films of PbMnS is crystalline but the crystallinity declined with increase in concentration of Mn^{2+}. The SEM morphology showed that the surfaces of the films are highly homogeneous in nature and particle sizes are uniform on the substrate with the majority of the particles been spherical in shape. These observed properties exhibited by the deposited thin films of PbMnS make the films good materials for many optoelectronic and electronic applications such as solar cell, light emitting diode (LED), photodetector etc.

Keywords: Electrodeposition, Optoelectronics, Bandgap.

1 Introduction

Devices made of semiconductor thin films have no doubt contributed immensely to the level of technology today and have demonstrated quite copious applications in various fields of science and technology. Few of these applications are solar cells, photoconductors, infrared detectors, waveguide coatings, temperature control of satellites, photo thermal solar coatings, magnetic films, superconducting films, anticorrosive films, anti-reflection coating, interference filters, polarizers, narrow band filters, microelectronics devices, diamond films, reduction of fabrication through coating or surface modification, high temperature wear resistance films, light sources (light emitting diodes -LED and light amplification by stimulated emission of radiation-LASER), "[1]-[7]". The performance of any semiconductor alloy for these applications is attributed to the electronic properties of the constituent elements of the material. The choice of the constituent elements of semiconductor thin film alloys can give rise to splits of materials with different performances for many applications. The basic electronic properties of elements are charge and spin properties of electrons. The charge property of electrons in semiconductor materials is basically produced

if the materials are composed of non-magnetic materials. In the other hand, the spin property of electrons is produced by magnetic elements that constitute the materials. Lead manganese sulphide (PbMnS) thin film semiconductor alloy is one of the semiconductor materials that is identified to constitute both magnetic and non-magnetic elements in its constituent. Ordinarily, lead sulphide (PbS) thin film is a very important binary IV–VI semiconductor material with a narrow band gap energy of 0.41 eV and relatively large excitation Bohr radius of 18 nm, "[8]". These properties result in strong quantum confinement of electrons and holes present in the crystal lattice of the material. The band gap energy of PbS thin films can be controlled simply by modifying particle size and shape. Quantum confinement in PbS thin films possessing significantly; broader band gaps gives rise to many interesting structural, optical and electrical properties much different from their bulk counterparts. These behaviors make it good material for light absorbers in solar cells, transistors, infrared detectors, biosensors devices, lasers, light emitting diode (LED) devices, telecommunications, optical switches, optical amplification as well as gas-sensing agents in the solid-state sensors, "[9], [10]". Incorporation of anti-ferromagnetic element-manganese into PbS crystal, grouped it into the new split of material called diluted magnetic semiconductor (DMS) thin films which have been identified as materials that have high performance potentials for many applications regarding the magnetic behaviors of their constituent elements "[11], [12]". This new form of material (PbMnS) can be prepared by varieties of methods. Mahashabde *et al.*, "[13]" used chemical bath method to deposit ternary thin films of $Pb_xMn_{1-x}S$ having composition (x = 0. 5) on Pyrex glass substrate at 45°C for 35-50 minutes using manganese acetate, lead acetate and thiourea as starting materials and studied their structural properties. Chidambara *et al.*, "[14]" used successive ionic layer adsorption and reaction method (SILAR) to grow manganese doped lead sulphide thin films on glass substrate and reported that stress exists for all the manganese doped PbS thin films deposited. Chidambara *et al.*, [15] investigated the structural, optical and magnetic properties of Mn doped PbS thin films fabricated using SILAR method. They reported that the films have preferential orientation along (2 0 0) plane, optical bandgap energy varied from 2.8 eV to 3.1 eV as manganese content increases and behave as a soft magnetic material according to the vibrating sample magnetometer (VSM) studies. The effect of bandgap broadening of Mn doped PbS quantum dots (QDs) reproduced using pulse laser deposition (PLD) synthesis have been reported by Yost *et al.*, "[16]" and they concluded that the variation in bandgap broadening is as a result of the Mn dopant locations, inside the surface of the QDs. They claim the results provide clear information on how the transition metal element doping locations in semiconducting QDs influence the electronic density of state (DOS) of the host QDs. The incorporation of other magnetic materials order than manganese into the PbS structure have demonstrated significantly enhanced performance of their device applications as reported by "[17]". In this work, we used electrodeposition method to deposit ternary chalcogenide thin film semiconductor alloys of PbMnS on florine doped tin oxide (FTO) conductive glass substrate to study their optical, electrical and structural properties for possible applications.

2 Materials and Method

The semiconductor thin films of PbMnS were deposited using an electrodeposition technique at room temperature using Potentiostat (model Zhaoxin: RXN-3010D). Lead acetate ($Pb(CH_3COO)_2$), Manganese sulphate ($MnSO_4.H_2O$) and Thiourea (CH_4N_2S) were the main starting materials used to source for lead (Pb) ions (Pb^{2+}), manganese (Mn) ions (Mn^{2+}), Sulphur (S) ions (S^{2-}). Sodium tri-sulphate (Na_2SO_3), Ethylenediaminetetraacetic acid (EDTA) ($C_{10}H_{16}N_2O_8$) and Distilled water were the secondary materials used as supporting electrolyte, complexing agent and reaction medium respectively. Floourine-doped tin oxide (FTO) conductive glass substrate was used as working electrode and washed with acetone in an ultrasonic machine for one hour and dried in an electric oven. Two digital multimeter (DT890C7 and mastech: MY60) were used for measuring current and voltage respectively. Three electrodes configuration systems of electrodeposition technique were employed to deposit the thin films of PbMnS on the FTO glass substrate.

2.1 Preparation of PbMnS Thin Films

To prepare the thin films of PbMnS, 10 ml of 0.2 M Lead acetate ($Pb(CH_3COO)_2$), 10 ml of 0.1 M CH_4N_2S, 10 ml of 0.1 M $Na_2S_3O_4$ and 5 ml of 0.025 M EDTA as a complexing agent with 0.05 M concentrations of $MnSO_4$ were reacted in an electrochemical cell. The deposition of the films was initiated on the surface of the working electrode at constant potential of 1.8 V by passage of current through the solution of the complexes and allowed to stay for 90 seconds. The process was repeated by varying the concentrations of Mn^{2+} source in the order of 0.05, 0.1, 0.15 and 0.25 M and the deposited films were removed from the cell and washed with distilled water and annealed in an oven at temperature of 250 ^{O}C for 5 minutes. These processes are summarized in the Table 1.

Table 1: *Preparation of PbMnS Thin Films at Varying Concentration of Mn^{2+}*

Bath Name	Pb-acetate		$MnSO_4.H_2O$		CH_4N_2S		EDTA		Na_2SO_4		Voltage (Volts)	Time (secs)
	Conc (mol)	Vol (ml)	Conc (mol)	Vol (ml)	Conc (mol)	Vol (ml)	Conc (mol)	Vol (ml)	Conc (mol)	Vol (ml)		
0.05 M Mn^{2+}	0.2	10	0.05	10	0.1	10	0.025	5.0	0.05	10	1.80	90.00
0.10 M Mn^{2+}	0.2	10	0.10	10	0.1	10	0.025	5.0	0.05	10	1.80	90.00
0.15 M Mn^{2+}	0.2	10	0.15	10	0.1	10	0.025	5.0	0.05	10	1.80	90.00
0.20 M Mn^{2+}	0.2	10	0.20	10	0.1	10	0.025	5.0	0.05	10	1.80	90.00
0.25 M Mn^{2+}	0.2	10	0.25	10	0.1	10	0.025	5.0	0.05	10	1.80	90.00

2.2 Characterizations of the Deposited Thin Films

To determine the optical, electrical and structural properties of the deposited thin films of PbMnS alloys, the films were subjected for optical analysis using UV-VIS Spectrophotometer of model U756S-19-018 to measure the absorbance of the films. The optical absorbance (A) was measured directly from the spectrophotometer machine and analyzed in the wavelength range of 200-1100 nm, while other optical properties were calculated using appropriate relations. The electrical properties were determine using four probe configurations connected to Keithley source meter of model 2400 LV to measure the resistivity of the films. EMPYREAN Diffractometer and MIRA 3 TESCAN scanning electron microscopy were used to measure the crystalline structure and morphology of the films respectively.

3 Results and Discussions.

3.1 Optical Properties of the as Deposited (PbMnS) Thin Films

The plot of absorbance as a function of wavelength for the deposited thin films of PbMnS is presented in figure 1.

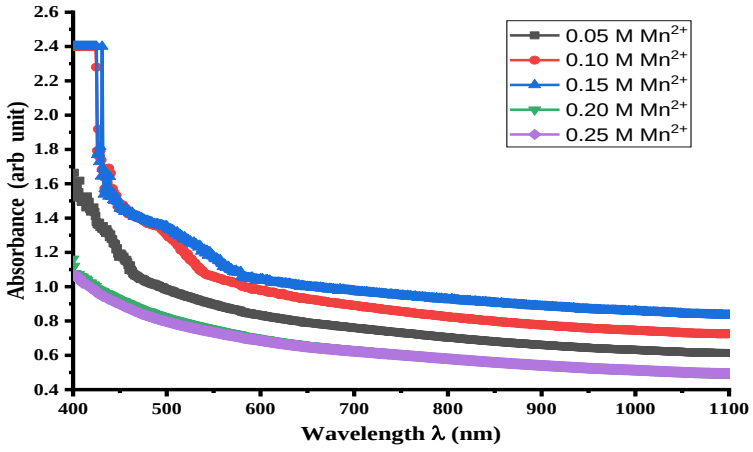

Figure 1: *Graph of Absorbance against wavelength for PbMnS thin films*

The figure showed that the absorbance of the films is high (in the order of 0.6-2.4) but decreases as wavelength increased. The absorbance initially increased as concentration of Mn^{2+} increased from 0.05 M to 0.15 M but decreased to lower values with further increase in Mn^{2+} concentration from 0.20 M to 0.25 M throughout the visible (VIS) and near infra-red (NIR) regions. High absorbance films of this nature have been reported by "[18]" and can be used for window coatings in the high temperature regions of the world such as sub-saharan Africa like Nigeria. This is because the harmful ultraviolet rays can be absorb by the device coated with the films thereby keeping the inside houses cool and subsequently replace the conventional air conditioning that are of high demand in the regions at cheap price.

Transmittance (T) of the deposited thin films of PbMnS was calculated using the relation as given by [19]

$$T = 10^{-A} \quad (1)$$

where A is the measured absorbance of the films.

The plot of the percentage transmittance of the films against wavelength is presented in Figure 2.

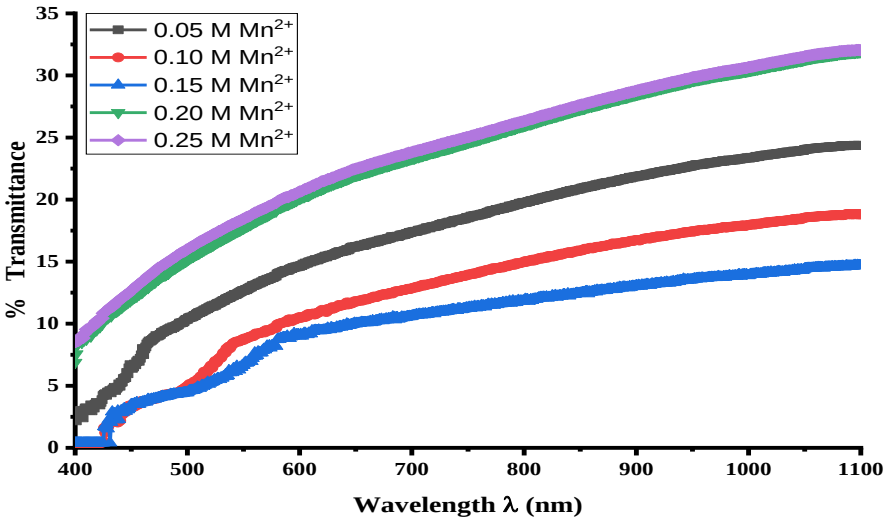

Figure 2: *Graph of % Transmittance against wavelength for PbMnS thin films*

The figure indicated that the transmittance of the films is low (in the range of 0 – 35 %). However, the transmittance increases with an increase in wavelength thereby suggesting higher transmittance values in the near infra-red (NIR) region. The low transmittance coupled with high absorbance of the films position them for photovoltaic solar cell application for solar energy haenessing. Similar results from manganese (Mn), chromium (Cr) and barium (Ba) doped PbS thin films deposited by chemical bath deposition and successive ionic layer adsorption reaction (SILAR) method respectively have been "reported by [20] - [22]".

Figure 3 is the graph showing the plot of absorption coefficient as a function of wavelength for the deposited thin films. The absorption coefficient (α) was calculated using the formula "as given by [23, 24]".

$$\alpha = \frac{1}{t_f}(logT^{-1}) \quad (2)$$

where t_f is the film thickness and T is the transmittance as calculated from equation (1). The figure showed that the films have high absorption coefficient which is in the order of 10^5 cm^{-1}. The absorption coefficient increased as concentration of Mn^{2+} increased up to the concentration of 0.15 M and thereafter decreased to lower values of 1.33 $\times 10^4$ cm^{-1} as concentration of Mn^{2+} increased passed 0.15 M throughout the VIS

and NIR regions. The high absorption coefficient exhibited by the films position them for solar cell application and other optoelectronic applications such as sensor devices.

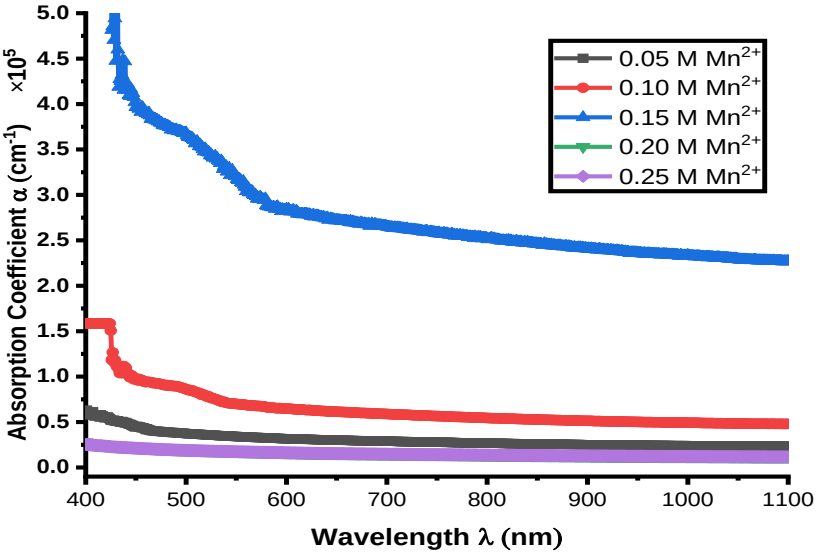

Figure 3: *Graph of Absorption coefficient against wavelength for PbMnS thin films*

The extinction coefficient of the deposited thin films which determines the rate at which light lost in the films was calculated using the relation "given by [25], [26]".

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

where λ is wavelength of light and α is the absorption coefficient of the films.

The plot of the extinction coefficient against wavelength is presented in figure 4. The figure indicates that the extinction coefficient of the films is low and initially increased as concentration of Mn^{2+} increased up to 0.15 M but started to decrease as the concentration of Mn^{2+} increased further throughout the VIS and NIR regions of electromagnetic spectrum. The low value of the extinction coefficient of the films make the films good material for photodetector application as the rate at which light energy is lost in the device made of the films for applications will be very low.

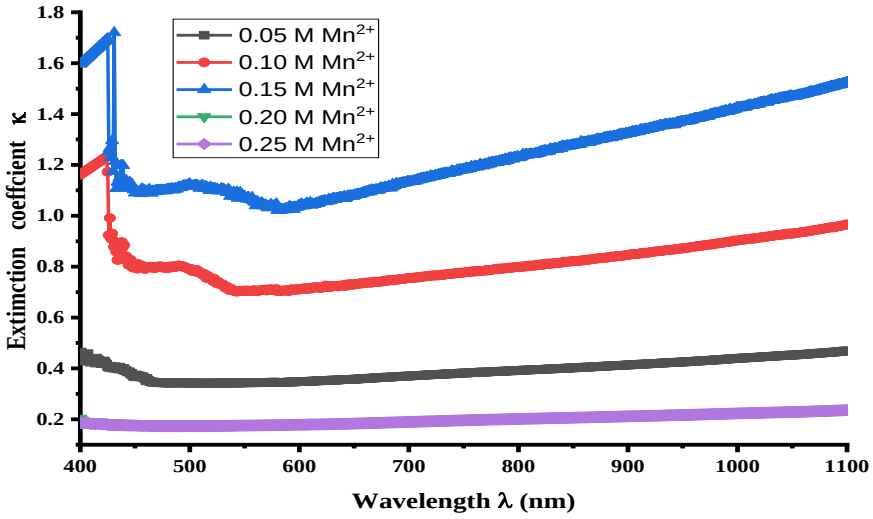

Figure 4: *Graph of Extinction coefficient against wavelength for PbMnS thin films*

The bandgap energy (E_g) of the films was estimated from the plot of Tauc relation "as given by [27] - [29]".

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

Where n is the transition factor which equals to 1/2 for direct band electronic transition, 2 for indirect band electronic transition, 3/2 for direct forbedden transition and 3 for indirect forbedden transition, A is a constant called the band trailing parameter, h is the plank constannt, v is the frequency and α is the absorption coefficient. The plot of $(\alpha h\nu)^2$ against photon energy (hv) (figure 5) was used to determine the direct bandgap energy of the deposited thin films of PbMnS by extrapolating the straight line portion of the photon energy axis at $(\alpha h\nu)^2$ equals to zero.

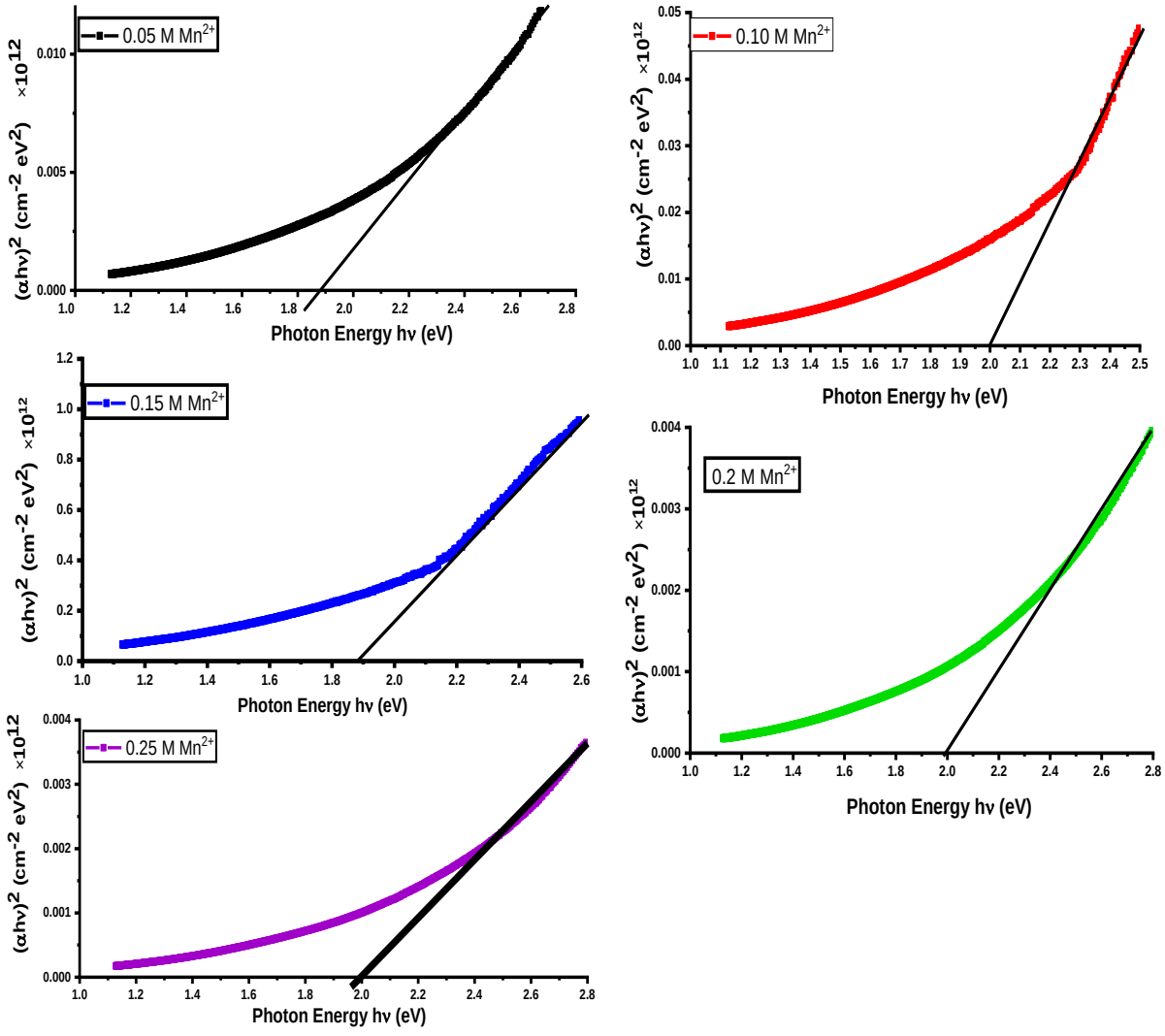

Figure 5: *Graph of $(\alpha h\nu)^2$ against Photon energy for PbMnS thin films*

From the figure, it is observed that the bandgap energy of all the films is 2.0 eV except for the films deposited with the 0.05 M and 0.15 M concentrations of Mn^{2+} whose values decreased to 1.9 eV each. Similar result of bandgap tunning to the values in this range in addition to high absorbance values for the thin films of PbS doped with rare earth element (terbium – Tb) have also been "reported by [30]". This tunned range of bandgap values for the deposited thin films of PbMnS is within the solar spectrum (UV-VIS regions) and are thus ideal materials for solar cell applications for solar energy harnessing and development.

3.2 Electrical Properties of the as deposited thin films of PbMnS

The electrical resistivity (ρ) and conductivity (σ) of the deposited films were obtained from the relation "as given by [31], [32]".

$$\rho = 4.53236 t_f \frac{V}{I} \quad (5)$$

$$\sigma = 1/\rho \quad (6)$$

Where t_f is the film thickness, V is the voltage drop measured across the inner probes and I is the current applied at the outer probes. The plot of electrical properties (electrical resistivity and conductivity) of the films against concentration of Mn^{2+} is shown in figure 6.

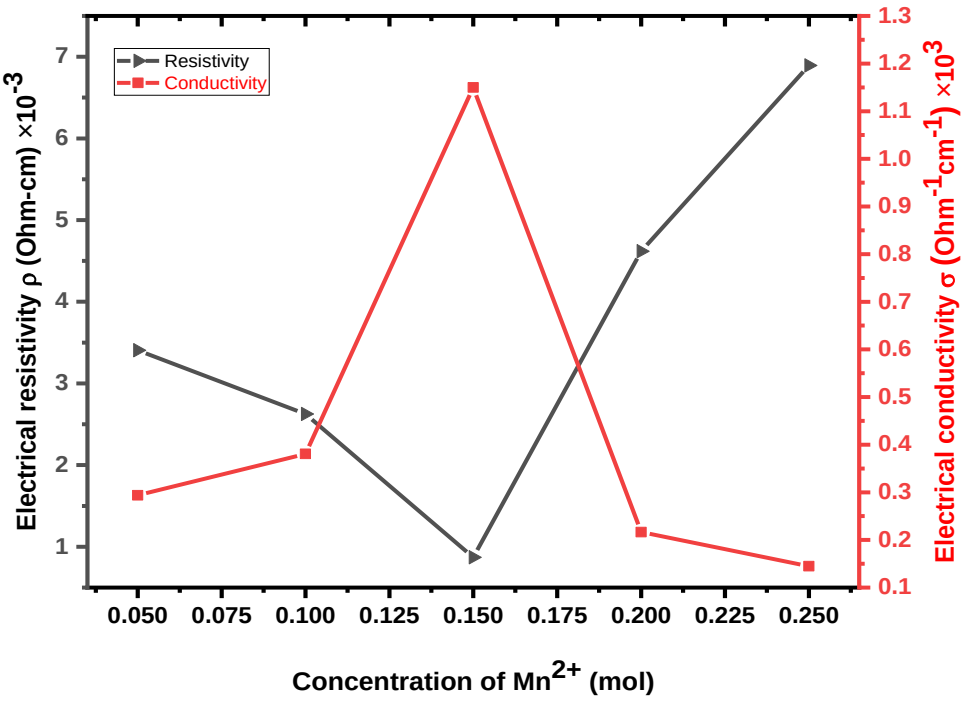

Figure 6: *Plot of Electrical properties against concentration of Mn^{2+} for the PbMnS thin films*

The figure showed that the resistivity of the films decreased to a minimum value of 1.0×10^{-3} ohm-cm at the film deposited with Mn^{2+} concentration of 0.15 M then increased to maximum value of 7.0×10^{-3} ohm-cm as concentration of Mn^{2+} increased further to 0.25 M. The electrical conductivity of the films increase to maximum value of 1.2×10^{3} $ohm^{-1}cm^{-1}$ at the film deposited with concentration of 0.15 M and thereafter decreased as concentration of Mn^{2+} increased. From the figure, it can be seen that the values of the electrical resistivity and conductivity of the films are within the range of values for semiconductor materials. The plot of electrical resistivity and conductivity of the films against film thickness presented in figure 7 showed that the electrical resistivity of the films is minimum at film thickness of 262.5 nm and then increased to higher value of 7.0×10^{-3} ohm-cm as film thickness increased. The electrical conductivity of the films increased to maximum value of 1.2×10^{3} $ohm^{-1}cm^{-1}$ as film thickness increased to a value of 262.5 nm then decreased as thickness increased further. The range of value of the thickness of the deposited thin films of PbMnS is 150 to 425 nm. The range of values of the electrical properties for the films are in the range for semiconductor materials, hence confirming the semiconducting nature of the films for device applications.

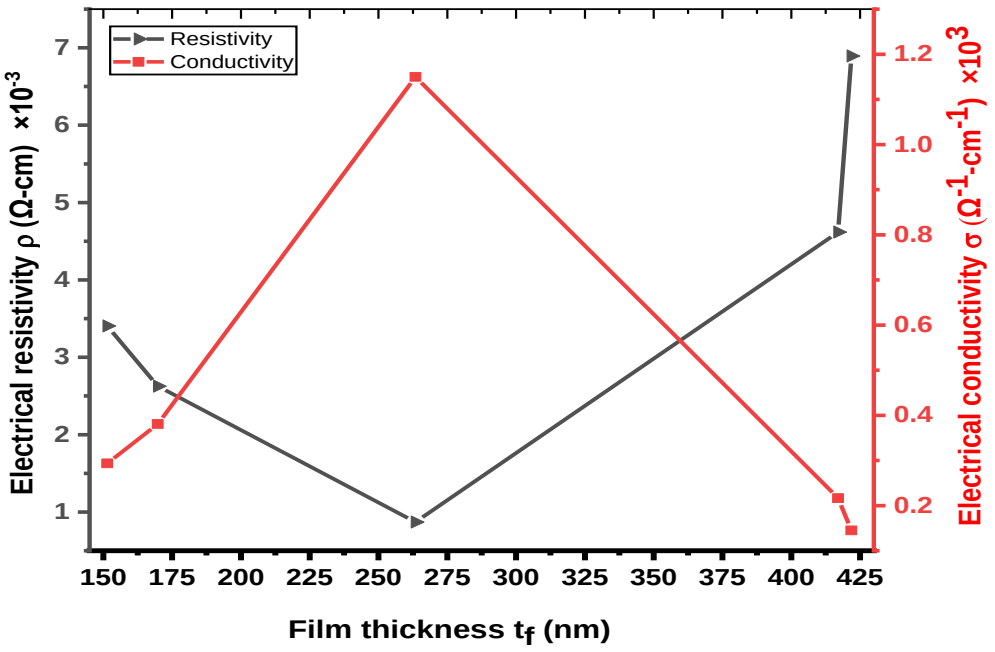

Figure 7: *Plot of Electrical properties against film thickness for the PbMnS thin films*

3.3 Structural Properties of the as Deposited Thin Films of PbMnS

The structural properties of the films were studied using X-ray diffraction (XRD) method. Figure 8 is the XRD pattern for the thin films of PbMnS deposited with different concentrations of Mn^{2+} (0.05 M, 0.10 M, 0.15 M, 0.20 M and 0.25 M).

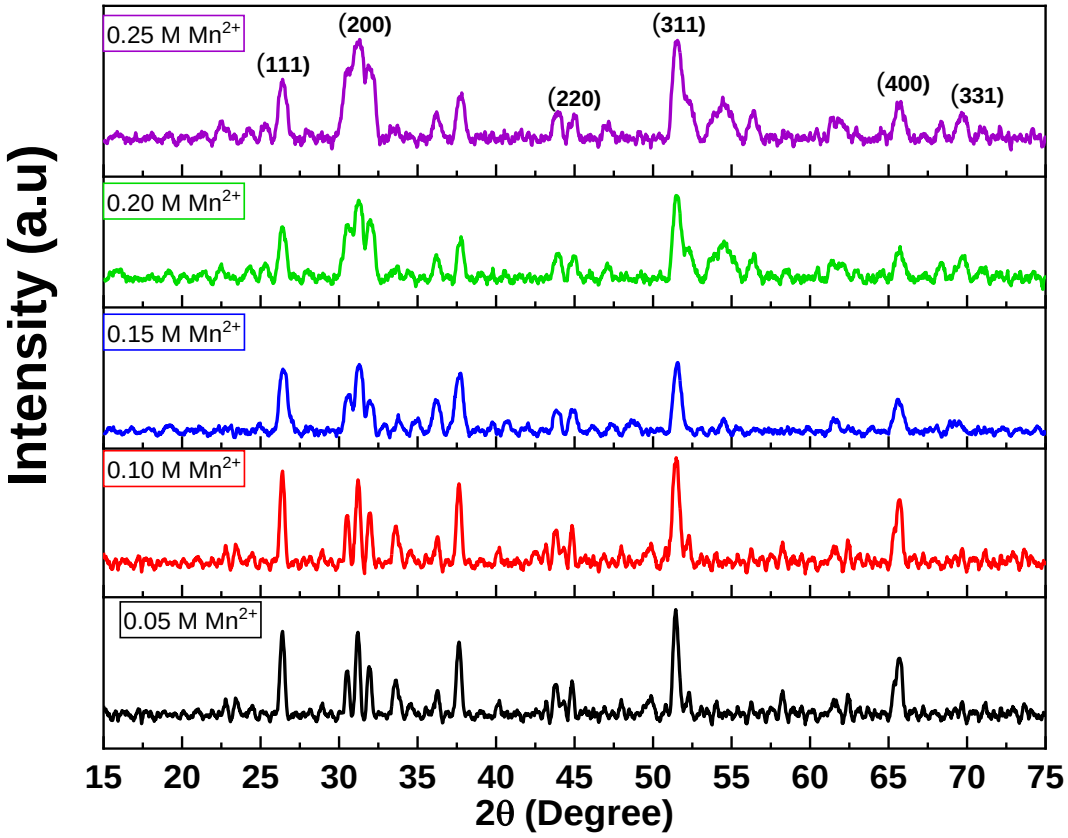

Figure 8: *XRD patterns of the deposited PbMnS thin films*

From the figure, it is observed that the deposited thin films of PbMnS are crystalline. However, the crystalline nature decreases with increase in concentration of Mn^{2+} as the peaks of the XRD pattern became broadened at the higher concentration of Mn^{2+}. The XRD pattern of the films showed preferential orientation at two theta angles 26.40^{o}, 31.30^{o}, 44.20^{o}, 51.43^{o}, 54.56^{o}, 65.71^{o} and 69.81^{o}; which are indexed to the crystal planes (111), (200), (220), (311), (222), (400) and (331) respectively. The additional peaks that emerged in the XRD pattern is evidencing the presence of manganese in the crystal of the material. The films are cubic with the space group Fm-3m. These values match well with standard data (JCPDS No: 00-002-1431). The average crystallite size, dislocation density and micro strain of the films calculated using the Dybe-Scherer and Williamson-Smallman relation "as given by [33] - [37]".

$$D = \frac{0.9\lambda}{\beta Cos\theta} \tag{7}$$

$$\delta = \frac{1}{D^2} \tag{8}$$

$$\varepsilon = \frac{\beta}{4tan\theta} \tag{9}$$

Where k is the shape factor, λ is the x-ray wavelength, **β** is the full weight at half maximum (FWHM) and θ is the Bragg's angle in radian are; 5.05 nm, 1442.38×10^{-3} lines/(nm)^2 and 121.36×10^{-3} respectively. The silmilar results of thin films of PbS doped with Mn with low crystallite size close to this work have been "reported by [38]".

3.4 Morphological Properties of the as Deposited (PbMnS) Thin Films

Figure 9 is the scanning electron microscopy (SEM) micrographs of the deposited PbMnS thin films. The figure showed that the films of PbMnS prepared with 0.05 M Mn^{2+} has uniform morphology that are of good quality and cover the entire glass substrate very well.

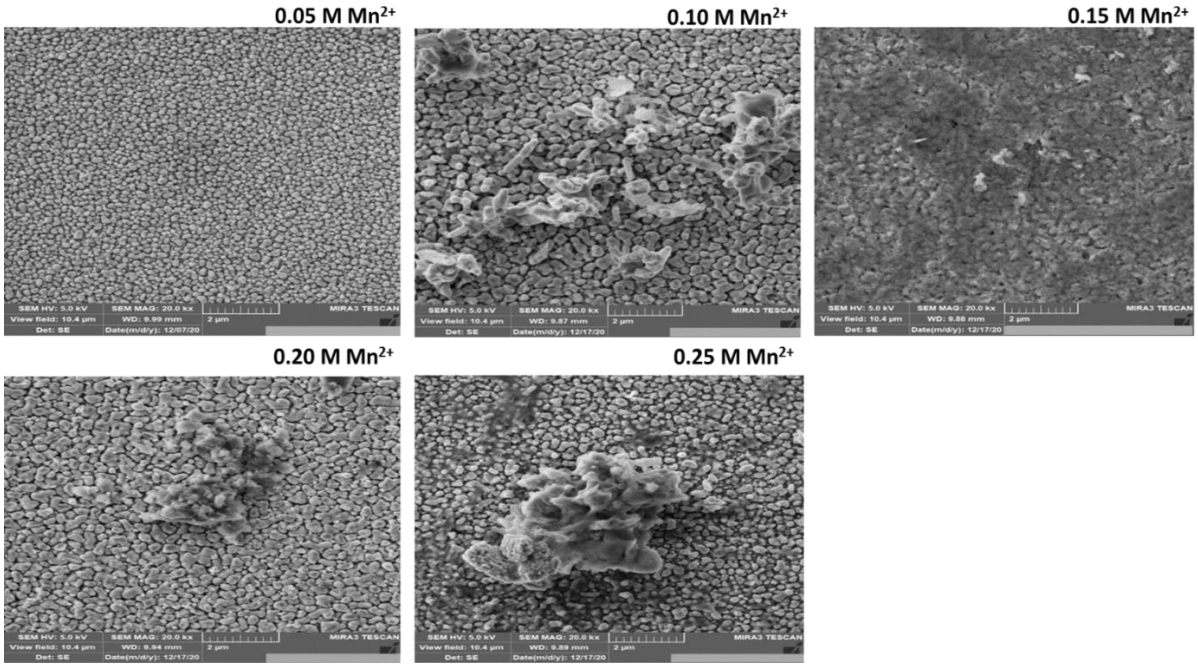

Figure 9: *SEM micrographs of the deposited PbMnS thin film*

The morphology composed of micro rod like particles that are irregular in shape as well as some smaller particles that are spherical in shapes and sizes. In the other hand the morphology of the films deposited with 0.10 M Mn^{2+} is also uniformly distributed but has particle sizes that are entirely irregular in shapes.

The morphology of the films deposited with 0.15 M Mn^{2+} is uniformly distributed on the surface of substrate and composed of particles that are irregular and spherical in shapes. The film deposited with 0.20 M Mn^{2+} is also uniformly distributed on the surface of the glass substrate. The particle sizes also consist of mixture of spherical and irregular shape but has a fibrous-like structure that is formed on top. In the other hand, the SEM micrographs of the thin film deposited with 0.25 M Mn^{2+} show that the surface of the film is highly homogeneous in nature and particle sizes are uniformly formed on the substrate. It can be seen that the majority of the particles are spherical in shape and are of good quality.

4 Conclusion

The analysis of the results of the characterisation of thin films of PbMnS deposited using an electrodeposition method for possible device applications has been carried out. The results showed that optical properties such as absorbance and absorption-coefficient of the films are high while the extinction coefficient is low in both the VIS and NIR regions. The percentage transmittance is low in the VIS region but increased towards the NIR region. The bandgap energy of the films was found to be in the range of 1.9 eV to 2.0 eV. The optical properties of the films investigated are found to be dependent on the concentration of Mn^{2+} as well as wavelength dependent. The films absorb high in the VIS region compare to NIR region of electromagnetic spectrum, consequently transmit is higher in the NIR. The results of the electrical characterization showed that the values of electrical properties (electrical resistivity and conductivity) of the films are within the range of values for semiconductor materials and equally dependent on the concentration of Mn^{2+} and film thickness. The minimum value of electrical resistivity and consequently the maximum electrical conductivity of the films were obtained when the films are deposited with the Mn^{2+} concentration of 0.15 M. The electrical resistivity of the films is found to increase as film thickness increased. The range of values of the electrical conductivity confirmed the semiconcting nature of the deposited thin films for semiconductor device applications. The XRD analysis revealed that the deposited thin films of PbMnS have cubic structure and are generally crystalline in nature but the crystallinity declined with increase in the concentration of Mn^{2+}. The SEM morphology show that the surfaces of the films are highly homogeneous and particle sizes are uniform but the majority of the particles are spherical in shape. These properties exhibited by the deposited thin films of PbMnS make them good materials for many opto-electronic and electronic applications such as in solar cells, light emitting diode (LED), photodetectors etc. In view of these observed properties of the deposited thin films, it is recommended that for optimal result to be achieved the films of this nature should be deposited with concentration of Mn^{2+} within 0.15 M region and film thickness should be within the range 250 nm to 300 nm.

5 Declarations

5.1 Limitations of the Study

Lack of research and development grants remain the potential treat to the study.

5.2 Acknowledgement

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5.3 Competing Interests

The authors declared that there is no conflict of interest that existed in the publication of the work.

How to Cite this Article:

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