

# Effects of Ligand on the Optical Properties of Manganese Sulphide Thin Films Prepared Using Chemical Bath Deposition (CBD) Technique

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## Abstract

Thin films of Manganese sulphide semiconductor material were successfully deposited on glass substrate using Chemical Bath Deposition (CBD) technique. The Films were optically characterized using PYE UNICAM SP8-100 Double Beam Spectrophotometer with uncoated glass substrate as a reference frame. The effects of various concentrations of ligand (TEA) on the optical properties of the deposited films were studied. The result shows that the absorbance was observed to decrease towards the infra-red region of electromagnetic spectrum with a value range of 17.5% -72.7%, and the film deposited at 4ml ligand concentration having a highest peak value of 72.7% at 380nm. The transmittance property of the films was found to be moderate and increases towards the infra-red region. The deposited films exhibited poor reflectance, extinction coefficient, and imaginary part dielectric function properties with film deposited at 2ml concentration of ligand possessing high optical conductivity value of  $1.08 \times 10^{14} \text{S}^{-1}$ . Refractive index and real part dielectric function of the films were observed to be also high with band gap energy of 2.80eV- 3.15eV. All these desirable properties made the semiconductor to be a good candidate for applications in photovoltaic devices.

**Keywords:** Ligand, semiconductor, electromagnetic spectrum, transmittance, reflectance, optical conductivity, and spectrophotometer.

## 1. Introduction

The discovery of semiconductor materials has revolutionized the opto-electronic industries. There is intense research by Scientists all over the world to discover semiconductor materials with desirable optical, electrical, structural, and electronic properties which will help solve societal problems like power supply, pollution in the world and at the same time be environmentally friendly. This has partly been achieved with the introduction of photovoltaic systems and optoelectronic devices. Manganese Sulphide thin film is a semiconductor material that belongs to II-VI compound which is increasingly attracting the attention of researchers due to its wide applications in such devices as sensors, optical mass memories, photoconductors, lithium sulfur batteries, electroluminescent displays, solar cell as well as blue light emitters [1-5]. There are different means of depositing thin films of manganese sulphide on a particular substrate. They include MBE [6], Solid-State Reaction [7], RF-sputtering [8] and Chemical Bath Deposition Technique [9]. It has also been discovered that the optical properties of thin films are dependent on bath temperature, nature of substrate, concentration of ligands, nature of salt and pH-value [10]. In this work, the effects of ligand (TEA) on the optical properties of MnS thin film were studied.

## 2. Experimental Details

Thin films of Manganese Sulphide were deposited on pre-cleaned glass substrates from the aqueous solution of Manganese (II) Chloride tetra hydrate, Ammonia solution, thiourea and in which triethanolamine (TEA) was employed as a ligand. The 50ml bath used contains in this order 5ml of 0.1M Manganese (II) Chloride Tetra Hydrate, 2ml of TEA, 5ml of Ammonia solution, 5ml of 0.1M thiourea and 30ml of distilled water. The substrate was later clamped vertically into the bath after proper stirring of the solution was done in order to achieve homogeneous state of the solution. And this particular bath was label bath 1 and allowed to stand for 12hours after which the substrate was removed from the bath, rinsed with distilled water and allowed to dry in open air. Other baths (2, 3, 4) preparation follows the same procedure at constant time of 12hours but with varying concentrations of the ligand and other parameters kept constant as shown in table 1. below.

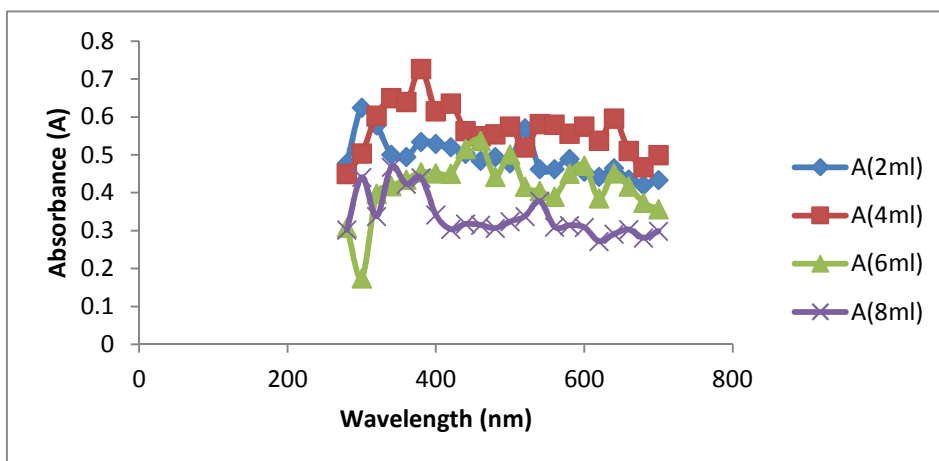
Table1. Bath parameters with varying concentration of ligand

Solution	Volume (ml)			
	Bath 1	Bath 2	Bath 3	Bath 4
MnCl <sub>2</sub> .4H <sub>2</sub> O	5	5	5	5
TEA	2	4	6	8
NH <sub>3</sub>	5	5	5	5
Thiourea	5	5	5	5
Distilled water	33	31	29	27
Total	50	50	50	50

After the deposition of the films, they were optically characterized using a PYE-UNICAM SP8 Double Beam Spectrophotometer to obtain the absorbance data in the wavelength range of 280nm- 700nm from which other optical properties of the films were determined.

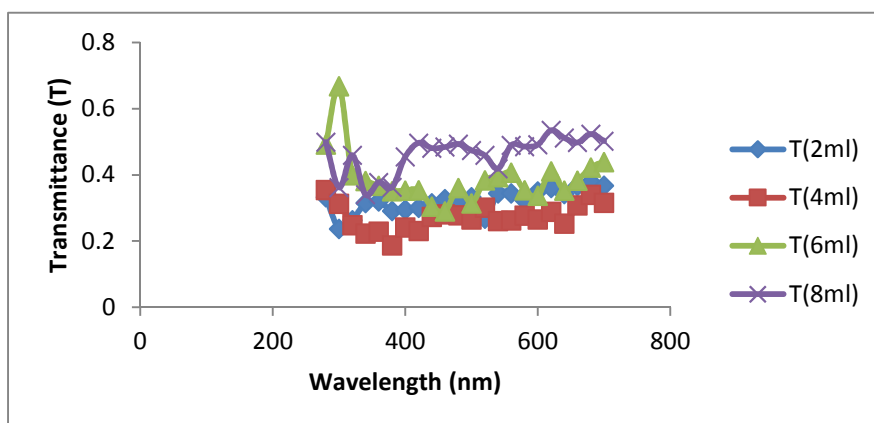
### 3. Results And Discussion

Some of the optical properties studied include; absorbance, transmittance, reflectance, refractive index, optical conductivity, extinction coefficient, Real and Imaginary parts of dielectric function and band gap energy as solid state property. Figure 1 shows the effect of ligand on the absorbance property of the film with respect to incident radiation. The absorbance spectra show that ligand has effect on the deposited films as the film deposited at 4m concentration has the highest peak of 0.727 at 380nm. This suggests that at this concentration of ligand there is uniform and homogenous reaction between  $Mn^{2+}$  and  $S^{2-}$  in the bath. It also shows that as the concentration of ligand increases the absorbance of the films decreases towards the infra-red region of electromagnetic spectrum as exhibited by films at 8ml concentration.



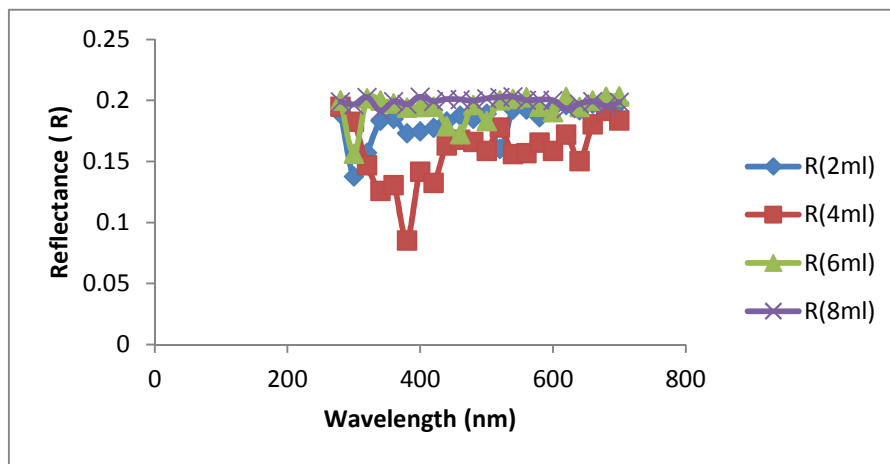
**Figure 1: Plot of Absorbance against Wavelength for the films deposited at different concentration of the ligand**

Figure 2 shows the transmittance spectra of the films to incident radiation. It shows that the film deposited at 6ml ligand concentration has better transmittance property than the rest of the films especial towards the infra-red region of electromagnetic spectrum. The film deposited at 6ml concentration exhibited a transmittance peak of 0.66634 at 300nm. From figure 2 it could be fathom that as the concentrations of the ligand increases the transmittance also increases.



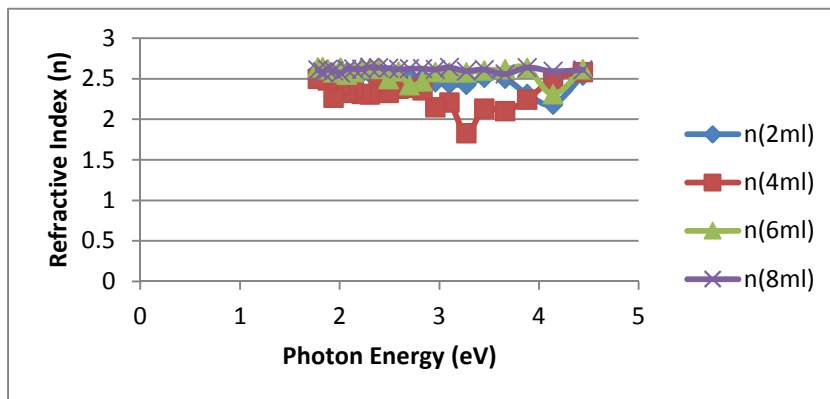
**Figure 2: The transmittance spectra of the deposited films at different concentrations of the ligand**

The plot of reflectance as a function of wavelength is illustrated in figure 3. The figure shows that the films deposited at 6ml and 8ml ligand concentrations have better reflectance properties than the rest of the films. From figure 3 it could be also seen that the reflectance of the films to incident radiation was generally low with the films deposited at 6ml and 8ml having a constant value of 0.202 at 320nm.



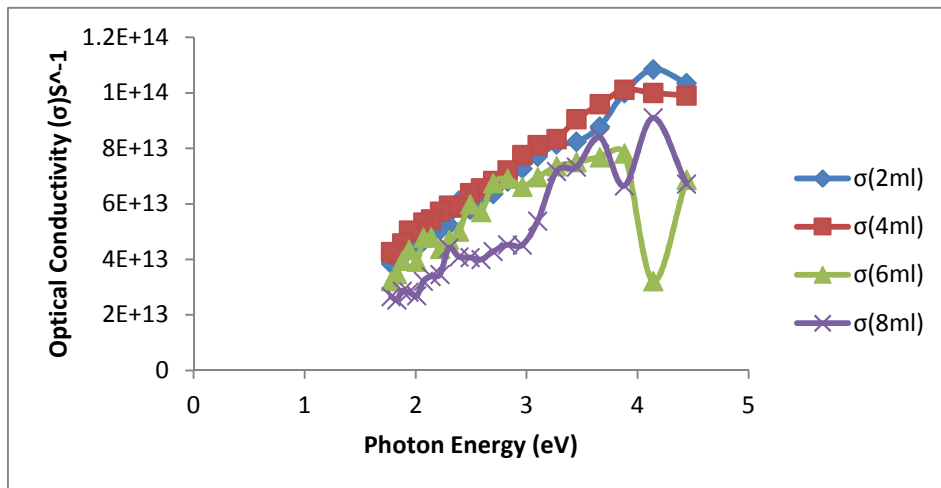
**Figure 3: Plot of Reflectance as a function of Wavelength for the deposited Films at different concentrations of ligand.**

The variation of refractive index with the photon energy is shown in figure 4. From the figure it can be deduced that almost all the films possess a high refractive index value of 2.50- 2.60 with the exception of the film deposited at 4ml concentration which exhibited a lowest value of 1.83 at 3.27eV



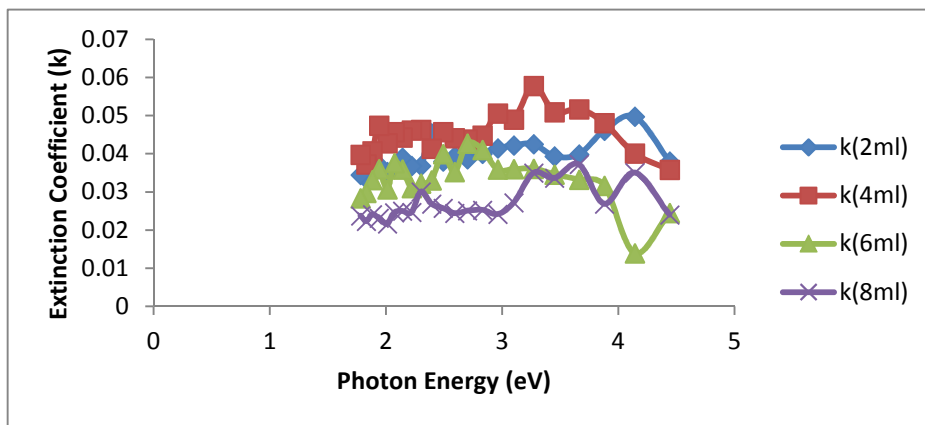
**Figure 4: The Variation of Refractive with the Photon Energy for all the deposited films at different ligand concentrations**

Figure 5 shows the plot of optical conductivity of the films at different ligand concentrations. The figures shows that as the optical conductivity increases the photon energy increases with the film deposited at 4ml ligand concentration having a better conductivity performance than the rest of the films. However, it was also observed that films exhibited high optical conductivity values with the highest being  $1.04 \times 10^{14} \text{S}^{-1}$  at 4.44eV for film deposited at 2ml ligand concentration.



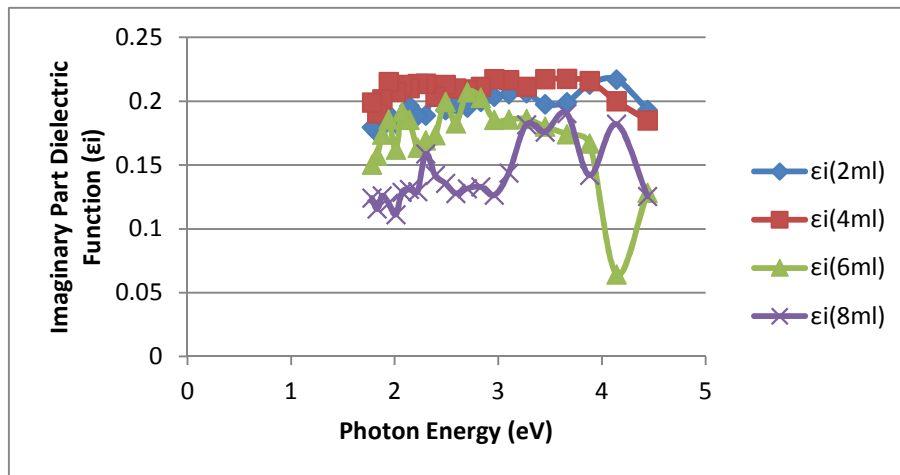
**Figure 5: Plot of optical conductivity as a function of Photon Energy for the films at different ligand concentrations.**

The variation of extinction coefficient with the photon energy is schematically portrayed in figure 6. From the figure it could be seen that the extinction coefficient of the deposited films was generally low with the film deposited at 4ml concentration of ligand having better extinction coefficient property than the rest of the films.



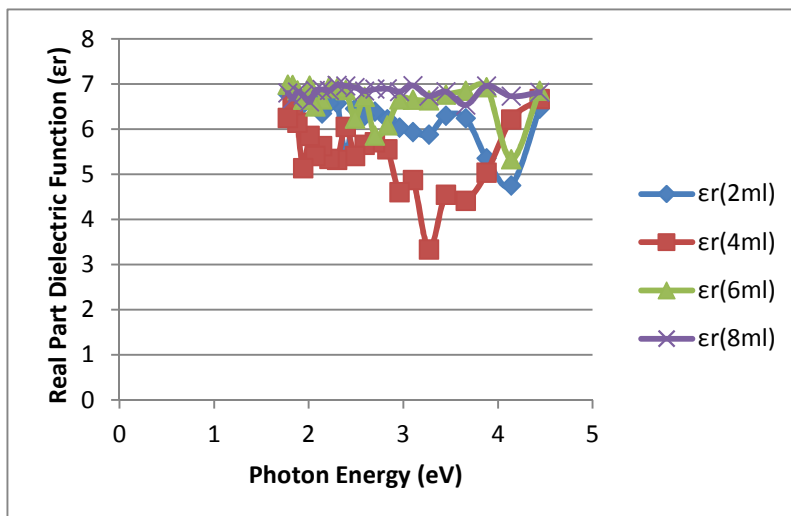
**Figure 6: The variation of Extinction coefficient with Photon Energy at different ligand concentrations.**

Figure 7 is the spectra of imaginary part dielectric function of the films at different ligand concentrations. The as-deposited films were generally found to exhibit low imaginary part dielectric function values with the films deposited at 2ml and 4ml ligand concentrations having the highest values of 0.2170 and 0.2174 respectively. It could also be seen that as the ligand concentrations increases the imaginary part dielectric function decreases.



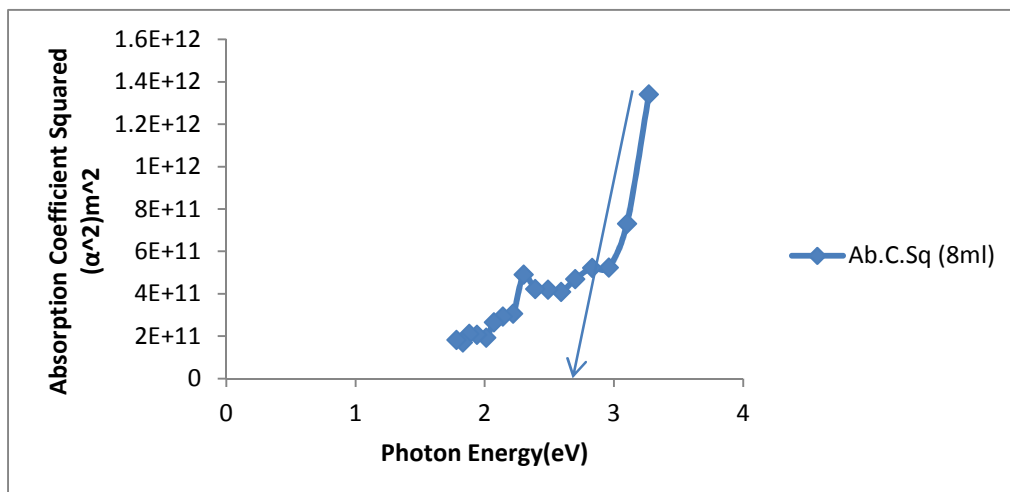
**Figure 7: The imaginary part dielectric function of the deposited films at Different ligand concentrations.**

Figure 8 show the spectra of the plot of real part dielectric function of the films at different ligand concentrations. The films were observed to exhibit high real part dielectric function values with the films deposited at 6ml and 8ml ligand concentrations having the highest values of 6.9868 and 6.9769 respectively. The illustration also shows that as the concentration of the ligand increases the real part dielectric function increases but with a different performance for film deposited at 4ml ligand concentration.

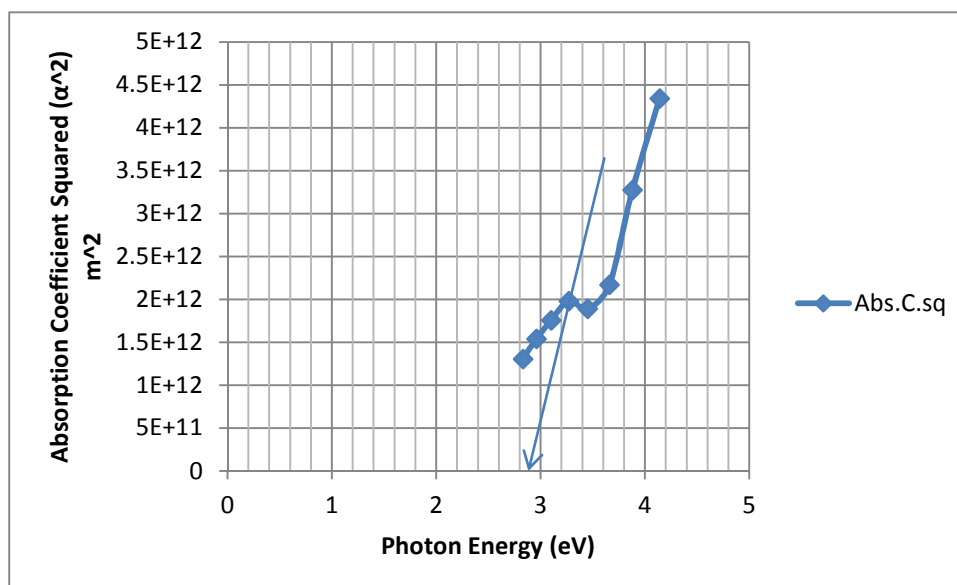


**Figure 8: Spectra of Real part Dielectric function of the films at different ligand concentrations.**

The band gap energy of the deposited films was obtained from the straight line of the plot of absorption coefficient squared against photon energy extrapolated to meet the photon energy axis. The values were found to be 2.80eV and 3.15eV for films at 8ml and 2ml ligand concentrations respectively. This shows that as the concentration of ligand increases the band gap energy decreases. This is as illustrated in figures 9 and 10 respectively.



**Figure 9: The Plot of Absorption coefficient squared against Photon Energy for the film deposited at 8ml concentration of ligand.**



**Figure 10: Plot of Absorption Coefficient Squared against Photon Energy for the film deposited at 2ml ligand concentration**

#### 4. Conclusion

Thin films of Manganese Sulphide were successfully deposited on glass substrate using Chemical Bath Deposition Technique. The effects of ligand on the optical properties of the deposited films were studied and the study shows that the concentration of the ligand in the bath has observable effects on the optical properties of the film. As the concentration of the ligand (TEA) increases, the absorbance, the band gap energy, imaginary part dielectric function decreases whereas as the concentration of the ligand increases, the transmittance, optical conductivity, real part dielectric function decreases. All these observations can be employed in obtaining film with desirable properties for application in opto-electronic devices.

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