Optical and Solid State Properties of Manganese Sulphide (MnS) Thin Film, Theoretical Analysis

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ABSTRACT

Analysis of the optical and Solid State properties of MgS thin film using theoretical approach of beam propagation technique in which a scalar wave is propagated through the material thin film deposited on a substrate with the assumption that the dielectric medium has homogenous reference dielectric constant term, ε_{ref} and a perturbed dielectric term, $\Delta\varepsilon_p(r)$ representing the deposited thin film medium is presented in this work. These two terms, constituted arbitrary complex dielectric function that describes dielectric perturbation imposed by the medium of for the system. This is substituted into a defined scalar wave equation in which the appropriate Green's Function was defined on it and solved using series solution technique in conjunction with Born approximation method in order to obtain a model equation of wave propagating through the thin film. This was used in computing the propagated field for different input regions of field wavelength such as ultraviolet, visible and infrared region respectively during which the influence of the dielectric constants of the thin film on the propagating field were considered. The results obtained from the computed field were used in turn to compute the band gaps, solid state and optical properties of the thin film such as reflectance, Transmittance and reflectance. The electrical and optical conductance was also computed.

1. INTRODUCTION

Recently it has been discovered that materials known as dilute magnetic semiconductors (DMS) have become a focus of intense research activity as they exhibit an interesting combination of magnetism and semiconductivity. MnS is such a DMS with (band gap energy, Eg, 3.1 eV) having potential use in solar cell applications as a window/buffer material as reported. The cubic α-phase of MnS appears to be stable above room temperature. The β-phase and ν -phase of MnS can be prepared at low temperature, but they transform to the o-phase above $200^{o}C$. The β-phase is retained at all the temperatures DMS material [1,2] Deposition of MnS is based on the slow release of Mn21and S22 ions in a solution which then condenses onto the substrate. For this, Mn salt with a suitable complexing agent as a Mn^{+2} and thioacetamide as $S^{-3}$are used in an aqueous medium just as usual. The depositions were carried out onto commercial glass slides,-uorine doped tin

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oxide (FTO) coated glass, and glassy carbon substrates. The glass and FTO coated glass substrates were cleaned with detergent dried and degreased with ethanol in an ultrasonic cleaner and kept immersed in distilled water prior to the deposition. The glassy carbon substrates were boiled in acetone. Chemicals were used as received; Mn acetate (Mn $(CH_3COO)_2$), (Alfa), 80% hydrazinehydrate (Riedel-de-Haen), thioacetamide (E. Merck),triethanolamine (TEA), (Alfa) and NH4Cl (Alfa). The following solutions were freshly prepared in distilled water prior to the deposition of MnS films; 1.0 M Mn acetate, 1.0 thioacetamide, and 1.4MNH4Cl. TEA and hydrazinehydrate solutions were used .Similarly Anuar and Ho who deposited same thin film using the same technique, but this time using ITO glass substrate reported the energy band gap to be 3.00eV.[3,4]

Based on the recent interest to use theoretical analysis on the study of thin films, the behavior of electromagnetic wave propagation through material thin film in relation to its solid state property had been veraciously studied in term of the influence of dielectric constants and in terms of assessment of beam propagation.[5,6,7]For instant, we have looked at the propagation of electromagnetic field through a conducting surface [8] where the behaviour of wave propagated through such material coupled with the influence of the dielectric function of the medium such on such material was analyzed. The effect of variation of refractive index of FeS2 had also been carried out theoretically for the purpose of getting a clear understanding of the how variation of refractive index of the tin film effects its application in optoelectronic and solar cell [9] From the study, a close look on the concept made it clear to recognize the importance of the effect of the refractive index of the medium in the reality of the two velocity components that normally give rise to phase and group refractive indices as considered study of wave propagation[10,11,12]

More complicated work had been embarked upon on the study of wave propagation through a modeled thin with dielectric perturbation in which W.K.B approximation in conjunction with with the application of numerical technique [This had gone a long way to reveal the efficacy of theoretical approach in understanding the mechanism on of wave propagating through thin film material due to the flexibility of green's function that facilitates the iterative process involved in the computation technique.[13,14,15]

Based on high cost of experimental analysis involved in the characterization of the grown thin films and sometimes non-availability of the machine especially in some parts of our third world countries because of their cost, we based this work on the use of theoretical concept to study the optical properties of manganese sulfide thin film in order to circumvents the use of experimental analysis and characterization. Our method here involves propagating an input field over a small distant representing the thin film thickness through the thin film medium using scalar wave equation with Born approximation method with which iteration technique is applied during the solution. This process of the computation involved iterating the propagating wave over and over through the propagation distant using Green's function technique, in which we derived equation $\psi k\,(z)$ representing the propagated wave in order to determine the absorption. Characteristics within the ultraviolet, visible and near infrared wavelength regions of electromagnetic wave spectrum as it traversed through the film medium. The computed the values were in turn used to obtain the band gap and some other solid state and optical properties of the MnS thin film.

2. THEORETICAL PROCEDURE

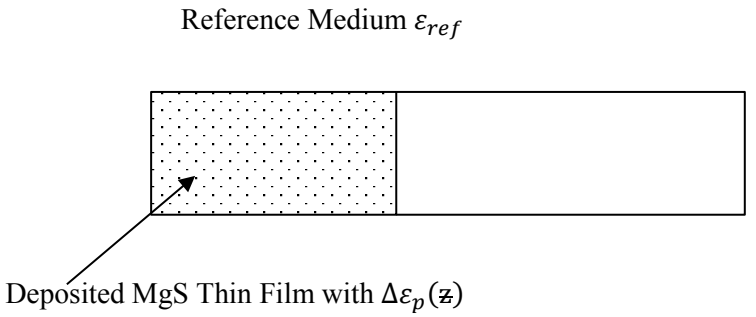

Fig.1; A model of MnS thin film deposited on Glass slide

General wave equation $$\nabla^2\psi(z) = \frac{1}{c^2}\frac{\partial^2\psi(z)}{\partial t^2} \tag{1}$$

$$\nabla^2\psi(z) + \omega^2\mu_o\varepsilon_o\psi(z) = 0 \tag{2}$$

From which we obtain the Helmholtz form of it as in equation (2) using separation of variable technique which is being used as of the method for solving wave propagating through a medium in which a dielectric function as defined in our model in fig.1 which shown in equation (3)

$$\varepsilon(z) = \varepsilon_{ref} + \Delta\varepsilon(z) \tag{3}$$

consisting of two parts is imposed on wave equation. The dielectric function consist of perturbed part, $\Delta\varepsilon(z)$ representing the part where the thin film is deposited and the reference section were no film is deposited, ε_{ref}. Substituting the dielectric function in equation (2), we obtain

$$\nabla^2\psi(z) + \mu_0\varepsilon_0\omega^2\psi(z) = -V(z) \tag{4}$$

where

$$V(z) = \gamma^2\varepsilon(z) \tag{5}$$

Green's function technique is used to obtain an expression for wave propagating through the film as

$$\psi(z) = \int_0^z G(z,z')V(z')\psi(z') \tag{6}$$

The Integral

$$\psi(z) = \int_0^z G(z,z')V(z')\psi(z') \tag{7}$$

This when critically considered is a homogeneous Volterra equation of second type with the kernel

$$k(z,z') = G(z,z')V(z') \tag{8}$$

In this equation, the Neumann series method is not applicable to this type of equation; hence, we apply Born approximation method that enables us to rewrite the equation as

$$\psi(z,z') \equiv I(z,z') = \int_o^{z'} \Phi(z,x)V(x)\psi(z,x)dx \tag{9}$$

However according to Born approximation procedure, we replace the unknown function $\psi(z,x)$ in integral with a known function say $\tilde{\Phi}(z,x)$ and use it to get an approximate solution of $\psi(z,z')$.
That is

$$\psi(z,z') = I(z,z') = \int_o^{z'} \Phi(z,x)V(x)\tilde{\Phi}(x) \tag{10}$$

The sign on $\Phi(z,x)$ is signify an indication of possible phase difference between the in-coming wave and the out-going wave. Thus if we use the Green's function as in the case of this work, we write

$$G(z,z') = \Phi(z,z') = \frac{2}{z}\sum_{n=1}^{\infty} \frac{\sin n\pi \, z'/z}{\gamma^2 - \dfrac{n^2\pi^2}{z^2}} \tag{11}$$

This results in the solution as given below,

$$\psi(z,z') = I(z,z') = -\sum_{n=1}^{\infty} \frac{\gamma^2}{\gamma^2 - \frac{n^{2\pi^2}}{z^2}} \left[\frac{(\varepsilon' + cz')\cos\left(\frac{n\pi}{z} + \frac{2\pi}{\lambda}\right)z'}{\frac{n\pi}{z} + \frac{2\pi}{\lambda}} + \frac{c}{\left(\frac{n\pi}{z} + \frac{2\pi}{\lambda}\right)} \right] \tag{12}$$

$\psi(\lambda)$ vs λ, when z and z' are fixed

In all use we considered in analysis the wavelength within λ= 250nm to 1200nm. From the equation, it is obvious that ($\psi(z)$ tends to 0 as the dielectric constant $\varepsilon' \to \infty$, therefore for fixed values of other parameters, the resultant solution can be approximated to any number of terms as may be required in relation to wave propagation terms.

This is used to obtain the absorption co-efficient using

$$I = I_o \exp \alpha z$$
$$\alpha = \frac{1}{z} In\left(\frac{1}{T}\right) \tag{13}$$

known as Lamber-Beer- Bouguer law [16].

The absorption coefficient is used in equation

$$(\alpha h\nu)^2 = A\left[h\nu - E_g\right] \text{[17]} \tag{13}$$

The band gap, spectral reflectance, transmittance absorbance, optical and electrical conductance were computed.

3. RESULT/DISCUSSION

The analytical solution was carried out from the result of the derivation based on the integral equation (6) as given in equation (12)[18] In computation and the analysis, the wavefunction was considered with respect to the variation of wavelength when z and z/ were fixed as t it was obvious from the analysis that $\psi(z) \to 0$ as the dielectric property of the film material, $\varepsilon' \to 0$. Under this condition, we fixed the values of other parameters in order to enables us approximate the result of wave propagating through the film material to a reasonable number of terms as required in the analysis. The efficacy of the assessment of the result obtained was based on analysis on the validated absorption co-efficient derived from Lambert-Beer- Bouguer law [16, 17] using our value. The energy band gap as shown in fig. 6 was obtained from extrapolation of the curves to intercept the wavelength axis

respectively as in figure 6. Each of this value was used correspondingly to computed the band gap accordingly as shown in Table 1.

Table 1: The band gap of magnesium sulphide thin film.

$\lambda(nm)$	**Band gap (eV)**	**Average Band Gap (eV) from computation**	**Band gap (eV) from experimental report**
MnS	250nm – 2.77 500nm – 2.33 750nm – 2.24 1000nm – 2.19	2.68	3.1– 3.40

Comparatively, the calculated band gap according to Lokhande is 3.02eV [19] in their experimental while some other researcher in their work obtained 3.20eV as their band gap which was also in consonance with that reported by Pathan and Lokhande [20] using CBD and SILAR of method of deposition respectively

The absorbance within the optical and near infrared appears linear with some portion showing negative value in the visible region as in fig.1 and 2. As observed in fig. 3 and fig.4, the transmittance exhibited the same trend in value [0.0 - 1.5 within 3.0eV to 6.0eV for all the three regions considered in the computation. From fig.4, it is seen that the reflectance appears negative all the wavelengths. The optical and electrical conductance of the film were also obtained and were found to be very high which is an indication of the low and in some cases negative values of the absorbance within the UV region coupled with the negative value of the reflectance for all the windows.

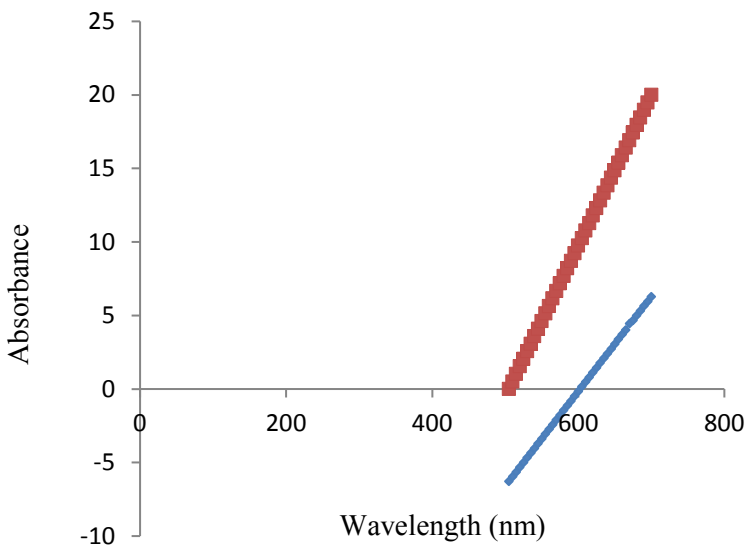

Fig 2; Absorbance of MnS vs Wavelength, λ (nm) for 2500nm and 500nm

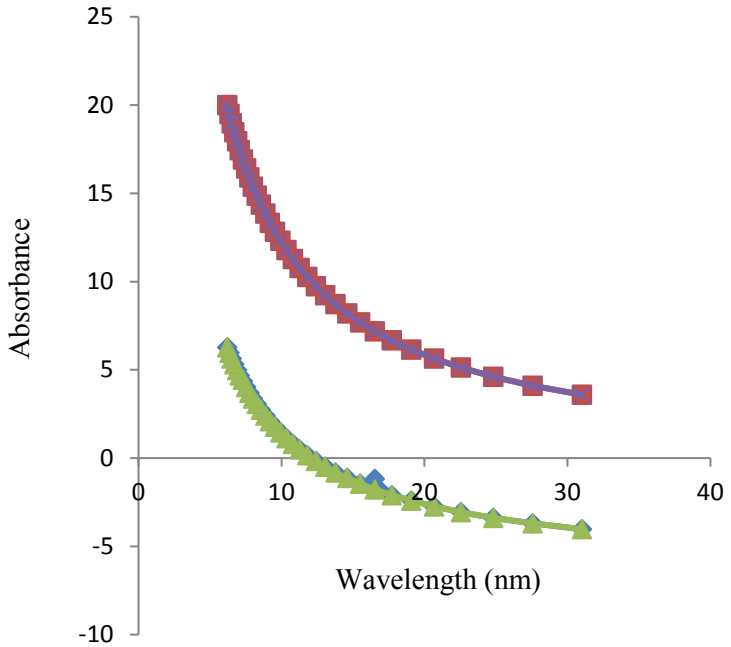

Fig.3: Absorbance of MnS vs Wavelength, λ (nm) for 750nm and 100nm

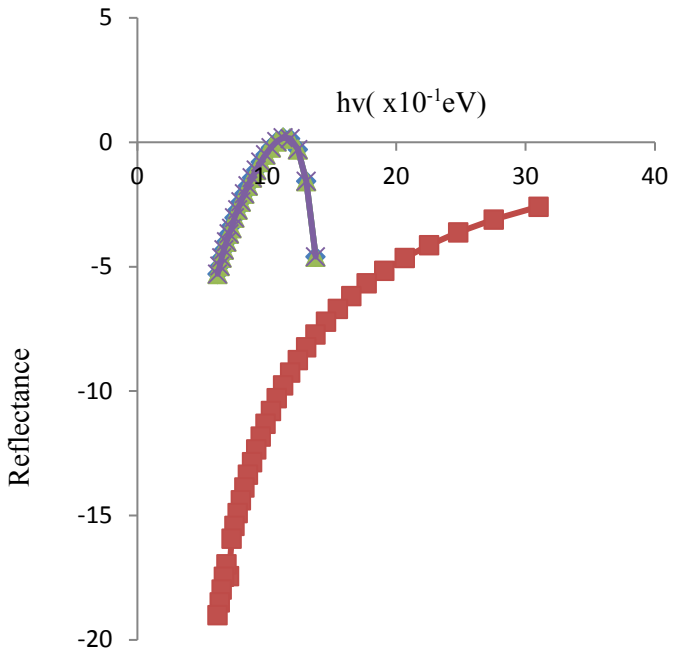

Fig.4: Reflectance as a function of Photon Energy for 250nm,500nm,750nm and 1000nm

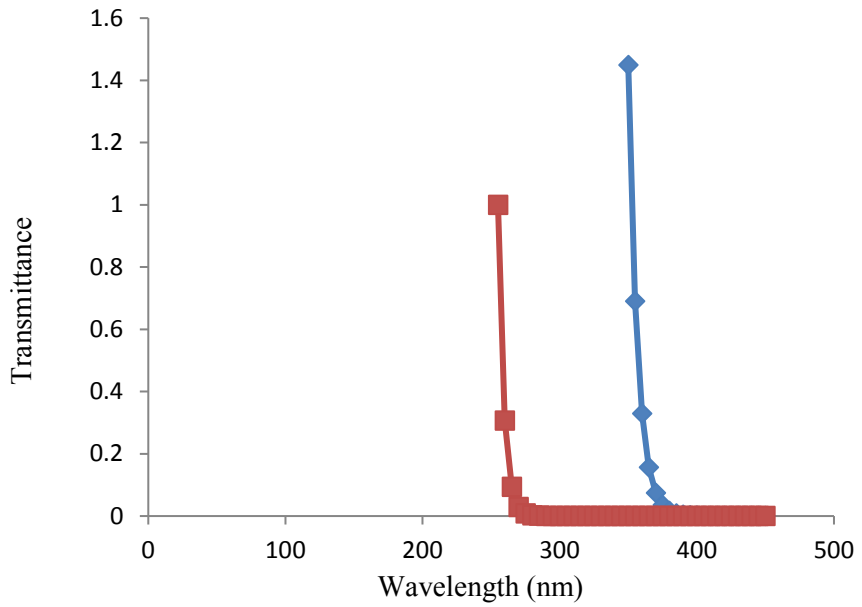

Fig.5: Graph of Transmittance as a function of wavelength for 250nm and 500nm

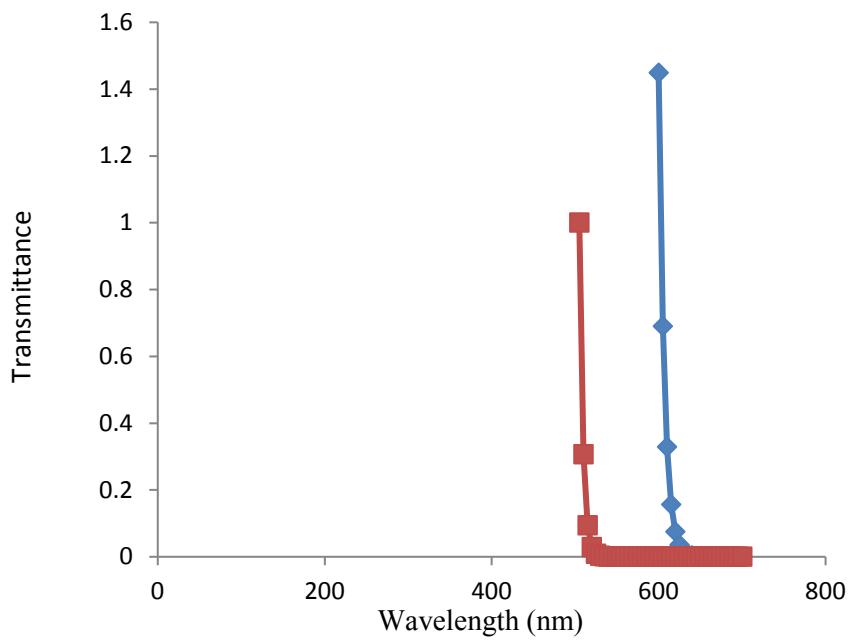

Fig.6: Graph of Transmittance as a function of wavelength for 750nm and 1000nm

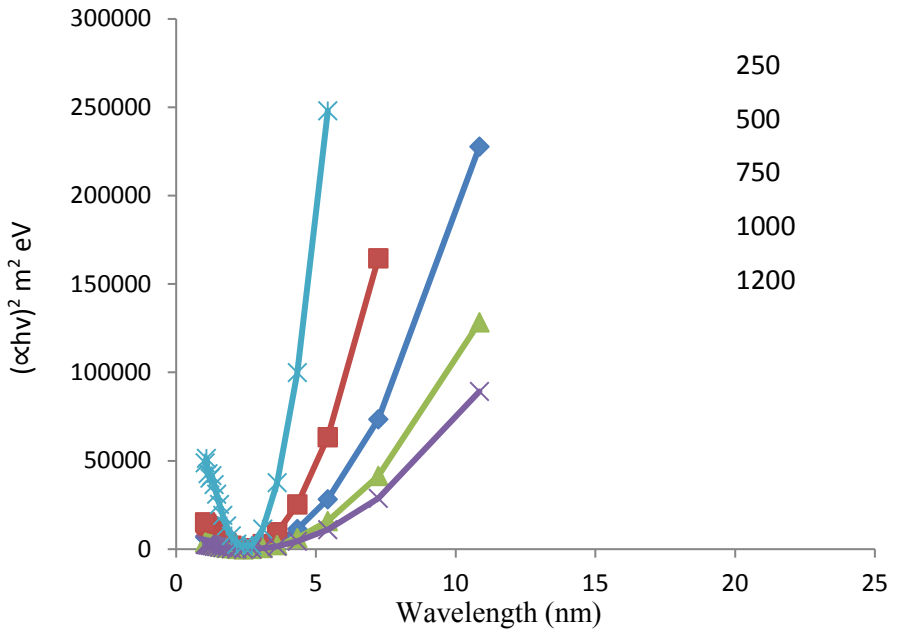

Fig.6: Graph of $(\alpha hv)^2$ of MnS as a function of wave length for 250nm.500nm, 750nm 1000nm and 1200nm

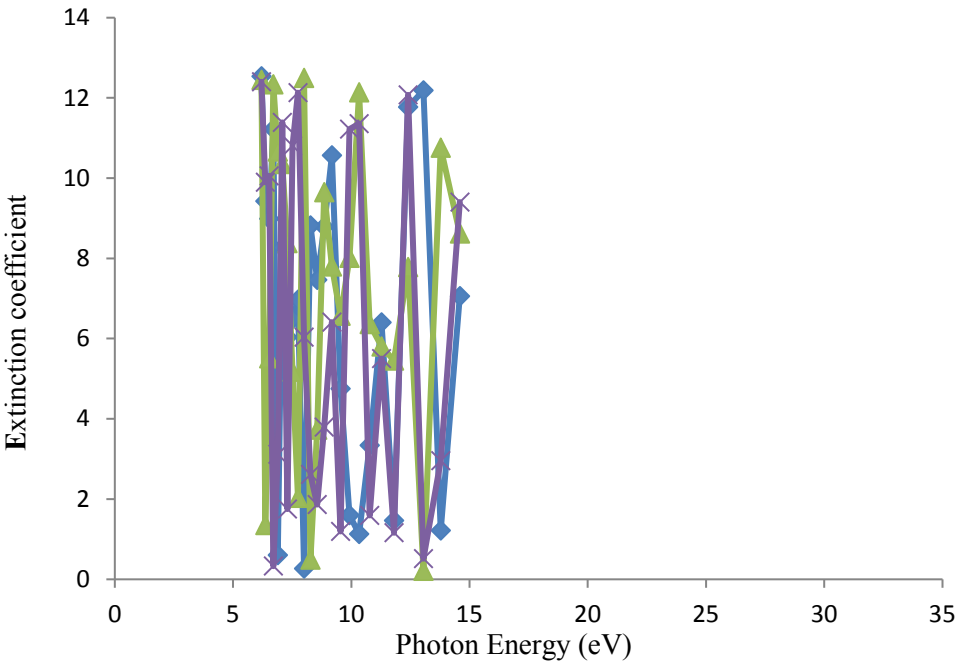

Fig.7: Extinction coefficient function of Photon Energy for 250nm, 500nm, 750nm and 1000nm

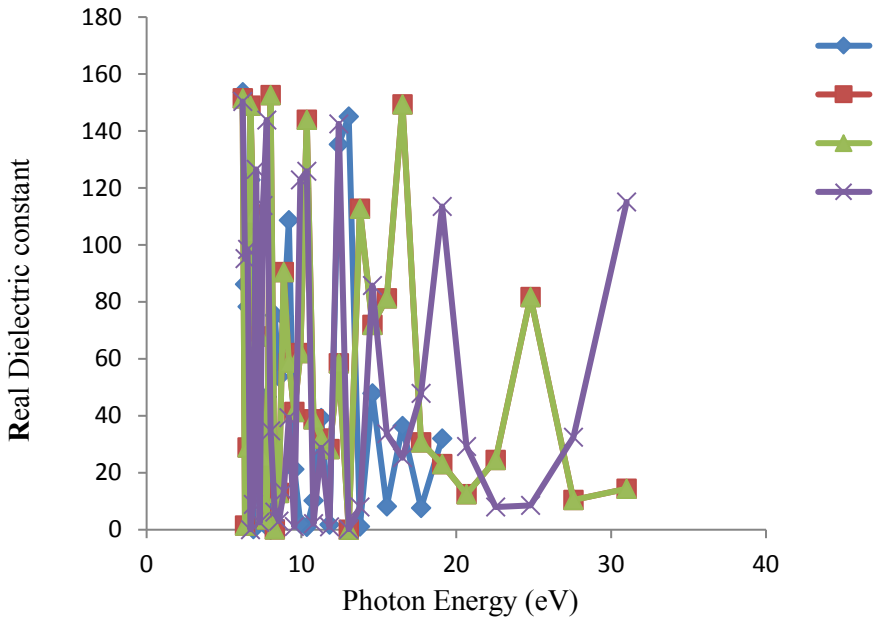

Fig.8: Real Dielectric Constant as a function of Photon Energy for 250nm, 500nm, 750nm and 1000nm

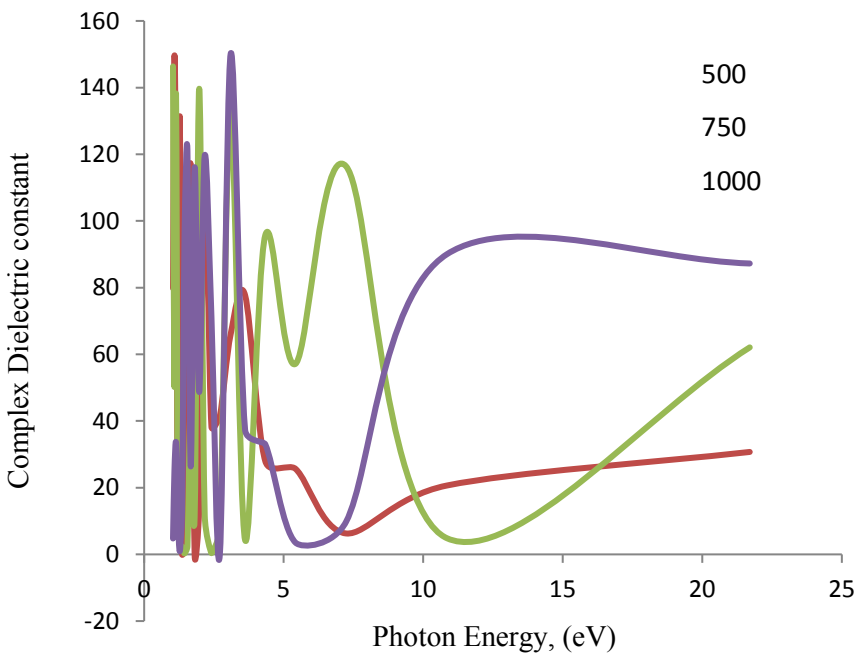

Fig.9: Graph of Complex Dielectric Constant as a function of Photon Energy, hv (eV)

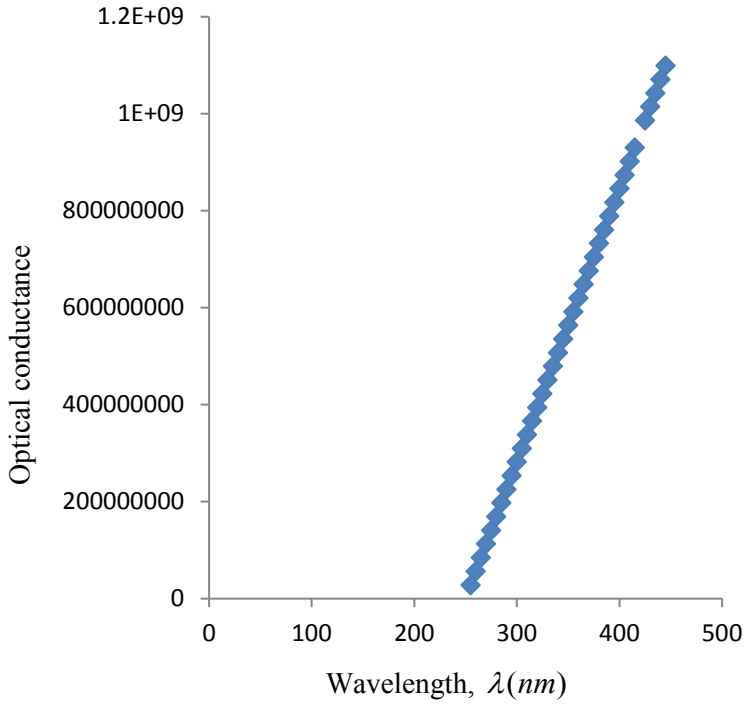

Fig.10: Optical Conductance of MnS as a Function of Wavelength for 750nm

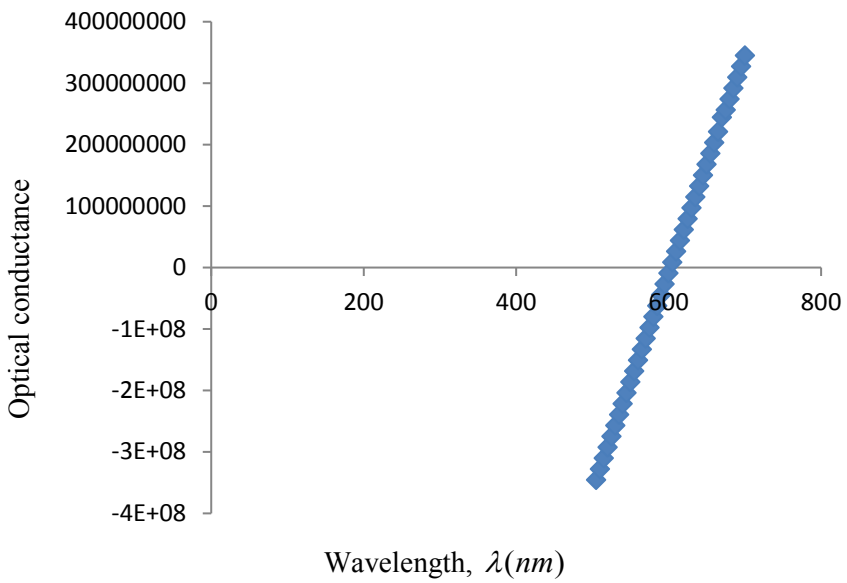

Fig.11: Optical Conductance of MnS as a Function of Wavelength for 1000nm

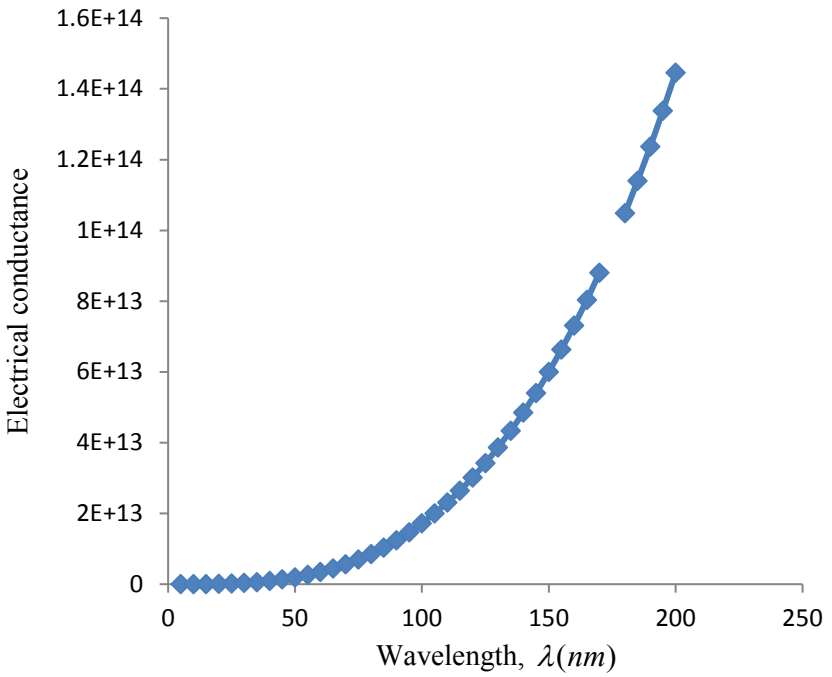

Fig.12: Electrical Conductance of MnS as a Function of Wavelength for 250nm

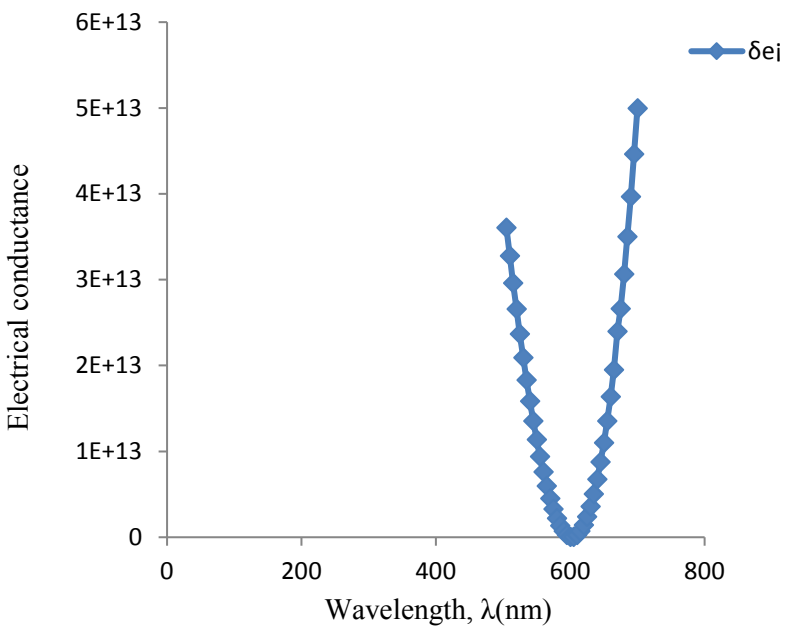

Fig.13: Electrical Conductance as a Function of Wavelength for 750nm

4. CONCLUSIONS

Theoretical model involving beam propagation was proposed in conjunction with Green's function technique to assess and study the optical and band gap of MnS thin film. Accordingly, Green's function was used to facilitate the computation of the propagating wave. The efficacy and the accuracy of the formalism was validated by the use of the result in Lambert-Beer-Bouguer law to obtain the absorption co-efficient which was utilized in computing the band gap according in accordance with the specified wavelength of the three windows. This enabled us to handle the numerical simulation of the spectral absorbance, transmittance, reflectance and conductance.

The result indicated that the computed band gap E_g from our formalism and the experimental characterization and analysis according to some other researchers is almost equivalent with just minimal deviation. While the value of computed band gap from our mechanism is 2.68eV that obtained from experiment is different within 3.1eV -3.45eV.

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